The chemistry and luminescence of antimony-containing calcium chlorapatite
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DOI:
10.6100/IR23899

Published: 01/01/1967

Document Version
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

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THE CHEMISTRY AND LUMINESCENCE OF ANTIMONY-CONTAINING CALCIUM CHLORAPATITE

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN DE TECHNISCHE WETENSCHAPPEN AAN DE TECHNISCHE HOGESCHOOL TE EINDHOVEN OP GEZAG VAN DE RECTOR MAGNIFICUS, DR. K. POSTHUMUS, HOOGLEERAAR IN DE AFDELING DER SCHEIKUNDIGE TECHNOLOGIE, VOOR EEN COMMISSIE UIT DE SENAAT TE VERDEDIGEN OP DINSDAG 6 JUNI 1967, DES NAMIDDAGS TE 4 UUR

DOOR

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SCHEIKUNDIG INGENIEUR
GEBOREN TE DEVENTER
DIET PROEFSCHRIFT IS GOEDGEKEURD DOOR DE PROMOTOR
PROF. DR. G. D. RIECK
CONTENTS

1. INTRODUCTION ............................................. 1
   References .............................................. 3

2. A SURVEY OF THE LITERATURE OF COMPOUNDS WITH
   THE APATITE CRYSTAL STRUCTURE ....................... 4
   2.1. The apatite minerals ............................... 4
   2.2. The apatite crystal structure ..................... 4
   2.3. Apatites made by reactions in the solid state .... 5
   2.4. Apatites made by reactions in solution .......... 9
   2.5. The presence of vacancies in the apatite crystal structure ... 11
   References .............................................. 12

3. MATERIALS USED AND METHODS EMPLOYED ............... 14
   3.1. Materials used ...................................... 14
       3.1.1. The starting materials ......................... 14
       3.1.2. The intermediates ............................. 15
       3.1.3. Other materials used ......................... 15
   3.2. Ball-milling ....................................... 15
   3.3. Measurement of the particle size and the particle-size distribution ... 17
   3.4. X-ray analysis ..................................... 17
   3.5. Chemical analytical methods ..................... 17
   3.6. Optical measurements ............................. 18
   References .............................................. 18

4. CALCIUM CHLORAPATITE .................................. 19
   4.1. Introduction ........................................ 19
   4.2. The reaction between CaHPO₄, CaCO₃ and NH₄Cl in stoichio-
        metrical proportions ............................... 20
   4.3. The reaction found in firing mixtures consisting ofCaHPO₄, CaCO₃
        and NH₄Cl with an excess of phosphate ............. 23
   4.4. The reaction between Ca₁₀(PO₄)₆(OH)₂ and NH₄Cl .... 27
   4.5. The reaction between Ca₁₀(PO₄)₆(OH)₂ and gaseous HCl; the
        preparation of calcium chlorapatite ............... 29
   4.6. The equilibrium between chlorapatite and hydroxyapatite .... 30
   4.7. The reaction of β-Ca₃(PO₄)₂ with HCl ............. 32
   4.8. The composition and the properties of mixed chlorhydroxyapatites . 33
   4.9. The atomic configuration of the various apatites .... 34
   References .............................................. 37
5. THE REACTION BETWEEN CHLORAPATITE AND GASEOUS ANTIMONY TRIOXIDE

5.1. Introduction ............................................. 38
5.2. Equipment ............................................... 39
5.3. Results and discussion ................................ 40
   5.3.1. The reaction between chlorapatite and gaseous antimony oxide carried out in an open system .... 40
   5.3.2. The reaction between chlorapatite and various gaseous antimony compounds carried out in a closed system ... 41
   5.3.3. The luminescence of the reaction products .................. 43

References ..................................................... 46

6. THE REACTION OF CHLORAPATITE MIXED WITH PYROPHOSPHATE OR ORTHOPHOSPHATE WITH GASEOUS ANTIMONY TRIOXIDE .................................................. 47

6.1. Introduction ............................................. 47
6.2. Experimental ........................................... 47
6.3. Results and discussion ................................ 47

References ..................................................... 51

7. THE REACTION OF GASEOUS ANTIMONY TRIOXIDE WITH A MIXTURE OF CALCIUM PYROPHOSPHATE AND ORTHOPHOSPHATE ................................................. 52

7.1. Introduction ............................................. 52
7.2. Experimental ........................................... 52
7.3. Results and discussion ................................ 52
   7.3.1. The chemical properties of the samples ................. 52
   7.3.2. The luminescence of the samples ....................... 55
   7.3.3. The effect of orthophosphate and pyrophosphate on the luminous efficiency of calcium-halophosphate phosphors 58
   7.3.4. The analogy of antimony and tin-activated \( \beta \)-calcium orthophosphate ...................................... 59
   7.3.5. The ratio of the intensities of the 415-nm and the 590-nm emission band in the spectrum of \( \beta \)-Ca\(_3\)(PO\(_4\))\(_2\)-Sb .......... 60
   7.3.6. Energy transfer in Ca\(_3\)(PO\(_4\))\(_2\) activated with antimony and manganese ........................................ 62

References ..................................................... 63
8. THE REACTION OF $\beta$-CALCIUM ORTHOPHOSPHATE WITH GASEOUS ANTIMONY TRICHLORIDE

8.1. Introduction
8.2. Equipment
8.3. Experimental
8.4. Results and discussion
  8.4.1. The effect of the SbCl$_3$ vapour pressure
  8.4.2. The effect of the temperature of the $\beta$-orthophosphate
  8.4.3. The conversion of orthophosphate by mixtures of gaseous SbCl$_3$ and Sb$_2$O$_3$
  8.4.4. The conversion of $\beta$-(Ca,Mn)$_3$(PO$_4$)$_2$ with gaseous SbCl$_3$

References

9. GENERAL CONCLUSIONS

References

Samenvatting

Dankwoord

Curriculum vitae
Abstract

The properties of calcium chlorapatite, both pure and antimony-activated, and of antimony-containing calcium phosphates are dealt with. This investigation was started in order to achieve a better insight into the complex reactions which occur during the preparation of calcium-halophosphate phosphors. A short introduction deals with the problems which arise in the preparation of this phosphor. The literature on compounds possessing the apatite crystal structure is reviewed and a survey of the materials used and the methods employed is given.

Unactivated calcium chlorapatite was prepared. This apatite is readily pyrohydrolysed to calcium hydroxyapatite. When the pyrohydrolysis occurs in the presence of Ca$_3$P$_2$O$_7$ it is followed by a decomposition of the apatite to orthophosphate. This reaction results in a distribution of calcium and phosphate between two contaminating phosphate phases, namely Ca$_2$P$_2$O$_7$ and Ca$_3$(PO$_4$)$_2$ when calcium chlorapatite is prepared with an excess of phosphate. Both the pyrohydrolysis and the decomposition of chlorapatite are found to be reversible reactions and a study of the first reaction leads to an improved method of preparing pure calcium chlorapatite.

In spite of a difference in structure between calcium chlorapatite and calcium hydroxyapatite there is a continuous range of solid solutions between these apatites which is attributed to the substitution of oxygen-vacancy pairs for either chlorine or hydroxyl ions.

Antimony-activated calcium chlorapatite was investigated. From the composition of samples obtained by heating Ca$_{10}$(PO$_4$)$_6$Cl$_2$ in gaseous Sb$_2$O$_3$ it follows that in addition to the substitution of SbO for CaCl an extra loss of chlorine occurs which is also attributable to the formation of oxygen-vacancy pairs. A hypothesis is given concerning the spectra of the luminescence of the samples, dealing with the location and the environment of the Sb$^{3+}$ ion in the chlorapatite. The presence of oxygen-vacancy pairs reduces the stability of the Sb-activated apatite and in the presence of Ca$_3$P$_2$O$_7$ it may be decomposed into Ca$_3$(PO$_4$)$_2$. This decomposition is a reversible reaction and Ca$_3$(PO$_4$)$_2$ can be converted by heating in gaseous SbCl$_3$ into chlorapatite and pyrophosphate.

The properties of Sb-containing calcium phosphates were examined. Activation of Ca$_3$P$_2$O$_7$ and Ca$_3$(PO$_4$)$_2$ with Sb$^{3+}$ gives rise to poor luminescence of the samples due to the small amount of antimony incorporated. A calcium-antimony orthophosphate of composition Ca$_{3-3x}$Sb$_{2x}$(PO$_4$)$_2$ ($x \approx 0.05$), however, is easily formed. This material also shows poor luminescence but the u.v. absorption is very high and, as compared with the halophosphate phosphors, the energy absorbed by this material can be considered a loss.

The stability of calcium chlorapatite is discussed in terms of the radius of the chlorine ion. Calcium chlorapatite has pyromorphite structure with chlorine ions located on the (000) and (001) positions. Both in the reaction with water vapour and gaseous antimony trioxide the remaining chlorine ions will try to force the substituents to occupy normal chlorine sites in spite of the preference of these ions for the (001) and (003) positions. When oxygen-vacancy pairs are present, however, the substituents involved can take their preferential positions and both pyrohydrolysis and antimony activation can proceed.
Artificial light sources based on the principles of incandescent lighting have been used since time immemorial. Oil lamps were known at Ur of the Chaldees as early as 3500 B.C. In the course of time candles and mineral-oil lamps were introduced. Better and much safer artificial lighting has been obtained by the introduction of the electric-filament lamp, in which the light is produced by heating a filament by means of an electric current. Every form of incandescent lighting, from the oil lamp to the electric-filament lamp, however, has a relatively low efficiency, due to the fact that most of the emitted radiation is located in the infrared part of the spectrum.

Much higher efficiencies may be obtained with gas-discharge lamps. Fluorescent lamps, belonging to the group of low-pressure mercury-vapour-discharge lamps, are widely used today. The 254-nm radiation emitted by the mercury vapour is converted into visible light by means of a coating of a luminescent material (commonly called a phosphor) on the inner side of the lamp.

The most widely used phosphor in fluorescent lamps is calcium halophosphate, $\text{Ca}_{10}(\text{PO}_4)_6(\text{F,Cl})_2$ activated by antimony and manganese. It was discovered by McKeag and Ranby in 1942. Its general application is attributed to the high efficiency of the transformation of ultraviolet radiation into visible light, to the acceptable spectral-energy distribution of the emitted light and to the good maintenance characteristics. The calcium-halophosphate phosphors whose crystal structure is closely related to those of the apatite minerals, belong to the group of double-activated or sensitized phosphors. Both $\text{Sb}^{3+}$ ions and $\text{Mn}^{2+}$ ions are incorporated into the apatite lattice. The 254-nm radiation is absorbed by $\text{Sb}^{3+}$ ions and it is partly transferred to $\text{Mn}^{2+}$ ions. Without antimony there is only a slight absorption of the 254-nm radiation. It is generally accepted that both kinds of "activator" ions are located on calcium lattice sites as suggested by Butler and Jerome for the manganese and by Ouweltjes for the antimony.

Halophosphate phosphors are prepared by a reaction at elevated temperatures, starting from a mixture of $\text{CaHPO}_4$, $\text{CaCO}_3$, $\text{CaF}_2$, $\text{NH}_4\text{Cl}$, $\text{MnCO}_3$ and $\text{Sb}_2\text{O}_3$. Wanmaker and Ouweltjes and Wanmaker found that these phosphors prepared with the precise stoichiometrical composition gave rise to poorly luminescent materials due to the extremely low amount of trivalent antimony dissolved in the apatite lattice. In order to increase the luminescence of the product the reaction mixture must have a smaller cation/phosphate mole ratio than corresponds to an apatite and consequently in the final product other phosphate phases will be present, too. In principle, this could be an orthophosphate or a pyrophosphate. Indeed X-ray-diffraction analysis reveals the
presence of Ca$_2$P$_2$O$_7$ in phosphors of good quality, whereas in rather poor materials a much larger quantity of Ca$_3$(PO$_4$)$_2$ is found.

The effect of contaminating phases on the efficiency of phosphors is readily explained by the fact that they may absorb the exciting radiation without contributing to the luminescence. The drop in efficiency is thus determined by the quantity of these contaminating phases and by their u.v. absorption.

If, for instance, we take a material with a cation/phosphate mole ratio of 1.617, an amount of 28 wt % of Ca$_3$(PO$_4$)$_2$ is found, whereas the quantity of the contaminating phase amounts only to 5.6 wt % when Ca$_2$P$_2$O$_7$ is present. Thus it is easy to understand that with respect to the quantity, Ca$_3$(PO$_4$)$_2$ is more harmful than Ca$_2$P$_2$O$_7$. Apart from the amount of contaminating materials their u.v. absorption is important. If the u.v. absorption is negligible a large amount of foreign material may be present without a noticeable effect on the efficiency. An example is MgWO$_4$ that is generally made with a 100% excess of MgO.

Little is known about the factors which control the distribution of the excess of phosphate between Ca$_3$(PO$_4$)$_2$ and Ca$_2$P$_2$O$_7$ in Ca-halophosphate phosphors. This also applies to the optical properties of these contaminating phases. The materials containing orthophosphate often have pinkish discolouration and in many cases they are obtained by "over-firing". In our experience this occurs more readily when a larger excess of phosphate is employed. Rabatin and Gillooly$^{1-9}$ attributed the discolouration to oxidation of divalent manganese present in $\beta$-(Ca,Mn)$_3$(PO$_4$)$_2$ which is formed by partial decomposition of the apatite lattice on prolonged firing. The greatly reduced efficiency cannot be explained by an inactive u.v. absorption of pure or partly oxidized $\beta$-(Ca,Mn)$_3$(PO$_4$)$_2$. Kinney$^{1-10}$ found that trivalent antimony can be incorporated in the Ca$_2$P$_2$O$_7$ lattice. Hence the question arises whether antimony can also be present in the $\beta$-Ca$_3$(PO$_4$)$_2$ lattice.

In order to achieve more insight into the distribution of the excess of phosphate between the contaminating phases several aspects of a simpler system were studied, viz. calcium chlorapatite, Ca$_{10}$(PO$_4$)$_6$Cl$_2$, both pure and activated with trivalent antimony. The incorporation of antimony into the orthophosphate lattice was also studied.

Halophosphate phosphors have the crystal structure of an apatite. A survey of materials known in the literature and having this structure is therefore given in chapter 2.

The starting materials and the measuring methods are reviewed in chapter 3.

The reversible conversion of calcium chlorapatite into hydroxyapatite is discussed in chapter 4. The investigation of this conversion leads to a new hypothesis concerning the solid solutions between these two kinds of apatite and to an improved synthesis of pure chlorapatite. Moreover, the reversible
conversion of a mixture of this apatite and pyrophosphate into orthophosphate is investigated.

The reaction between chlorapatite and antimony trioxide is discussed in chapter 5. From chemical analysis of antimony-containing apatites the conclusion is drawn that a variable proportion of the chlorine lattice sites is unoccupied; moreover, the emission spectra of the luminescence differ. This led us to a hypothesis concerning the environment of the Sb$^{3+}$ centre in the apatite lattice.

The incorporation of antimony into a mixture of chlorapatite and pyrophosphate is dealt with in chapter 6. The effect of the vapour pressure of antimony chloride follows from this investigation. A partial decomposition of the apatite into orthophosphate takes place when the SbCl$_3$ is removed continuously; a certain vapour pressure of the SbCl$_3$(P$_{SbCl_3}$) achieves the opposite.

The incorporation of trivalent antimony into orthophosphate is discussed in chapter 7. Antimony-containing $\beta$-calcium orthophosphate may easily be formed. These phosphates show a poor luminescence in spite of a high u.v. absorption.

The reversible reaction between orthophosphate and antimony trichloride into chlorapatite, pyrophosphate and antimony trioxide is discussed in chapter 8. The effect of both the vapour pressure of the antimony chloride and the temperature of the orthophosphate is given.

Finally the general conclusions are briefly reviewed in chapter 9.

REFERENCES

2. A SURVEY OF THE LITERATURE OF COMPOUNDS WITH THE Apatite CRYSTAL STRUCTURE

2.1. The Apatite Minerals

At the beginning of the 19th century the name "apatite" was given to a group of minerals which can be represented by the general formula $M_{10}(XO_4)_6Z_2$. According to Van Waser 2-1):

- $M$ stands for Ca, Sr, Pb, Mn, Cd, Mg, Fe, Al, La, Y, the rare-earth elements Ce and Dy, and Na, K;
- $X$ stands for P, As, V, S and Si;
- $Z$ stands for F, Cl and OH.

According to recent investigations by Winand 2-2) and Kühl and Nebergall 2-3) the $CO_3$ group may also stand for $XO_4$.

The name "apatite" was derived from the Greek verb ἀπατάω which means "to deceive", for the apatites were often confused with other minerals. Mineralogists have classified the apatite minerals into two main groups, the apatite and the pyromorphite group with $Ca_{10}(PO_4)_6F_2$ and $Pb_{10}(PO_4)_6Cl_2$, as characteristic prototypes, respectively. From a chemical point of view there is no basic difference between those groups. Generally it can be said that the pyromorphite group starts with atoms having a higher atomic number. Both groups are closely related, as follows from the fact that they readily form solid solutions.

2.2. The Apatite Crystal Structure

The crystal structure of the major member of the apatite group, $Ca_{10}(PO_4)_6F_2$, was determined by Mehmel 2-4) and by Náray Szabó 2-5). These authors had different opinions about the positions of the F atoms in the unit cell. According to Náray Szabó these atoms are located at lattice sites having the coordinates $(00\frac{1}{2})$ and $(00\frac{3}{2})$ while Mehmel proposed that they occupy the $(000)$ and $(00\frac{1}{2})$ positions. Hendricks et al. 2-6) and Beevers and McIntyre 2-7) accepted the positions of the fluorine atoms as proposed by Náray Szabó. Hendricks 2-6) applied the Mehmel-type structure to $Ca_{10}(PO_4)_6Cl_2$ with chlorine atoms in the $(000)$ and $(00\frac{1}{2})$ positions and suggested that $Ca_{10}(PO_4)_6Cl_2$ is a member of the pyromorphite group. Nacken 2-8) found that there is a linear relationship between composition and index of refraction of mixed calcium hydroxychlorapatites. Wallaeys 2-9) found that this also applied to the lattice constants $a$ and $c$. This author concluded from these findings that the structures of $Ca_{10}(PO_4)_6F_2$ and $Ca_{10}(PO_4)_6Cl_2$ are closely related.

A more accurate determination of the structure of $Ca_{10}(PO_4)_6F_2$ was made by Beevers and McIntyre 2-7) by using more extensive X-ray data. The unit cell belongs to the hexagonal $P6_3/m$ type and contains one mole of
Ca_{10}(PO_4)_6F_2; values of $a = 9.37$ Å and $c = 6.88$ Å were found for the lattice constants. Two kinds of Ca lattice sites are found in this structure, commonly referred to as Ca$_I$ and Ca$_{II}$. The local symmetry around these sites for Ca$_{10}$(PO$_4$)$_6$F$_2$ and Ca$_{10}$(PO$_4$)$_6$Cl$_2$, respectively, is given in fig. 2.1. The

![Diagram of Ca$_{10}$(PO$_4$)$_6$F$_2$ and Ca$_{10}$(PO$_4$)$_6$Cl$_2$ sites](image)

Fig. 2.1. The local symmetry around the two calcium sites in fluorapatite and chlorapatite (Johnson 2-10).

Ca$_I$ sites are situated in planes perpendicular to the $c$-axes at $z = 0$ and $z = \frac{1}{2}$ and are located on trigonal symmetry axes parallel to the $c$-axes; six oxygen atoms are the nearest neighbours. The symmetry around the Ca$_{II}$ sites is much lower. These sites, situated in mirror planes perpendicular to the $c$-axes at $z = \frac{1}{4}$ and $z = \frac{3}{4}$, are surrounded by oxygen atoms and either by one F site in the same plane for fluorapatite or by two Cl sites situated in planes at $z = 0$ and $z = \frac{1}{2}$ for chlorapatite.

2.3. Apatites made by reactions in the solid state

A wide variety of apatites, covering the normal composition M$_{10}$(XO$_4$)$_6$Z$_2$ as well as compounds like Pb$_2$Na$_2$(PO$_4$)$_6$ for which the apatite structure is less obvious, has been prepared by solid-state reactions. A survey of the apatites of the composition M$_{10}$(XO$_4$)$_6$Z$_2$ is given in table 2-1. These apatites have been prepared by heating a mixture of three moles of M$_3$(XO$_4$)$_2$ and one mole of MZ$_2$ to elevated temperatures or, when Z stands for OH, by heating a mixture of three moles of M$_3$(XO$_4$)$_2$ and one mole of MO in air saturated with water vapour. Wallaeys 2-9) demonstrated that Ca$_{10}$(PO$_4$)$_6$F$_2$ and Ca$_{10}$(PO$_4$)$_6$Cl$_2$ are also formed when Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ or hydrated tricalcium phosphate is heated with CaF$_2$ and CaCl$_2$, respectively. Montel 2-26) found that Ca$_{10}$(PO$_4$)$_6$F$_2$ can also be prepared by heating a mixture of Ca$_2$P$_2$O$_7$ + CaF$_2$, Ca(PO$_3$)$_2$ + CaF$_2$ and even P$_2$O$_5$ + CaF$_2$, respectively. In the absence of water vapour the excess of phosphorus and fluorine volatilises as POF$_3$. Kinh 2-27) found that Sr$_{10}$(PO$_4$)$_6$F$_2$ can be formed in a similar way. Ditte 2-28) reported the preparation of M$_{10}$(PO$_4$)$_6$J$_2$, but the existence of these apatites in which M stands for Ca, Sr and Ba is doubtful. Neither Wilke Dörfurt 2-29)
TABLE 2-I

A survey of apatites represented by formula $M_{10}(XO_4)_6Z_2$

<table>
<thead>
<tr>
<th>apatite</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$c/a$</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$_{10}$(PO$_4$)$_6$(OH)$_2$</td>
<td>9.403</td>
<td>9.666</td>
<td>0.730</td>
<td>2-9</td>
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<tr>
<td>Sr$_{10}$(PO$_4$)$_6$(OH)$_2$</td>
<td>9.74</td>
<td>7.20</td>
<td>0.739</td>
<td>2-11</td>
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<tr>
<td>Ba$_{10}$(PO$_4$)$_6$(OH)$_2$</td>
<td>10.19</td>
<td>7.70</td>
<td>0.756</td>
<td>2-12</td>
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<tr>
<td>Cd$_{10}$(PO$_4$)$_6$(OH)$_2$</td>
<td>9.0</td>
<td>6.6</td>
<td>0.73</td>
<td>2-13,14</td>
</tr>
<tr>
<td>Pb$_{10}$(PO$_4$)$_6$(OH)$_2$</td>
<td>9.90</td>
<td>7.29</td>
<td>0.736</td>
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<tr>
<td>Ca$_{10}$(PO$_4$)$_6$F$_2$</td>
<td>9.37</td>
<td>6.88</td>
<td>0.735</td>
<td>2-5,7</td>
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<tr>
<td>Ca$_{10}$(PO$_4$)$_6$F$_2$</td>
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<td>6.87</td>
<td>0.735</td>
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<td>Ca$_{10}$(PO$_4$)$_6$Cl$_2$</td>
<td>9.48</td>
<td>7.15</td>
<td>0.754</td>
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<tr>
<td>Ca$_{10}$(PO$_4$)$_6$Cl$_2$</td>
<td>9.52</td>
<td>6.85</td>
<td>0.719</td>
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<td>Cd$_{10}$(PO$_4$)$_6$Cl$_2$</td>
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<td>6.76</td>
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<td>Cd$_{10}$(PO$_4$)$_6$Cl$_2$</td>
<td>9.7</td>
<td>6.4</td>
<td>0.771</td>
<td>2-17</td>
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<tr>
<td>Mn$_{10}$(PO$_4$)$_6$Cl$_2$</td>
<td>9.30</td>
<td>6.20</td>
<td>0.667</td>
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</tr>
<tr>
<td>Ca$_{10}$(PO$_4$)$_6$Cl$_2$</td>
<td>9.30</td>
<td>7.18</td>
<td>0.753</td>
<td>2-16</td>
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<tr>
<td>Ca$_{10}$(PO$_4$)$_6$F$_2$</td>
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<td>Ca$_{10}$(PO$_4$)$_6$Cl$_2$</td>
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<td>6.76</td>
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<tr>
<td>Ca$_{10}$(PO$_4$)$_6$Br$_2$</td>
<td>9.714</td>
<td>6.75</td>
<td>0.696</td>
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<tr>
<td>Sr$_{10}$(PO$_4$)$_6$F$_2$</td>
<td>9.719</td>
<td>7.2</td>
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<td>Sr$_{10}$(PO$_4$)$_6$Cl$_2$</td>
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<td>Ba$_{10}$(PO$_4$)$_6$F$_2$</td>
<td>10.22</td>
<td>7.66</td>
<td>0.750</td>
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<tr>
<td>Ba$_{10}$(PO$_4$)$_6$Cl$_2$</td>
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<td>7.64</td>
<td>0.744</td>
<td>2-20</td>
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<tr>
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<td>7.64</td>
<td>0.737</td>
<td>2-20</td>
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<td>Cd$_{10}$(AsO$_4$)$_6$Cl$_2$</td>
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<td>7.21</td>
<td>0.752</td>
<td>2-18</td>
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<td>Sr$_{10}$(AsO$_4$)$_6$Cl$_2$</td>
<td>10.12</td>
<td>7.49</td>
<td>0.741</td>
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<tr>
<td>Ba$_{10}$(AsO$_4$)$_6$Cl$_2$</td>
<td>10.44</td>
<td>7.59</td>
<td>0.726</td>
<td>2-20</td>
</tr>
<tr>
<td>Ba$_{10}$(AsO$_4$)$_6$Br$_2$</td>
<td>10.46</td>
<td>7.62</td>
<td>0.729</td>
<td>2-20</td>
</tr>
<tr>
<td>Pb$_{10}$(PO$_4$)$_6$F$_2$</td>
<td>9.76</td>
<td>7.29</td>
<td>0.746</td>
<td>2-21</td>
</tr>
<tr>
<td>Pb$_{10}$(PO$_4$)$_6$Cl$_2$</td>
<td>9.97</td>
<td>7.32</td>
<td>0.734</td>
<td>2-21</td>
</tr>
<tr>
<td>Pb$_{10}$(PO$_4$)$_6$Br$_2$</td>
<td>10.07</td>
<td>7.37</td>
<td>0.732</td>
<td>2-21</td>
</tr>
<tr>
<td>Pb$_{10}$(AsO$_4$)$_6$F$_2$</td>
<td>10.07</td>
<td>7.42</td>
<td>0.737</td>
<td>2-21</td>
</tr>
<tr>
<td>Pb$_{10}$(AsO$_4$)$_6$Cl$_2$</td>
<td>10.25</td>
<td>7.46</td>
<td>0.727</td>
<td>2-21</td>
</tr>
<tr>
<td>Pb$_{10}$(AsO$_4$)$_6$Br$_2$</td>
<td>10.31</td>
<td>7.47</td>
<td>0.725</td>
<td>2-21</td>
</tr>
<tr>
<td>Pb$_{10}$(V$_2$O$_4$)$_6$F$_2$</td>
<td>10.37</td>
<td>7.54</td>
<td>0.727</td>
<td>2-21</td>
</tr>
</tbody>
</table>

Pb$_{10}$(VO$_4$)$_6$F$_2$ | 10.40 | 7.34 | 0.727 | 2-21 |
TABLE 2-I (continued)

<table>
<thead>
<tr>
<th>apatite</th>
<th>lattice constants</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a (Å)</td>
<td>c (Å)</td>
</tr>
<tr>
<td>(\text{Pb}_{10}(\text{VO}_4)_6\text{Cl}_2)</td>
<td>10·32</td>
<td>7·33</td>
</tr>
<tr>
<td>(\text{Pb}_{10}(\text{VO}_4)_6\text{Br}_2)</td>
<td>10·39</td>
<td>7·36</td>
</tr>
<tr>
<td>(\text{Pb}_{10}(\text{VO}_4)_6\text{J}_2)</td>
<td>10·41</td>
<td>7·46</td>
</tr>
<tr>
<td>(\text{Ba}_{10}(\text{VO}_4)_6(\text{OH})_2)</td>
<td>10·44 *)</td>
<td>7·95 *)</td>
</tr>
<tr>
<td>(\text{Ba}_{10}(\text{CrO}_4)_6(\text{OH})_2)</td>
<td>10·44 *)</td>
<td>7·84 *)</td>
</tr>
<tr>
<td>(\text{Ba}_{10}(\text{MnO}_4)_6(\text{OH})_2)</td>
<td>10·44 *)</td>
<td>7·74 *)</td>
</tr>
<tr>
<td>(\text{Sr}_{10}(\text{MnO}_4)_6(\text{OH})_2)</td>
<td>9·94 *)</td>
<td>7·42 *)</td>
</tr>
<tr>
<td>(\text{Ca}_{10}(\text{CrO}_4)_6(\text{OH})_2)</td>
<td>9·67</td>
<td>7·01</td>
</tr>
<tr>
<td>(\text{Sr}_{10}(\text{CrO}_4)_6(\text{OH})_2)</td>
<td>9·98</td>
<td>7·40</td>
</tr>
<tr>
<td>(\text{Ba}_{10}(\text{CrO}_4)_6(\text{OH})_2)</td>
<td>10·34</td>
<td>7·77</td>
</tr>
<tr>
<td>(\text{Ba}_{10}(\text{CrO}_4)_6\text{F}_2)</td>
<td>10·33</td>
<td>7·77</td>
</tr>
<tr>
<td>(\text{Ca}_{10}(\text{CrO}_4)_6\text{F}_2)</td>
<td>10·09</td>
<td>6·78</td>
</tr>
<tr>
<td>(\text{Sr}_{10}(\text{CrO}_4)_6\text{Cl}_2)</td>
<td>10·12</td>
<td>7·32</td>
</tr>
<tr>
<td>(\text{Ba}_{10}(\text{CrO}_4)_6\text{Cl}_2)</td>
<td>10·50</td>
<td>7·73</td>
</tr>
</tbody>
</table>

*) kX units

nor Harth \(2-20\) succeeded in preparing them. Probably the iodine atom is too big to be incorporated into these apatites. Merker and Wondratschek \(2-21\) did not succeed in preparing \(\text{Pb}_{10}(\text{PO}_4)_6\text{J}_2\). They found that \(\text{Pb}_{10}(\text{AsO}_4)_6\text{J}_2\) appeared in two modifications, a white modification with apatite structure and a yellow one possessing an orthorhombic structure.

From the work of McConnell \(2-30\), Hägele and Machatschki \(2-31\) and Klement \(2-32\) it follows that the phosphorus atoms in the \(\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2\) lattice can be replaced by other atoms. Charge compensation can be achieved in various ways:

2P⁵⁺ replaced by Si⁴⁺ and S⁶⁺, e.g. \(\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3\text{F}_2\), ellestadite \(2-30\); Ca²⁺ and P⁵⁺ replaced by Me³⁺ and Si⁴⁺, e.g. \(\text{Ca}_4\text{Ce}_6(\text{SiO}_4)_6\text{F}_2\), britholite \(2-31\); Ca²⁺ and P⁵⁺ replaced by Me⁺ and S⁶⁺, e.g. \(\text{Ca}_4\text{Na}_6(\text{SO}_4)_6\text{F}_2\), calcium-sodium-sulphate apatite \(2-32\).

Following these substitution methods, new apatites were found and some of them have been tabulated in table 2-II. It may be mentioned that Cr⁶⁺ is present in the apatites as found by Pascher \(2-34\). On the other hand, however, pentavalent chromium is present in the apatites as found by Banks and Jaunarajs \(2-24\) as a result of magnetic-susceptibility measurements.

All the apatites of tables 2-I and 2-II have in common the presence of the “correct” amount of two halogen atoms per ten M or per six X atoms.
### TABLE 2-II

A survey of some substituted apatites

<table>
<thead>
<tr>
<th>apatite</th>
<th>lattice constants</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a) (Å)</td>
<td>(c) (Å)</td>
</tr>
<tr>
<td>(\text{Na}_6\text{Ca}_4(\text{SO}_4)_6\text{F}_2)</td>
<td>9.515</td>
<td>7.015</td>
</tr>
<tr>
<td>(\text{Ca}_4\text{Y}_6(\text{SiO}_4)_6(\text{OH})_2)</td>
<td>9.31</td>
<td>6.58</td>
</tr>
<tr>
<td>(\text{Ca}_4\text{Nd}_6(\text{SiO}_4)_6(\text{OH})_2)</td>
<td>9.53</td>
<td>6.825</td>
</tr>
<tr>
<td>(\text{Ca}_4\text{La}_6(\text{SiO}_4)_6(\text{OH})_2)</td>
<td>9.65</td>
<td>6.84</td>
</tr>
<tr>
<td>(\text{K}_6\text{Pb}_4(\text{CrO}_4)_6\text{F}_2)</td>
<td>10.32*</td>
<td>7.58*</td>
</tr>
<tr>
<td>(\text{Na}_6\text{Pb}_4(\text{SeO}_4)_6\text{F}_2)</td>
<td>10.15*</td>
<td>7.46*</td>
</tr>
<tr>
<td>(\text{Pb}_{10}(\text{SiO}_4)_3(\text{CrO}_4)_3\text{F}_2)</td>
<td>10.10*</td>
<td>7.43*</td>
</tr>
<tr>
<td>(\text{Pb}_{10}(\text{SiO}_4)_3(\text{SeO}_4)_3\text{F}_2)</td>
<td>10.13*</td>
<td>7.46*</td>
</tr>
<tr>
<td>(\text{Pb}_{10}(\text{GeO}_4)_3(\text{CrO}_4)_3\text{F}_2)</td>
<td>10.23*</td>
<td>7.47*</td>
</tr>
<tr>
<td>(\text{Pb}_{10}(\text{GeO}_4)_3(\text{SeO}_4)_3\text{F}_2)</td>
<td>10.29*</td>
<td>7.55*</td>
</tr>
<tr>
<td>(\text{Pb}_{10}(\text{SiO}_4)(\text{GeO}_4)(\text{PO}_4))</td>
<td>10.16*</td>
<td>7.44*</td>
</tr>
</tbody>
</table>

*) kX units

Interesting classes of apatites are represented by the formulas \(\text{Pb}_{10}(\text{XO}_4)_4(\text{YO}_4)_2\) and \(\text{Pb}_8\text{A}_2(\text{XO}_4)_6\) (\(X\) stands for P, As and V; \(Y\) stands for Si and Ge and \(A\) stands for Na, K, Rb, Cs and Tl). Materials corresponding to the first formula have been found by Paetsch and Dietzel \(2-35\) and by Wondratschek and Merker \(2-36\). The compounds with monovalent ions on \(M\) lattice sites were described by Merker and Wondratschek \(2-37\). Both groups of materials have in common that the \(Z\) sites are unoccupied. A survey of apatites with halogen vacancies is given in table 2-III. Attention may be drawn to the boron silicate \(\text{Pb}_{10}(\text{BO}_3)_4(\text{SiO}_4)_2\) prepared by Moore and Eitel \(2-38\). According to this formula unoccupied oxygen lattice sites should also be present.

Merker and Wondratschek \(2-39\) succeeded in incorporating trivalent atoms into the class of compounds represented by the formulas \(\text{Pb}_8\text{A}_2(\text{PO}_4)_6\) and \(\text{Pb}_{10}(\text{PO}_4)_4(\text{YO}_4)_2\). Oxypyroborate \(\text{Pb}_{10}(\text{PO}_4)_6\text{O}\) was also prepared by Merker and Wondratschek \(2-40\). The lattice constants are \(a = 9.84\) Å and \(c = 14.86\) Å. The lattice constant \(c\) is about twice that of a normal apatite. According to the authors this indicates an ordered distribution of the oxygen atoms over half of the \(Z\) sites.

Compounds with the formula \(\text{Ca}_6\text{Na}_2(\text{XO}_4)_6\), where \(X\) stands for P, As and V, have been reported by Harth \(2-20\), whereas Klement and Haselbeck \(2-18\) reported sodium apatites of Mn, Co and Mg. These authors also described the mixed apatites \(\text{Me}_x\text{Ca}_{10-x}(\text{PO}_4)_6\text{Cl}_2\) where \(\text{Me}\) stands for Zn and Cu (\(x\) up to 4) and for Co (\(x\) up to 3).
### TABLE 2-III
Apatites with unoccupied Z lattice sites

<table>
<thead>
<tr>
<th>apatite</th>
<th>lattice constant</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$a$ (Å)</td>
<td>$c$ (Å)</td>
</tr>
<tr>
<td>$\text{Pb}_1\text{O}_2(\text{SiO}_4\text{PO}_4)_4$</td>
<td>9.79</td>
<td>7.32</td>
</tr>
<tr>
<td>$\text{Pb}_1\text{O}_2(\text{SiO}_4\text{VO}_4)_4$</td>
<td>9.99</td>
<td>7.35</td>
</tr>
<tr>
<td>$\text{Pb}_1\text{O}_2(\text{SiO}_4\text{AsO}_4)_4$</td>
<td>10.02</td>
<td>7.38</td>
</tr>
<tr>
<td>$\text{Pb}_1\text{O}_2(\text{GeO}_4\text{PO}_4)_4$</td>
<td>9.88</td>
<td>7.32</td>
</tr>
<tr>
<td>$\text{Pb}_1\text{O}_2(\text{GeO}_4\text{VO}_4)_4$</td>
<td>10.06</td>
<td>7.37</td>
</tr>
<tr>
<td>$\text{Pb}_1\text{O}_2(\text{GeO}_4\text{AsO}_4)_4$</td>
<td>10.10</td>
<td>7.40</td>
</tr>
<tr>
<td>$\text{Pb}_1\text{O}_2(\text{SiO}_4\text{VO}_4\text{PO}_4)_2$</td>
<td>9.88</td>
<td>7.33</td>
</tr>
<tr>
<td>$\text{Pb}_1\text{O}_2(\text{SiO}_4\text{GeO}_4\text{PO}_4)_4$</td>
<td>9.81</td>
<td>7.30</td>
</tr>
<tr>
<td>$\text{Pb}_1\text{O}_2(\text{SiO}_4\text{GeO}_4\text{AsO}_4\text{PO}_4)_2$</td>
<td>9.92</td>
<td>7.34</td>
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<tr>
<td>$\text{Pb}_8\text{Na}_2\text{PO}_4_6$</td>
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<td>7.18</td>
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<td>9.76</td>
<td>7.24</td>
</tr>
<tr>
<td>$\text{Pb}_8\text{K}_2\text{PO}_4_6$</td>
<td>9.80</td>
<td>7.28</td>
</tr>
<tr>
<td>$\text{Pb}_8\text{Rb}_2\text{PO}_4_6$</td>
<td>9.86</td>
<td>7.37</td>
</tr>
<tr>
<td>$\text{Pb}_8\text{Na}_2\text{AsO}_4_6$</td>
<td>10.02</td>
<td>7.31</td>
</tr>
<tr>
<td>$\text{Pb}_8\text{K}_2\text{AsO}_4_6$</td>
<td>10.12</td>
<td>7.43</td>
</tr>
<tr>
<td>$\text{Pb}_8\text{Na}_2\text{VO}_4_6$</td>
<td>10.05</td>
<td>7.46</td>
</tr>
<tr>
<td>$\text{Pb}_8\text{K}_2\text{VO}_4_6$</td>
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</tr>
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<td>$\text{Pb}_8\text{TI}_2\text{VO}_4_6$</td>
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<td>7.40</td>
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<td>$\text{Pb}_8\text{Rb}_2\text{AsO}_4_6$</td>
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<td>7.52</td>
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<td>7.47</td>
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<td>7.49</td>
</tr>
<tr>
<td>$\text{Pb}_8\text{TI}_2\text{PO}_4_6$</td>
<td>9.81</td>
<td>7.36</td>
</tr>
<tr>
<td>$\text{Pb}_1\text{O}_2(\text{BO}_3)_4(\text{SiO}_4)_2$</td>
<td>9.61</td>
<td>7.10</td>
</tr>
<tr>
<td>$\text{Pb}_8\text{Bi}_2\text{TI}_2(\text{PO}_4)_4(\text{SiO}_4)_2$</td>
<td>9.78</td>
<td>7.34</td>
</tr>
<tr>
<td>$\text{Pb}_8\text{Bi}_2(\text{PO}_4)_2(\text{SiO}_4)_4$</td>
<td>9.76</td>
<td>7.26</td>
</tr>
<tr>
<td>$\text{Pb}_8\text{Na}_2(\text{SO}_4)_2(\text{PO}_4)_2(\text{SiO}_4)_2$</td>
<td>9.79</td>
<td>7.29</td>
</tr>
<tr>
<td>$\text{Pb}_8\text{Bi}_4(\text{PO}_4)_2(\text{SiO}_4)_6$</td>
<td>9.7-9.8</td>
<td>7.2-7.3</td>
</tr>
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</table>

### 2.4. Apatites made by reactions in solution

Although we prepared all our samples by solid-state reactions, it is worth while studying the work done on apatites and other phosphates formed in solution, because of the conclusions that may be drawn with regard to the nature of the various defects that occur in these lattices.
According to the chemical concepts of the apatites, the Ca/P mole ratio of Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ should be 1.67. Nevertheless, Arnold$^{2-41}$ reported mole ratios from 1.33 up to 1.95 for materials showing the apatite structure. According to Schleede et al.$^{2-42}$ calcium phosphates are hydrolysed in aqueous suspension to Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ especially at higher temperatures. When the initial mole ratio differs from 1.67, the final suspension contains either Ca$^{2+}$ or PO$_4^{3-}$ ions. The PO$_4^{3-}$ ions may give rise to a further hydrolysis PO$_4^{3-}$ → HPO$_4^{2-}$ → H$_2$PO$_4^{-}$, depending upon the pH of the suspension. Trömel and Möller$^{2-25}$ calculated that a monomolecular layer of phosphate ions, when adsorbed on the surface of apatite crystals with a mean particle size of 10$^{-2}$ μ, would change the analytical chemical composition of the apatite from a Ca/P mole ratio of 1.67 to 1.50. Bale et al.$^{2-43}$ and Hendricks and Hill$^{2-44}$ agreed with this surface-adsorption hypothesis. Mattson et al.$^{2-45}$ showed that the finely divided particles of a precipitated Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ behaved like those of an amphoteric colloid.

Posner and Perloff$^{2-46}$ challenged the surface-sorption hypothesis by means of a calculation dealing with particle sizes and chemical composition. Moreover, Posner and Stephenson$^{2-47}$ showed that hydrothermal crystal growth of an apatite with a Ca/P mole ratio of 1.5 did not lead to desorption of any phosphate. Weikel and Neuman$^{2-48}$, using radioactive-tracer techniques, found that the ratio of Ca exchange as compared to P exchange was the same for two different hydroxyapatites having Ca/P mole ratios of 1.50 and 1.67, respectively. From these references it may be concluded that the adsorption hypothesis as proposed by Trömel$^{2-25}$ is not correct.

Dallemagne and Brasseur$^{2-49,50}$ assumed that two hydrogen ions are substituted for a Ca$^{2+}$ ion. This hypothesis, however, is not supported by crystallographic considerations. Arnold$^{2-41}$ proposed that two hydrogen ions and three moles of water replace two Ca$^{2+}$ ions and two OH$^{-}$ ions.

Neuman and Neuman$^{2-51}$ reviewed both the adsorption and the isomorphic-substitution hypothesis. These authors assumed that the variable composition of hydroxyapatites may be explained by a surface substitution on tiny crystallites. A detailed calculation based on measured surface area showed that this hypothesis can explain the data in the case of a tricalcium phosphate with apatite structure and a Ca/P mole ratio of 1.5 which was studied critically. An isomorphic substitution of a hydronium ion for a calcium ion was postulated in the surface positions and it can explain the existence of precipitates possessing the apatite structure with a Ca/P mole ratio smaller than 1.67. The existence of precipitates with a higher Ca/P mole ratio than 1.67 was ascribed to a surface substitution of carbonate for phosphate.

From X-ray-diffraction and index-of-refraction data Posner and Perloff$^{2-46}$ and Posner$^{2-52}$ have put forward the hypothesis that calcium atoms located on Ca$_1$ sites are missing at random throughout the lattice. Electric neutrality
is achieved through hydrogen ions, probably present as hydrogen bonds between the oxygens of adjacent phosphate tetrahedra. Winand \(^2\) proposed that "non-stoichiometric" calcium hydroxyapatite may be represented by the formula \(\text{Ca}_{10-x}\text{H}_x(\text{PO}_4)_6(\text{OH})_{2-x}\). According to Winand and Brasseur \(^2\) and to Taves \(^2\) this formula also applies to octacalcium phosphate \((x = 2)\). Winand's \(^2\) substitution hypothesis is in good agreement with the experiments of Baudrienghien and Brasseur \(^2\). These authors found that a non-stoichiometrical calcium hydroxychlorapatite, \(\text{Ca}_{10-x}\text{H}_x(\text{PO}_4)_6\text{OH}_{2-x-y}\text{Cl}_y\), was formed when hydrated tricalcium phosphate, \(\text{Ca}_9\text{H}(\text{PO}_4)_6\text{OH}\cdot x\text{H}_2\text{O}\) is heated in an aqueous solution of calcium chloride. When heated to 900°C this non-stoichiometrical hydroxychlorapatite decomposes forming a stoichiometrical hydroxychlorapatite and orthophosphate. Both the molar ratio apatite/\(\text{Ca}_3(\text{PO}_4)_2\) and the lattice constants of the apatite depend upon the temperature at which the hydrated tricalcium phosphate is treated with the \(\text{CaCl}_2\) solution.

A survey of some precipitated materials with the apatite crystal structure is given in table 2-IV.

<table>
<thead>
<tr>
<th>apatite</th>
<th>lattice constants</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2)</td>
<td>9·42 6·94 0·737</td>
<td>2-6</td>
</tr>
<tr>
<td>(\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2)</td>
<td>9·410 6·865 0·730</td>
<td>2-9</td>
</tr>
<tr>
<td>(\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2)</td>
<td>9·423 6·884 0·731</td>
<td>2-58</td>
</tr>
<tr>
<td>(\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2)</td>
<td>9·418 6·883 0·731</td>
<td>2-59</td>
</tr>
<tr>
<td>(\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2)</td>
<td>9·432 6·881 0·730</td>
<td>2-60</td>
</tr>
<tr>
<td>(\text{Sr}_{10}(\text{PO}_4)_6(\text{OH})_2)</td>
<td>9·761 7·277 0·746</td>
<td>2-58</td>
</tr>
<tr>
<td>(\text{Sr}_{10}(\text{PO}_4)_6(\text{OH})_2)</td>
<td>9·760 7·284 0·746</td>
<td>2-59</td>
</tr>
</tbody>
</table>

2.5. The presence of vacancies in the apatite crystal structure

From the structural data mentioned before it follows that the unit cell of an apatite has 42 sites. In the complete apatite 10 of these sites are occupied by M atoms, 6 by X atoms, 24 by oxygen atoms and 2 by Z atoms. In all the apatites studied so far it is presumably necessary for the M and X sites to be occupied. A proportion of the M sites may be occupied by H atoms, e.g. in materials prepared in aqueous solution, but these materials are less stable at
elevated temperatures and decompose into an apatite with an M/P mole ratio of 1.67 and orthophosphate. On the other hand the Z sites may be completely unoccupied. It follows from table 2-III that Z vacancies occur in some leadapatites and in compounds corresponding to the formula $M_8Na_2(PO_4)_6$.

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2-4) M. Mehmel, Z. Krist. 75, 323-331, 1930.
2-7) C. A. Bevers and D. B. McIntyre, Mineral Mag. 27, 254-257, 1946.
2-8) R. Nacken, Zent. Min. Geol., 545-559, 1912.
2-17) A. H. McKee, U.S. Patent 2,201,698, 1940.
2-31) G. Hägele and F. Machatschki, Naturw. 27, 132-133, 1939.
3. MATERIALS USED AND METHODS EMPLOYED

3.1. Materials used

The calcium and phosphorus compounds used in our investigations were either CaCO$_3$ and CaHPO$_4$ or phosphates prepared from these materials.

3.1.1. The starting materials

The starting materials CaHPO$_4$ and CaCO$_3$ were those normally used in the preparation of Ca-halophosphate phosphors.

The chemical analysis of the CaHPO$_4$ was CaO: 41·15%, P$_2$O$_5$: 51·0% (theor. CaO: 41·22%, P$_2$O$_5$: 52·17%). The Ca/P mole ratio of the CaHPO$_4$ used is 1·024, which is probably due to a contamination of the CaHPO$_4$ by a small amount of apatite, or hydrated tricalcium phosphate that can be represented by the formula Ca$_9$H(PO$_4$)$_6$OH. $x$H$_2$O according to Winand $^3$-1). When preparing mixtures with this CaHPO$_4$, the excess of Ca is compensated for either by adding a smaller amount of CaCO$_3$ or by adding an additional quantity of phosphate, such as (NH$_4$)$_2$HPO$_4$. The average particle diameter as measured by the Fisher sub-sieve sizer is 6·4 $\mu$. The particle-size distribution as found by the Bahco analyser is given in table 3-1.

The CaCO$_3$ employed had the calcite crystal lattice and contained 56·05 wt % of CaO (theor. 56·10%). The average particle diameter is 5·8 $\mu$ and the particle-size distribution is also shown in table 3-1.

| Table 3-I |
| The particle-size distribution of the CaHPO$_4$ and CaCO$_3$ employed (Bahco method) |

<table>
<thead>
<tr>
<th>fraction in $\mu$</th>
<th>CaHPO$_4$ wt % in the fraction</th>
<th>CaCO$_3$ wt % in the fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>$&lt;$ 2·4</td>
<td>1·6</td>
<td>0·5</td>
</tr>
<tr>
<td>2·4- 3·6</td>
<td>4·9</td>
<td>0·6</td>
</tr>
<tr>
<td>3·6- 6·0</td>
<td>13·8</td>
<td>8·9</td>
</tr>
<tr>
<td>6·0-12·0</td>
<td>38·0</td>
<td>46·6</td>
</tr>
<tr>
<td>12·0-18·0</td>
<td>26·7</td>
<td>33·5</td>
</tr>
<tr>
<td>18·0-28·0</td>
<td>10·4</td>
<td>8·3</td>
</tr>
<tr>
<td>$&gt;$ 28·0</td>
<td>4·6</td>
<td>1·6</td>
</tr>
</tbody>
</table>
3.1.2. The intermediates

The other calcium phosphates were prepared from a mixture of CaHPO₄ and either (NH₄)₂HPO₄ or CaCO₃. The reaction mixtures were heated in open quartz-glass crucibles and a survey concerning composition and firing conditions is given in table 3-11. Between two firings the reaction products were dry ball-milled in order to get a thorough mixture. It may be noticed that firing at relatively low temperatures and ball-milling before the material is submitted to a higher temperature prevents any blasting of the final product. X-ray-diffraction analysis confirmed that pure compounds are obtained.

3.1.3. Other materials used

The phosphate (NH₄)₂HPO₄ was of analytical grade and had been obtained from Union Chimique Belge S.A. This material contained 53.8 wt % of P₂O₅, which corresponds to the theoretical content. It was rather coarsely crystallized and in order to obtain homogeneous mixtures it was mortar-ground before adding it to the reaction mixtures.

The materials NH₄Cl, Sb₂O₃ and MnCO₃ were of luminescent grade as normally used in the production of Ca-halophosphate phosphors. The Cl percentage of the NH₄Cl used amounted to 66.45 wt % (theor. 66.36 %). The Sb₂O₃ content of the Sb₂O₃ employed was found as 99.9-100%. The MnCO₃ contained 45.1 % Mn²⁺ (theor. 47.8 %). Spectrochemical analysis did not show any impurities present.

Antimony oxychloride approximately corresponding to the formula Sb₄O₃Cl₂ was obtained from British Drug Houses Ltd. The Sb percentage was 75.7 % (theor. 76.3 %) and the Cl percentage was 12.5 % (theor. 11.1 %).

The compound SbCl₃ was supplied by Hooker, New York. The Sb percentage was 53.0 % (theor. 53.4 %) and the Cl percentage was 47.0 % (theor. 46.6 %). This material is very hygroscopic and therefore it was stored in a desiccator over P₂O₅.

When heating experiments were carried out in nitrogen, “lamp-grade” nitrogen was used. The “oxygen content”, including H₂O and CO₂, was lower than 0.003 %.

3.2. Ball-milling

Ball mills may be used for mixing, in which the particle size of the ingredients is not affected, or for real grinding in which the purpose is to break up the particles. About 20 % of the mill’s volume is filled with ½” pebbles when it is employed as a mixer for dry powdered materials. For grinding, about 45 % of its volume is filled with ½” pebbles. The speeds of the mills in mixing and grinding for the 1-5-1 and the 5-1 mills were 42 and 34 r.p.m, respectively.

When preparing small amounts of mixtures, e.g. 10-20 g, a cylindrical glass
TABLE 3-II
Survey of the preparation of various phosphates

<table>
<thead>
<tr>
<th>phosphate</th>
<th>$\beta$ - Ca(PO$_3$)$_2$</th>
<th>$\beta$ - Ca$_2$P$_2$O$_7$</th>
<th>$\beta$ - Ca$_3$(PO$_4$)$_2$</th>
<th>$\beta$ -(Ca,Mn)$_3$(PO$_4$)$_2$</th>
<th>Ca$_{10}$(PO$_4$)$_6$(OH)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>composition of the</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>firing mixture</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>moles of CaHPO$_4$</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>moles of (NH$_4$)$_2$HPO$_4$</td>
<td>1</td>
<td>very small</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>moles of CaCO$_3$</td>
<td></td>
<td>1</td>
<td>1 - x</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>moles of MnCO$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>firing conditions</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>first firing</td>
<td>2 h to 400 °C</td>
<td>2 h to 600 °C</td>
<td>3 h to 1000 °C</td>
<td>3 h to 1000 °C</td>
<td>3 h to 900 °C wet air</td>
</tr>
<tr>
<td>second firing</td>
<td>4 h to 600 °C</td>
<td>3 h to 900 °C</td>
<td>16 h to 1000 °C</td>
<td>16 h to 1000 °C</td>
<td>16 h to 1000 °C wet air</td>
</tr>
<tr>
<td>third firing</td>
<td>16 h to 800 °C</td>
<td></td>
<td></td>
<td>3 h to 1000 °C in N$_2$</td>
<td></td>
</tr>
</tbody>
</table>
bottle with a diameter of 5 cm and a height of 4 cm, provided with a plastic screw lid and filled with 30 g of steatite balls with a diameter of 5 mm, was used. This bottle was shielded by a steel cylinder of the same outer diameter as the 1·5-1 porcelain mill.

A milling time of 3 hours was employed in making mixtures whereas the milling time in grinding depends upon the desired decrease in particle size.

3.3. Measurement of the particle size and the particle-size distribution

The average particle diameter \( d_m \) of a powdered material was determined by the Fisher sub-sieve sizer, an instrument made by Fisher Scientific Corp., Pittsburgh, U.S.A. This instrument employs what is generally known as the air-permeability method. The principles of this method have been established by Gooden and Smith \(^3\). The particle-size distribution of powdered materials was determined by the Bahco centrifugal dust classifier. This apparatus is made by Messrs. Etablissements Neu, Lille, France, as licensee for B. A. Hjorth and Co., Bahco, Sweden \(^3\). This apparatus is essentially a centrifugal air elutriator. Air and dispersed powder particles are drawn through the cavity of a rotating hollow disc in a radially inward direction against centrifugal forces. The particles are thus divided into undersized and oversized fractions, collected and weighed. Separation into fractions of different size is made by altering the air velocity. The theoretical basis for this method of sifting a powdered material has been studied by Wolf and Rumpf \(^3\).

3.4. X-ray analysis

The X-ray-diffraction patterns are powder patterns obtained with nickel-filtered CuK\(\alpha\) radiation using a North American Philips Geiger-counter X-ray diffractometer.

3.5. Chemical analytical methods

The Ca content of CaHPO\(_4\) and CaCO\(_3\) was determined by complexometric titration employing Erio T-black as an indicator \(^3\). The absolute difference in duplex determinations did not exceed 0·1\%.

The P\(_2\)O\(_5\) content in calcium phosphates was also determined by complexometric titration \(^3\) after removing the Ca ions from the hydrochloric-acid solution by means of an Amberlite I.R. 120 resin \(^3\). The absolute difference in duplex determinations did not exceed 0·1\%.

The Cl percentage was determined by the Volhard method \(^3\). The absolute difference in duplex determinations did not exceed 0·04\%.

The Sb\(^{3+}\) percentage was determined by bromometric titration. This method has been described elsewhere \(^3\). The absolute difference in duplex determinations did not exceed 0·02\%.
The Ca$_2$P$_2$O$_7$ percentage in reaction products was determined by colorimetric titration in a perchloric-acid solution before and after the hydrolysis of the P$_2$O$_7^{4-}$ ions; Sb$^{3+}$ incorporated into either one of the phases present in the sample gives rise to erroneous results, probably due to the fact the sample dissolves too slowly, so that the P$_2$O$_7^{4-}$ ions partly hydrolyse before their determination has been carried out\(^{3-9}\).

### 3.6. Optical measurements

Spectral-energy distribution (s.e.d.) curves of the luminescence of final reaction products were normally determined over the range of 380-640 nm by a single grating monochromator provided with a recorder. The excitation source was a quartz-glass low-pressure mercury-vapour-discharge lamp with an appropriate filter, mainly emitting 254-nm radiation.

The apparatus employed for the measurement of the brightness, in respect to blue Ca halophosphate, and of the u.v. absorption, in respect to ZnO, has been described elsewhere\(^{3-10}\).

### REFERENCES

3-3) U.S. Patent 2,546,068, 1951.
3-5) G. Schwarzenbach and H. Flaschka, Die komplexometrische Titration, Enke, Stuttgart, 1965, pp. 144(a) and 234(b).
3-9) E. G. Berns, private communication.
4. CALCIUM CHLORAPATITE

4.1. Introduction

Nacken \(^4\) has given a survey of the preparation methods of calcium chlorapatite as carried out by several investigators, all employing the method of melting \(\text{CaCl}_2\) and \(\text{Ca}_3(\text{PO}_4)_2\) and using \(\text{NaCl}\) and \(\text{Na}_3\text{PO}_4\) as a flux. Hendricks et al. \(^2\) prepared it in the form of microscopic hexagonal crystals by heating a mixture of the theoretical amounts of \(\text{CaCl}_2\) and \(\text{Ca}_3(\text{PO}_4)_2\) to about 1400 °C in air. From X-ray-diffraction analysis the lattice constants of the hexagonal unit cell were calculated as \(a = 9.52 \text{ Å}\) and \(c = 6.05 \text{ Å}\).

Wallaeys \(^3\) found from X-ray-diffraction analysis that a mixture of 3 moles of \(\text{Ca}_3(\text{PO}_4)_2\) and 1 mole of \(\text{CaCl}_2\) starts to react when heated to 600 °C. Complete reaction was obtained by a firing process at 900 °C during twelve hours. Absence of water vapour was necessary since chlorapatite is very subject to pyrohydrolysis at temperatures higher than about 800 °C according to the overall reaction

\[
\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2 + 2x \text{H}_2\text{O} \rightarrow \text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2 - 2x(\text{OH})_{2x} + 2x \text{HCl}. \quad (4.1)
\]

Wallaeys also found that when an equimolar mixture of \(\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2\) and \(\text{CaCl}_2\) is heated to 800-900 °C, chlorapatite is formed according to the reaction equation

\[
\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + \text{CaCl}_2 \rightarrow \text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2 + \text{CaO} + \text{H}_2\text{O}. \quad (4.2)
\]

However, no pure chlorapatite is obtained like this; moreover, it was found that the final product contains less chlorine than corresponds to the chemical formula.

In large-scale halophosphate production the starting mixture contains \(\text{CaHPO}_4\), \(\text{CaCO}_3\), \(\text{CaF}_2\), \(\text{NH}_4\text{Cl}\), \(\text{Sb}_2\text{O}_3\) and \(\text{MnCO}_3\). A considerable loss of chlorine and antimony is always observed. This may be due to various effects: the \(\text{HCl}\) formed during the dissociation of the ammonium chloride may not completely react with the calcium carbonate, part of it may react with the antimony trioxide and volatilize as antimony trichloride, pyrohydrolysis may occur at higher temperatures, and so on. The possibilities are too many to be unravelled from thermoanalysis curves or experiments in which the firing is interrupted at various stages. It was therefore decided to study the simpler problems encountered in the synthesis of pure unactivated calcium chlorapatite, starting from the ingredients \(\text{CaHPO}_4\), \(\text{CaCO}_3\) and \(\text{NH}_4\text{Cl}\) commonly used in halophosphate manufacture. Moreover, we studied the reaction between calcium hydroxyapatite and ammonium chloride, hoping that this reaction would lead to pure calcium chlorapatite. This turned out to be impossible, but a reliable method of preparing chlorapatite was found in firing hydroxyapatite.
in a stream of gaseous hydrochloric acid. The results obtained in this work induced us to study the reaction between calcium orthophosphate and hydrochloric acid also. Finally we shall discuss the structure of the calcium hydroxychlorapatites.

4.2. The reaction between CaHPO₄, CaCO₃ and NH₄Cl in stoichiometrical proportions

A mixture of 6 moles of CaHPO₄, 4 moles of CaCO₃ and 2 moles of NH₄Cl was heated in amounts of about 500 mg in a covered crucible of about 2 ml on a Stanton thermobalance. This type of thermobalance has been described by Duval. The weight loss determined and expressed as a percentage of the original weight of the mixture has been plotted as a function of temperature. A typical curve is shown in fig. 4.1. From the weight loss found in the region

\[ \text{CaCO}_3 + 2 \text{NH}_4\text{Cl} \rightarrow \text{CaCl}_2 + 2 \text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O}. \quad (4.3) \]

Other weight losses are recorded at 400-500 °C and at 500-900 °C. These are

![Graph showing weight loss as a function of temperature](image-url)
TABLE 4-I

Heating experiments using a mixture of 6 moles of CaHPO₄, 4 moles of CaCO₃ and 2 moles of NH₄Cl to various temperatures in air

<table>
<thead>
<tr>
<th>reaction temp. (°C)</th>
<th>weight loss (%)</th>
<th>chlorine present (fraction of original amount)</th>
<th>water-soluble chlorine</th>
<th>calcite detected by microscope</th>
<th>phases as found by X-ray-diffraction analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CaCO₃</td>
</tr>
<tr>
<td>300</td>
<td>5·08</td>
<td>1·00</td>
<td>++</td>
<td>+++</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>7·70</td>
<td>0·98</td>
<td>++</td>
<td>+++</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>13·37</td>
<td>0·88</td>
<td>++</td>
<td>+++</td>
<td>+</td>
</tr>
<tr>
<td>600</td>
<td>15·18</td>
<td>0·915</td>
<td>+</td>
<td>++</td>
<td>+</td>
</tr>
<tr>
<td>700</td>
<td>18·55</td>
<td>0·93</td>
<td>+</td>
<td>++</td>
<td>+</td>
</tr>
<tr>
<td>800</td>
<td>21·64</td>
<td>0·94</td>
<td>+?</td>
<td>+?</td>
<td>+?</td>
</tr>
<tr>
<td>1100</td>
<td>21·90</td>
<td>0·925</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>1200</td>
<td>22·06</td>
<td>0·90</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Relative quantities and relative intensities of the strongest diffraction lines: +++ very high, ++ high, + medium, +? trace, ? questionable, — absent.
attributed to the dehydration of the CaHPO₄ and the dissociation of the CaCO₃ and have been described by Wanmaker and Verheyke⁴⁻⁵. The theoretical weight loss of the firing mixture when all reactions have been completed, is calculated as 21·72%. From fig. 4.1 it may be seen that this weight loss is reached at 900 °C. When the firing was interrupted at this temperature, and the sample analysed, it was found that the chlorine content is only 6·2% (theoretical chlorine content of Ca₁₀(PO₄)₆Cl₂ is 6·81%). Microscopic investigation under polarized light showed that some undissociated calcium carbonate was still present. Apparently a loss of chlorine occurs at temperatures below 900 °C.

In order to get more detailed information about these reactions, quantities of about 20 g of the mixture consisting of 6 moles of CaHPO₄, 4 moles of CaCO₃ and 2 moles of NH₄Cl have been heated to various temperatures in covered quartz-glass crucibles of 50 ml for two hours. The weight loss (wt%) and the amount of chlorine ions in the reaction product, expressed as the fraction of the amount originally present are given in table 4-I.

The presence of water-soluble chloride (indicating CaCl₂ not reacted to Ca₁₀(PO₄)₆Cl₂), unreacted CaCO₃ (as detected by microscopic analysis) and the phases as found by X-ray analysis are also given in this table. From these figures it follows that the chloride is taken up quantitatively by the calcium carbonate to a reaction temperature of 400 °C *).

At higher reaction temperatures, viz. temperatures of 500 °C and above, a loss of chloride is found. This loss must be ascribed partly to pyrohydrolysis of chlorapatite at low temperatures, partly to a reaction of the CaCl₂ present and the water formed by dehydrating the CaHPO₄. This statement follows from the observation that this loss of chlorine was proved to be lower when the CaHPO₄ is replaced by an equivalent amount of Ca₂P₂O₇.

From the data of table 4-I it can be seen that calcium chlorspodiosite, Ca₃(PO₄)₂·CaCl₂, is present as an intermediate in the temperature range of 500-800 °C. Obviously the reaction

\[
3 \text{Ca}_2\text{P}_2\text{O}_7 + 3 \text{CaCO}_3 + \text{CaCl}_2 \rightarrow \text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2 + 3 \text{CO}_2
\]  \hspace{1cm} (4.4)

takes place in two steps; first spodiosite is formed according to the reaction

\[
\text{Ca}_2\text{P}_2\text{O}_7 + \text{CaCO}_3 + \text{CaCl}_2 \rightarrow \text{Ca}_4(\text{PO}_4)_2\text{Cl}_2 + \text{CO}_2,
\]  \hspace{1cm} (4.5)

then spodiosite is converted into apatite according to

\[
\text{Ca}_4(\text{PO}_4)_2\text{Cl}_2 + 2 \text{Ca}_2\text{P}_2\text{O}_7 + 2 \text{CaCO}_3 \rightarrow \text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2 + 2 \text{CO}_2.
\]  \hspace{1cm} (4.6)

From fig. 4.1 it is clear that the dissociation of the CaCO₃ between 500 °C and

---

*) This is also a matter of the reactivity of the CaCO₃; with a coarser, less reactive CaCO₃ (\(d_m = 22 \mu\)) part of the hydrochloric acid escaped.
900 °C takes place in two steps. In the first step (500-700 °C) a weight loss of about 3.5% (absolute) is found; this is followed by a second one of about 7%. The fact that the second weight loss is twice the first one is in agreement with reactions (4.5) and (4.6).

As already mentioned, a small amount of calcium carbonate is still present after the mixture has been heated to 900 °C. Consequently part of the weight loss found above this temperature must be ascribed to the decomposition of these traces of carbonate. As the amount of chloride present in the reaction product decreases with increasing reaction temperature, the other part of the weight loss must be ascribed to other reactions. Presumably a certain amount of the Ca₁₀(PO₄)₆Cl₂ is hydrolysed to Ca₁₀(PO₄)₆(OH)₂ and HCl by water vapour present in the surrounding air. In order to estimate the contribution of the pyrohydrolysis we carried out the following experiment. A mixture of 6 moles of CaHPO₄, 4 moles of CaCO₃ and 2 moles of NH₄Cl was heated to 600 °C for two hours. From the data in table 4-I it may be expected that the water formed by reaction (4.3) and by the dehydration of CaHPO₄ has been completely removed. The dehydrated material was fired to 1180 °C for another two hours in a stream of dry nitrogen, in atmospheric air and in wet air, respectively. From the weight loss and the Cl percentage we found that the heating process in wet air causes a considerable loss of chlorine (about 1 mole/mole of apatite), whereas this loss is either rather small (0.06 mole/mole) or negligible if the firing takes place in normal air or in dry nitrogen, respectively.

No Ca₁₀(PO₄)₆Cl₂ could be prepared in this way with the stoichiometrical amount of chloride. Even using twice the theoretical amount of NH₄Cl did not give good results.

4.3. The reaction found in firing mixtures consisting of CaHPO₄, CaCO₃ and NH₄Cl with an excess of phosphate

As discussed in chapter 1, commercial halophosphates are generally made with an excess of phosphate. It was therefore also interesting to study the behaviour of undoped mixtures using an excess of phosphate. The result will be mainly chlorapatite and pyrophosphate.

Samples of about 25 g of mixtures containing 6 moles of CaHPO₄, 2-3.7 moles of CaCO₃ and 2 moles of NH₄Cl, were heated in covered 50-ml crucibles to 1180 °C for various lengths of time. The theoretical amounts of chlorapatite and pyrophosphate can be calculated from the chemical composition of the original mixture. These theoretical amounts are defined as the amounts present if the calcium and the phosphorus are distributed only between an apatite and a pyrophosphate phase. The actual amounts of the chlorine and the pyrophosphate present in the final product are given in figs 4.2 and 4.3, respectively, as percentages of the calculated theoretical amounts (percentages retained) for various Ca/P mole ratios M. Note that \( M = 1.67 \) applies to the theoretical mole ratio...
Fig. 4.2. The percentage of chlorine retained after heating a mixture of CaHPO$_4$, CaCO$_3$ and NH$_4$Cl with a Ca/P mole ratio $M$ to 1180 °C in air.

Fig. 4.3. The percentage of pyrophosphate retained after heating a mixture of CaHPO$_4$, CaCO$_3$ and NH$_4$Cl with a Ca/P mole ratio $M$ to 1180 °C in air.

of an apatite. From the figures it is clear that the chlorine and pyrophosphate content decrease on prolonged heating.

The phases, as found by X-ray analysis, have been recorded in table 4-II for $M = 1.616$ and in table 4-III for $M = 1.500$. In addition to the pyrophosphate and the apatite, we find reflections characteristic of orthophosphate. The actual distribution of the phosphate between the apatite, the orthophosphate and the pyrophosphate phases can be calculated from the overall composition, the chlorine and the pyrophosphate content. From tables 4-II and 4-III it follows that these calculated amounts agree reasonably well with the relative quantities as found by X-ray analysis.

In fig. 4.4 the molar fractions of the phosphorus present in the apatite, the pyrophosphate and the orthophosphate phases have been plotted as a function of reaction time for various values of $M$. The mole fractions of the phosphorus present in the theoretical amounts as defined above have been put in at reaction time zero. From fig. 4.4 it appears that when $M < 1.67$ the amounts of apatite and pyrophosphate decrease whereas the amount of orthophosphate increases with prolonged firing. This can be explained as follows: in a separate experiment
TABLE 4-II
Phases found by X-ray analysis and by calculation after heating a mixture of CaHPO$_4$, CaCO$_3$ and NH$_4$Cl with a Ca/P mole ratio $M = 1.616$ in air

<table>
<thead>
<tr>
<th>reaction time (h)</th>
<th>theoretical amounts</th>
<th>0.5</th>
<th>2</th>
<th>4</th>
<th>8</th>
<th>16</th>
<th>96</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X-ray-diffraction pattern</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>apatite</td>
<td>s</td>
<td>s</td>
<td>s</td>
<td>s</td>
<td>s</td>
<td>s</td>
<td>s</td>
</tr>
<tr>
<td>$\beta$ - Ca$_2$P$_2$O$_7$</td>
<td>m</td>
<td>vw</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>$\beta$ - Ca$_3$(PO$_4$)$_2$</td>
<td>vw?</td>
<td>vw?</td>
<td>w</td>
<td>w-m</td>
<td>a</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>$\alpha$ - Ca$_3$(PO$_4$)$_2$</td>
<td>a</td>
<td>vw</td>
<td>w</td>
<td>w-m</td>
<td>m</td>
<td>m</td>
<td>m</td>
</tr>
<tr>
<td>molar quantities calculated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>apatite</td>
<td>0.925</td>
<td>0.84</td>
<td>0.79</td>
<td>0.76</td>
<td>&lt;0.72</td>
<td>&lt;0.72</td>
<td>&lt;0.72</td>
</tr>
<tr>
<td>pyrophosphate</td>
<td>0.225</td>
<td>0.14</td>
<td>0.09</td>
<td>0.06</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>orthophosphate</td>
<td>0</td>
<td>0.34</td>
<td>0.54</td>
<td>0.66</td>
<td>&gt;0.82</td>
<td>&gt;0.82</td>
<td>&gt;0.82</td>
</tr>
</tbody>
</table>

Relative intensities of the strongest diffraction lines: s = strong, m = medium, w = weak, vw = very weak, ? = questionable, a = absent.

TABLE 4-III
Phases found by X-ray analysis and by calculation after heating a mixture of CaHPO$_4$, CaCO$_3$ and NH$_4$Cl with a Ca/P mole ratio $M = 1.500$ in air

<table>
<thead>
<tr>
<th>reaction time (h)</th>
<th>theoretical amounts</th>
<th>0.5</th>
<th>2</th>
<th>4</th>
<th>8</th>
<th>16</th>
<th>96</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X-ray-diffraction pattern</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>apatite</td>
<td>s</td>
<td>s</td>
<td>m</td>
<td>m</td>
<td>m</td>
<td>w</td>
<td>a</td>
</tr>
<tr>
<td>$\beta$ - Ca$_2$P$_2$O$_7$</td>
<td>m</td>
<td>m</td>
<td>w</td>
<td>w</td>
<td>w</td>
<td>vw</td>
<td>a</td>
</tr>
<tr>
<td>$\alpha$ - Ca$_3$(PO$_4$)$_2$</td>
<td>vw</td>
<td>w</td>
<td>w-m</td>
<td>m</td>
<td>s</td>
<td>s</td>
<td>s</td>
</tr>
<tr>
<td>molar quantities calculated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>apatite</td>
<td>0.750</td>
<td>0.67</td>
<td>0.60</td>
<td>0.53</td>
<td>0.45</td>
<td>0.16</td>
<td>0</td>
</tr>
<tr>
<td>pyrophosphate</td>
<td>0.750</td>
<td>0.67</td>
<td>0.60</td>
<td>0.53</td>
<td>0.45</td>
<td>0.16</td>
<td>0</td>
</tr>
<tr>
<td>orthophosphate</td>
<td>0</td>
<td>0.33</td>
<td>0.60</td>
<td>0.88</td>
<td>1.19</td>
<td>2.36</td>
<td>3.00</td>
</tr>
</tbody>
</table>

Relative intensities of the strongest diffraction lines: s = strong, m = medium, w = weak, vw = very weak, a = absent.
Fig. 4.4. The mole fraction of phosphorus actually present in the various phases of samples prepared by heating a mixture of CaHPO$_4$, CaCO$_3$ and NH$_4$Cl with a Ca/P mole ratio $M$ to 1180 °C in air.

it was found by X-ray analysis and from weight loss that when equimolar amounts of calcium hydroxyapatite and calcium pyrophosphate were heated to 1180 °C for one hour, complete conversion into calcium orthophosphate takes place according to the equation

$$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + \text{Ca}_2\text{P}_2\text{O}_7 \rightarrow 4 \text{Ca}_3(\text{PO}_4)_2 + \text{H}_2\text{O}. \quad (4.7)$$
In the experiments involved the chlorine content decreases, which must be attributed to partial hydrolysis of the chlorapatite. Apparently the hydroxyapatite formed reacts with pyrophosphate according to eq. (4.7). From the calculated amounts of the various phases actually present (tables 4-II and 4-III) it appears that the decrease in the molar amounts of the apatite and the Ca$_3$P$_2$O$_7$ is the same within the experimental error. Moreover, the sum of these decreases amounts to half the amount of Ca$_3$(PO$_4$)$_2$ formed. From table 4-II it follows, e.g. that for a firing time of half an hour

the decrease in apatite is 0·925 mole—0·84 mole = 0·085 mole,
the decrease in pyrophosphate is 0·225 mole—0·14 mole = 0·085 mole,
the quantity of orthophosphate is 0·34 mole.

These results are in agreement with reaction (4.7).

4.4. The reaction between Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ and NH$_4$Cl

In our first attempts to make pure chlorapatite we employed a mixture of Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ and NH$_4$Cl. We preferred to replace the CaCl$_2$, which had been used by Wallaeys$^{4-3}$, by NH$_4$Cl in order to avoid contamination of the reaction products with CaO. Thorough mixtures of one mole of Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ and a variable amount of NH$_4$Cl ($y$ moles) were made by ball-milling. The coarsely crystallised NH$_4$Cl was mortar-ground beforehand. A quantity of about 25 g of these mixtures was heated to 1180 °C in air in a covered crucible for half an hour. From the change in weight we determined the weight of the apatite obtained (per mole). The amount of chlorine (moles per mole of apatite) incorporated in it follows from the chemical analysis. These data have been entered in table 4-IV.

Assuming that the reaction equation is

$$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + y \text{ NH}_4\text{Cl} \rightarrow \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 - y - z \text{Cl} + (y - z)\text{NH}_3 + (y - z)\text{H}_2\text{O} + z \text{NH}_4\text{Cl},$$

(4.8)

we calculated the theoretical weight ($G_{\text{th}}$) of the reaction product from the experimental amount of chlorine. When these data are compared with the actual weight ($G_{\text{exp}}$) of the samples, a deficit in weight is observed. This figure is also reported in table 4-IV and will be discussed in sec. 4.8. It follows that under our experimental conditions even a high excess of NH$_4$Cl does not effectuate a complete conversion of the hydroxyapatite into Ca$_{10}$(PO$_4$)$_6$Cl$_2$. Half the Cl$^-$ ions are taken up according to the reaction

$$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + \text{NH}_4\text{Cl} \rightarrow \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})\text{Cl} + \text{H}_2\text{O} + \text{NH}_3.$$

(4.9)

With a larger amount of NH$_4$Cl added an increasing loss of chlorine is found.
### TABLE 4-IV

Heating experiments using mixtures of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ and various amounts of NH$_4$Cl in air

<table>
<thead>
<tr>
<th>mole ratio NH$_4$Cl/apatite</th>
<th>actual weight per mole of apatite</th>
<th>molar amount of chlorine per mole of apatite</th>
<th>deficit weight $G_{\text{m}} - G_{\text{exp}}$</th>
<th>composition of the apatite</th>
<th>lattice constants $a$ (Å)</th>
<th>$c$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1001.7</td>
<td>0.00</td>
<td>3.3</td>
<td>$\text{Ca}_{10}(\text{PO}<em>4)<em>6(\text{OH})</em>{1.63}O</em>{0.185}$</td>
<td>9.411</td>
<td>6.879</td>
</tr>
<tr>
<td>0.25</td>
<td>1005.7</td>
<td>0.25</td>
<td>3.9</td>
<td>$\text{Ca}<em>{10}(\text{PO}<em>4)<em>6(\text{OH})</em>{1.30}O</em>{0.22}\text{Cl}</em>{0.26}$</td>
<td>9.423</td>
<td>6.868</td>
</tr>
<tr>
<td>0.50</td>
<td>1009.9</td>
<td>0.48</td>
<td>4.0</td>
<td>$\text{Ca}<em>{10}(\text{PO}<em>4)<em>6(\text{OH})</em>{1.08}O</em>{0.22}\text{Cl}</em>{0.48}$</td>
<td>9.442</td>
<td>6.856</td>
</tr>
<tr>
<td>0.75</td>
<td>1013.7</td>
<td>0.73</td>
<td>4.8</td>
<td>$\text{Ca}<em>{10}(\text{PO}<em>4)<em>6(\text{OH})</em>{0.74}O</em>{0.265}\text{Cl}</em>{0.73}$</td>
<td>9.490</td>
<td>6.843</td>
</tr>
<tr>
<td>1.00</td>
<td>1017.6</td>
<td>0.98</td>
<td>5.5</td>
<td>$\text{Ca}<em>{10}(\text{PO}<em>4)<em>6(\text{OH})</em>{0.38}O</em>{0.32}\text{Cl}</em>{0.98}$</td>
<td>9.522</td>
<td>6.828</td>
</tr>
<tr>
<td>1.50</td>
<td>1024.4</td>
<td>1.28</td>
<td>4.3</td>
<td>$\text{Ca}<em>{10}(\text{PO}<em>4)<em>6(\text{OH})</em>{0.26}O</em>{0.23}\text{Cl}</em>{1.28}$</td>
<td>9.550</td>
<td>6.806</td>
</tr>
<tr>
<td>2.00</td>
<td>1029.7</td>
<td>1.52</td>
<td>3.4</td>
<td>$\text{Ca}<em>{10}(\text{PO}<em>4)<em>6(\text{OH})</em>{0.12}O</em>{0.18}\text{Cl}</em>{1.52}$</td>
<td>9.589</td>
<td>6.793</td>
</tr>
<tr>
<td>3.00</td>
<td>1034.6</td>
<td>1.73</td>
<td>2.4</td>
<td>$\text{Ca}<em>{10}(\text{PO}<em>4)<em>6(\text{OH})</em>{0.01}O</em>{0.13}\text{Cl}</em>{1.73}$</td>
<td>9.612</td>
<td>6.781</td>
</tr>
<tr>
<td>4.00</td>
<td>1036.7</td>
<td>1.82</td>
<td>2.0</td>
<td>$\text{Ca}_{10}(\text{PO}<em>4)<em>6O</em>{0.09}\text{Cl}</em>{1.82}$</td>
<td>9.621</td>
<td>6.777</td>
</tr>
<tr>
<td>8.00</td>
<td>1040.6</td>
<td>1.94</td>
<td>0.3</td>
<td>$\text{Ca}<em>{10}(\text{PO}<em>4)<em>6(\text{OH})</em>{0.04}O</em>{0.01}\text{Cl}</em>{1.94}$</td>
<td>9.636</td>
<td>6.765</td>
</tr>
</tbody>
</table>

$\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$

$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$

9.638 6.770

9.421 6.882
4.5. The reaction between $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ and gaseous $\text{HCl}$; the preparation of calcium chlorapatite

Remembering the decomposition of chlorapatite with water vapour, it will be clear that there is an equilibrium

$$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + 2 \text{ HCl} \rightleftharpoons \text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2 + 2 \text{ H}_2\text{O}, \quad (4.10)$$

from which it follows that the only way to obtain a pure chlorapatite is to drive the reaction to completeness by means of a continuous supply of $\text{HCl}$ passing through or over the material. Hydroxyapatite may be used as a starting material or a mixed hydroxychlorapatite, for instance as obtained by heating hydroxyapatite with ammonium chloride. We used the hydroxychlorapatite obtained by heating a mixture of 6 moles of $\text{CaHPO}_4$, 4 moles of $\text{CaCO}_3$ and 2 moles of $\text{NH}_4\text{Cl}$, as described in sec. 4.2, and then proceeded as follows.

About 200 g of this material was heated to 1050 °C in a crucible provided with an inlet in the bottom (fig. 4.5) for 3 hours. Per minute a mixture of

450 ml dry nitrogen and 50 ml gaseous hydrochloric acid was passed through the bulk of the apatite. The reaction product was cooled in a nitrogen stream and leached in water to remove adsorbed hydrochloric acid. A pure chlorapatite is obtained by this method. The weight percentage of chlorine was $6.79 \pm 0.02\%$ as compared with the theoretical value of $6.81\%$. 

![Fig. 4.5. The reaction vessel used to heat hydroxyapatite or orthophosphate in a continuous stream of gaseous HCl.](image-url)
4.6. The equilibrium between chlorapatite and hydroxyapatite

In the preceding section the equilibrium between hydroxyapatite and chlorapatite in an atmosphere consisting of HCl and H₂O was briefly mentioned. More information on this equilibrium was obtained in the experiment described below.

Two open quartz-glass boats A and B containing 0.005 mole of Ca₁₀(PO₄)₆Cl₂ and 0.005 mole of Ca₁₀(PO₄)₆(OH)₂, respectively, were put together into a quartz-glass tube which could be evacuated. After evacuating, the tube was closed and heated to 1100 °C for various periods of time. After cooling, the content of each boat was weighed and analysed for Cl. The experimental results are given in table 4-V.

TABLE 4-V

The weight and the Cl percentage of the apatites obtained by heating Ca₁₀(PO₄)₆(OH)₂ and Ca₁₀(PO₄)₆Cl₂ in two separate boats in a closed evacuated system

<table>
<thead>
<tr>
<th>Reaction time (h)</th>
<th>Boat A started from Ca₁₀(PO₄)₆(OH)₂</th>
<th>Boat B started from Ca₁₀(PO₄)₆Cl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight per mole of apatite (g)</td>
<td>% Cl</td>
</tr>
<tr>
<td>0</td>
<td>1005.0</td>
<td>0.00</td>
</tr>
<tr>
<td>2.5</td>
<td>1007.0</td>
<td>0.90</td>
</tr>
<tr>
<td>7.5</td>
<td>1018.1</td>
<td>3.16</td>
</tr>
<tr>
<td>24</td>
<td>1019.2</td>
<td>3.43</td>
</tr>
</tbody>
</table>

It is clear that the two samples approximate to the same overall composition. Moreover, the X-ray diagrams are identical. Since practically all of the chlorine is recovered in the solid contents of the boats, very little HCl remained in the gas phase. After cooling, the wall of the tube in which the experiment had been performed was coated with small drops of water, the quantity of which was found from the weight loss of the two boats taken together. The reaction of the water was only slightly acidic. Consequently in the equilibrium condition $P_{H₂O}$ is considerably greater than $P_{HCl}$. As we start with two solids, the reaction can only proceed by means of the gaseous products, water and hydrochloric acid. At 1100 °C the hydroxyapatite will partially decompose and lose some water. This will diffuse towards the chlorapatite, cause pyrohydrolysis and liberate HCl. The HCl will diffuse back, react with the hydroxyapatite, liberate more water
TABLE 4-VI

Reaction mechanism found when heating separate samples of chlorapatite and hydroxyapatite in a closed evacuated tube

<table>
<thead>
<tr>
<th>boat A</th>
<th>boat B</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})<em>2 \rightarrow \text{Ca}</em>{10}(\text{PO}_4)_6\text{O} + \text{H}_2\text{O}$</td>
<td>$\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2 + \text{H}<em>2\text{O} \rightarrow \text{Ca}</em>{10}(\text{PO}_4)_6\text{ClOH} + \text{HCl}$</td>
</tr>
<tr>
<td>$\text{Ca}_{10}(\text{PO}<em>4)<em>6\text{O} + \text{HCl} \rightarrow \text{Ca}</em>{10}(\text{PO}<em>4)<em>6(\text{OH})</em>{0.60}\text{O}</em>{0.20}\text{Cl}</em>{1.00} + \text{+ 0.2H}_2\text{O}$</td>
<td>$\text{Ca}_{10}(\text{PO}<em>4)<em>6\text{ClOH} \rightarrow \text{Ca}</em>{10}(\text{PO}<em>4)<em>6\text{Cl}</em>{1.00}\text{O}</em>{0.20}(\text{OH})</em>{0.60} + \text{+ 0.2H}_2\text{O}$</td>
</tr>
<tr>
<td>$\text{Ca}_{10}(\text{PO}_4)<em>6(\text{OH})<em>2 \rightarrow \text{Ca}</em>{10}(\text{PO}<em>4)<em>6(\text{OH})</em>{0.60}\text{O}</em>{0.20}\text{Cl}</em>{1.00}$</td>
<td>$\text{Ca}_{10}(\text{PO}_4)<em>6\text{Cl}<em>2 \rightarrow \text{Ca}</em>{10}(\text{PO}<em>4)<em>6\text{Cl}</em>{1.00}\text{O}</em>{0.20}(\text{OH})</em>{0.60}$</td>
</tr>
</tbody>
</table>

solid phase in boat A                     solid phase in boat B

$+ 0.40 \text{H}_2\text{O}$ (gaseous phase)
and so on. In this way the equilibrium condition is gradually built up. The mechanism is given in table 4-VI. In sec. 4.8 we shall have a closer look at the composition and the properties of the final solid reaction products.

4.7. The reaction of $\beta$-$\text{Ca}_3(\text{PO}_4)_2$ with HCl

As already mentioned, the pyrohydrolysis of chlorapatite in the presence of pyrophosphate leads to the formation of orthophosphate and gaseous hydrochloric acid. The overall reaction can be represented as follows:

$$\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2 + 2 \text{H}_2\text{O} \rightarrow \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + 2 \text{HCl}$$

$$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + \text{Ca}_2\text{P}_2\text{O}_7 \rightarrow 4 \text{Ca}_3(\text{PO}_4)_2 + \text{H}_2\text{O}$$

$$\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2 + \text{Ca}_2\text{P}_2\text{O}_7 + \text{H}_2\text{O} \rightarrow 4 \text{Ca}_3(\text{PO}_4)_2 + 2 \text{HCl}. \quad (4.11)$$

It should be noted that in the absence of water no reaction between chlorapatite and pyrophosphate occurs.

The question arises as to whether this reaction is reversible, in other words, is a mixture of chlorapatite and pyrophosphate formed when calcium orthophosphate is heated in an atmosphere containing HCl? The following experiment will show that reaction (4.11) is indeed reversible.

A sample of 18 g of $\beta$-$\text{Ca}_3(\text{PO}_4)_2$ was heated at various temperatures for two hours in a crucible as shown in fig. 4.5. During the heating a flow of 500 ml N$_2$/min and 50 ml HCl/min passed through the bulk of the powdered orthophosphate. Both the weight and the amount of chloride present in the reaction product have been plotted as a function of reaction temperature as curve a and curve b, respectively, in fig. 4.6. The chlorine contents found in the materials prepared at reaction temperatures up to 800 °C were differentiated into a water-insoluble form (curve c) and into a water-soluble form (curve d). At lower reaction temperatures the chlorine is completely present in the water-soluble form. X-ray analysis shows that only the $\beta$-$\text{Ca}_3(\text{PO}_4)_2$ lattice is found. It is suggested that the water-soluble chlorine is present as adsorbed HCl, as the weight of the reaction product corrected for the weight of the water-soluble chlorine (curve e) equals the weight of the orthophosphate originally present. At higher reaction temperatures, however, the weight and the chlorine percentage increase. X-ray analysis shows that part of the $\beta$-$\text{Ca}_3(\text{PO}_4)_2$ is transformed into chlorapatite and pyrophosphate. Calcium orthophosphate is absent in the samples heated to 1000 °C and higher; the chlorine content remains constant, proving that the reaction has been complete.

In a subsequent series of experiments, in which the temperature was kept constant at 1000 °C and the reaction time was varied, it was found that after
Fig. 4.6. Heating experiments with $\beta$-Ca$_3$(PO$_4$)$_2$ in gaseous HCl.

Half an hour about 95% of the orthophosphate was converted into chlorapatite and pyrophosphate.

This conversion of orthophosphate by HCl may be one of the reasons why, under manufacturing conditions, the excess of phosphate in halophosphate is present as pyrophosphate and not as orthophosphate. To this aspect we shall refer again in chapters 6 and 8.

4.8. The composition and the properties of mixed chlorhydroxyapatites

In the preceding sections we have repeatedly dealt with mixed chlorhydroxyapatites. May these samples be considered as mixed crystals and, if so, will there be a continuous series of these mixed crystals? Wallaeyts$^{4-5}$) answered the latter question in the affirmative.

A closer study of our samples of mixed hydroxylchlorapatites obtained by firing hydroxyapatite with NH$_4$Cl or from the equilibrium experiment described in a preceding section, has shown that these materials cannot be considered as members of a continuous series of mixed crystals between calcium chlorapatite and calcium hydroxyapatite. This is immediately clear if we take a closer look at the material balance in the equilibrium experiment of sec. 4.6. If the solids were members of a continuous series of mixed crystals, the composition
of both would be $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_x\text{Cl}_{2-x}$, and taken together the boats should show no loss in weight (table 4-V). Actually there is a noticeable weight loss, and as we have seen, it is due to water. Now, as already briefly mentioned in table 4-IV, the hydroxyapatite also loses water when heated. Bredig et al. found that when hydroxyapatite is heated to 1300 °C some weight loss occurs. The material formed is hydroxyoxyapatite, a divalent oxygen ion replacing two monovalent hydroxyl ions and it can be schematically represented by the formula

$$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{2-z}\text{PO}^{II}_{1/2} V$$

where $V$ stands for a unoccupied hydroxyl site.

As will be discussed in the next section, this formulation does not quite represent the actual situation of the oxygen-ion-vacancy pair in the crystal lattice.

A clear illustration of the conditions prevailing in the mixed chlorhydroxyapatites is provided by the properties of the products obtained by firing hydroxyapatite with various amounts of ammonium chloride (table 4-IV). These samples cover nearly the whole range of compositions from hydroxyapatite to chlorapatite. Compared with the theoretical weight ($G_{th}$), the actual samples show a weight loss due to a loss of water as discussed in sec. 4.6. Similar to the oxyapatite we assume that for each molecule of water lost we get an oxygen ion and a vacancy. If this is correct, we can find the complete composition of the apatite (table 4-IV). The fractions of two Z(halogen) sites of the apatite occupied by $\text{OH}^-$ and $\text{Cl}^-$ ions, by oxygen ions and by vacancies (the number of vacancies equals the number of oxygen ions) have been plotted in fig. 4.7 as a function of the mole ratio ammonium chloride/hydroxyapatite of the firing mixtures. Note that the ratio of the hydroxyl ions to the oxygen ions rapidly decreases with increasing amounts of chlorine incorporated, indicating that the hydroxychlorapatite loses water even more rapidly than the hydroxyapatite. This can be easily understood from the atomic configurations of the various apatites, which will be discussed in the next section. It explains the high $p_{\text{H}_2\text{O}}/p_{\text{HCl}}$ ratio in the equilibrium experiment as described in sec. 4.6.

4.9. The atomic configuration of the various apatites

According to Náray Szabó the fluorine ions in the fluorapatite are situated on lattice sites with coordinates (00$\frac{1}{4}$) and (00$\frac{3}{4}$). The same applies to the hydroxyl ions in the hydroxyapatite. Hence the fluorine and the hydroxyl ions are to be found in the same plane as the $\text{Ca}_{11}$ ions. Schematically the situation around the fluorine and the hydroxyl ions may be represented by

$$-\text{Ca} - \text{F} - \text{Ca} -$$

and

$$-\text{Ca} - \text{OH} - \text{Ca} -.$$
Fig. 4.7. The fraction of the two halogen lattice sites occupied by hydroxyl and chlorine ions and oxygen-vacancy pairs in apatite obtained by heating a mixture of Ca₁₀(PO₄)₆(OH)₂ and adding variable amounts of NH₄Cl.

In the chlorapatite the chlorine ions take up positions between the planes at \( z = \frac{1}{4} \) and \( z = \frac{3}{4} \) in which the Ca₉ ions are located

\[
-\text{Ca} \quad \text{Ca} \quad -
\quad \text{Cl}
\quad -\text{Ca} \quad \text{Ca} - .
\]

When calcium hydroxyapatite loses water, for instance when heated in air to 1050 °C or higher, the lattice constant \( a \) decreases, as was found by Lagergren and Carlström⁴⁻⁸. Apparently the Ca₁₁ ions are no longer pushed apart by the hydroxyl ions, but are drawn closer together by the oxygen ions located in “between” planes at \( z = 0 \) and \( z = \frac{1}{2} \) just like the chlorine ions in chlorapatite. Schematically this picture can be represented as follows

\[
-\text{Ca} \quad \text{OH} \quad \text{Ca} - \quad -\text{Ca} \quad \text{Ca} -
\quad -\text{Ca} \quad \text{OH} \quad \text{Ca} - \quad -\text{Ca} \quad \text{Ca} -
\quad \text{O} \quad + \text{H₂O} .
\]

Therefore, strictly speaking, the oxyapatites should not be represented by the formula \( \text{Ca}_{10}(\text{PO}_4)_6 \text{O} \frac{1}{2} \text{V}_{\text{OH}} \), which suggests that the oxygen ion is in the same position as the hydroxyl ion (see the preceding section).
What happens if the fluorine is replaced by chlorine appears from the work of Hill\(^{4-9}\) and Apple and Ishler\(^{4-10}\). According to Hill 50 mole \(\%\) of the fluorine in \(\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2\) can be replaced by chlorine, resulting in a change of the lattice constant \(a\) from 9·39 Å to 9·47 Å. Only 25 mole \(\%\) of the chlorine in \(\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2\) can be replaced by fluorine, the crystal structure of chlorapatite remaining and the lattice constant \(a\) being altered from 9·63 Å to 9·57 Å. Products with an \(\text{F}/(\text{F} + \text{Cl})\) mole ratio ranging from 0·25 to 0·50 consist of two apatites, one with the chlorapatite, the other with the fluorapatite structure so that a region of non-miscibility must occur. Apple and Ishler assumed that the lattice of mixed fluorchlorapatites is expanded sufficiently at high temperature to allow a chlorine ion to occupy a normal fluorine site with coordinates \((00\frac{1}{2})\) and \((00\frac{3}{2})\). By rapid cooling (quenching) the high-temperature structure can be frozen in.

The question of miscibility in the chlorhydroxyapatites was studied by us by means of X-ray-diffraction analysis. The apatites given in table 4-IV and also pure \(\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2\) and pure \(\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2\) were thoroughly mixed with about 25 \(\%\) of very pure KCl. An extensive X-ray-diffraction analysis was carried out for each mixture. The KCl served as a standard so that the observed values of \(\sin \theta\) for the diffraction lines of each sample could be directly corrected for instrumental errors. The lattice constant of KCl was taken to be 6·2931 Å\(^{4-11}\). A least-square calculation on the corrected values of \(\sin \theta\) for ten or more reflections then gives the lattice constants of each sample. These data are given in table 4-IV. The lattice constants of pure \(\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2\) and \(\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2\) as found by us are in accordance with the figures given in the literature, viz. for \(\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2\): \(a = 9·423\) Å, \(c = 6·884\) Å\(^{4-9}\) and \(a = 9·418\) Å, \(c = 6·883\) Å\(^{4-12}\) and \(\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2\): \(a = 9·629\) Å, \(c = 6·776\) Å\(^{4-13}\).

The lattice constants of the various samples have been plotted in fig. 4.8. It is obvious that Végard’s law does not apply, confirming the result of the chemical analysis that the samples cannot simply be considered as mixed crystals. Nor, on the other hand, is there any indication of a region of non-miscibility as found by Hill for the fluorchlorapatites.

So we may propose the following scheme when chlorine ions replace the hydroxyl ions in calcium hydroxyapatite. A very limited number of chlorine ions may replace \(\text{OH}^-\) ions on the normal \(\text{OH}\) sites. Very soon, however, the chlorine ions will occupy their normal positions between the planes, pushing the \(\text{OH}^-\) ions apart. Considering the instability of the pure hydroxyapatite it is not surprising that the presence of chlorine ions will result in an increased tendency to lose water, thus generating vacancies. In this way ample room is created for the chlorine ions, and there is no reason why a region of non-miscibility should occur as in the fluorchlorapatites.
Fig. 4.8. The lattice constants (in Å) of various hydroxychloroxyapatite samples.

REFERENCES

4-1) R. Nacken, Zent. Min. Geol., 545-549, 1912.
4-7) S. Náray Szabó, Z. Krist. 75, 387-398, 1930.
5. THE REACTION BETWEEN CHLORAPATITE AND GASEOUS ANTIMONY TRIOXIDE

5.1. Introduction

Trivalent antimony can be incorporated into the lattice of Ca$_{10}$(PO$_4$)$_6$Z$_2$, when Z stands for Cl, F, OH or mixtures thereof, giving rise to a blue-green-luminescent material. It is generally assumed that the antimony ions are located at calcium lattice sites. As already mentioned in sec. 2.2 the Ca$^{2+}$ ions are distributed between two kinds of lattice positions. With four of the ten, each Ca$^{2+}$ ion is surrounded by six oxygen ions (Ca$_I$ position), whereas with the other six, each Ca$^{2+}$ ion is surrounded by an irregular polyhedron of oxygen and halogen ions (Ca$_II$ position).

Butler and Jerome found the position of the antimony emission band to be only slightly dependent on the nature of the halogen ion, and therefore suggested that two antimony ions may substitute for two calcium ions in adjacent Ca$_I$ positions, an extra oxygen ion being incorporated interstitially near the substituents in order to achieve electric neutrality. This can be represented schematically by

$$2 \text{Ca}^{2+} \rightarrow 2 \text{Sb}^{3+} + \text{O}^2-. $$

Ouweltjes pointed out that the relative insensitivity of the antimony emission band to the F/Cl ratio could also be explained if the Sb$^{3+}$ ion replaces a Ca$_{II}$ ion, and if at the same time the adjacent halogen ion is substituted by an O$^{2-}$ ion, the latter being of the same size as the F$^-$ ion. This is represented schematically by

$$\text{Ca}_{I} \rightarrow \text{Sb}_{F}^{O}. $$

Prener and Williams independently expressed the same opinion. The hypothesis of Ouweltjes was put forward for the fluorapatite, but it can equally well apply to the chlorapatite.

Johnson concluded from the spontaneous polarization of the luminescence of big synthetic single crystals, activated by antimony and manganese, that the Sb$^{3+}$ ion is probably at a Ca$_{II}$ position in the fluorapatite. In the chlorapatite and in the mixed fluorochlorapatites its position is uncertain. According to Johnson there are reasons for assuming it to be distributed between both kinds of position but predominantly at the Ca$_I$ positions.

In this investigation the reaction of chlorapatite with Sb$_2$O$_3$, Sb$_4$O$_5$Cl$_2$ or SbCl$_3$ has been studied. The quantity of the Sb$^{3+}$ and Cl$^-$ ions present in the reaction products has been determined by chemical analytical methods and a hypothesis concerning the reaction mechanism is given based on these data. The spectral-energy-distribution (s.e.d.) curves of the luminescence under 254-nm excitation have been determined. From these data a hypothesis is put forward concerning the environment of the Sb$^{3+}$ ion.
5.2. Equipment

The experiments were carried out both in open and closed systems. The open system is represented by fig. 5.1. A quartz-glass tube is surrounded by two tubular furnaces, the temperature of which can be regulated independently. A variable air gap between the furnaces, shielded by a steel cylinder, prevents heat conduction from one furnace to the other. The Sb$_2$O$_3$ is evaporated in the low-temperature section and is passed over the chlorapatite by means of dry nitrogen as a carrier gas. The flow of nitrogen is produced by boiling liquid nitrogen and the flow rate can be varied by changing the voltage over the heating coil. It was maintained at 50 ml/min. Figure 5.2 represents the closed system used to heat the apatite in gaseous Sb compounds. It consists of a quartz-glass tube with both ends widened. The volume is approximately 50 ml. Before use, the quartz-glass tube and vessels were heated overnight at 1150 °C in order to remove as much absorbed water as possible. The dimensions lengthwise have been chosen such that the centres of the widened ends lie in the centres of the tubular furnaces shown in fig. 5.1. The apatite (0.005 mole) and a variable amount of an antimony compound were placed separately in the widened ends of the tube. In all these experiments the apatite was kept at a constant temperature of 1100 °C for three hours. The vapour pressure of the antimony compound is determined by the temperature of the low-temperature section.
5.3. Results and discussion

5.3.1. The reaction between chlorapatite and gaseous antimony oxide carried out in an open system

The chemical analysis of the samples obtained by heating chlorapatite in an open system in gaseous \( \text{Sb}_2\text{O}_3 \) for various periods of time is given in table 5-1. Clearly the amount of antimony incorporated into the chlorapatite is much smaller than the loss of chlorine.

If only the configuration

\[
\begin{array}{c}
\text{Cl} \\
\text{Ca} \quad \text{Ca}
\end{array}
\]

were to be replaced by

\[
\begin{array}{c}
\text{O} \\
\text{Sb} \quad \text{Ca}
\end{array}
\]

these quantities could be expected to be equal on a molar basis. As chlorapatite heated in pure nitrogen will not lose any chlorine, the extra loss of Cl ions must be due to the formation of a larger amount of \( \text{SbCl}_3 \) than expected from an equation of the type

\[
3 \text{Ca}_6\text{(PO}_4\text{)}_6\text{Cl}_2 + 2 \text{Sb}_2\text{O}_3 \rightarrow 3 \text{Ca}_6\text{Sb(PO}_4\text{)}_6\text{ClO} + 3 \text{CaO} + \text{SbCl}_3. \quad (5.1)
\]

One might assume another type of reaction in which oxygen replaces the

\[
\begin{array}{c}
\text{Cl} \\
\text{Ca} \quad \text{Ca}
\end{array}
\]

### TABLE 5-1

Reaction of \( \text{Ca}_6\text{(PO}_4\text{)}_6\text{Cl}_2 \) with gaseous \( \text{Sb}_2\text{O}_3 \) in an open system

<table>
<thead>
<tr>
<th>heating time (min)</th>
<th>30</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>number of the experiment</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td><strong>final product</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>chemical analysis</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Sb}^{3+} ) (wt%)</td>
<td>0.48</td>
<td>0.93</td>
</tr>
<tr>
<td>( \text{Cl}^- ) (wt%)</td>
<td>6.05</td>
<td>5.50</td>
</tr>
<tr>
<td><strong>calculated changes in composition</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(mole/mole of apatite)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \Delta \text{Sb} ) (q)</td>
<td>0.041</td>
<td>0.080</td>
</tr>
<tr>
<td>( \Delta \text{Cl} ) (2p + q)</td>
<td>-0.217</td>
<td>-0.376</td>
</tr>
<tr>
<td>number of Cl vacancies (p)</td>
<td>0.088</td>
<td>0.148</td>
</tr>
</tbody>
</table>

The Cl percentage of the \( \text{Ca}_6\text{(PO}_4\text{)}_6\text{Cl}_2 \) employed was 6.79 wt%. 

chlorine, with the simultaneous introduction of a vacancy at a neighbouring halogen site:

\[ 3 \text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2 + \text{Sb}_2\text{O}_3 \rightarrow 3 \text{Ca}_{10}(\text{PO}_4)_6\text{O} \bar{V}_{\text{Cl}} + 2 \text{SbCl}_3. \]  
(5.2)

In practice both types of substitution may occur simultaneously, resulting in an antimony-activated chlorapatite, with additional halogen vacancies. The overall reaction can be given by the equation

\[ 3 \text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2 + (p + 2q)\text{Sb}_2\text{O}_3 \rightarrow 3 \text{Ca}_{10-q}\text{Sb}_q(\text{PO}_4)_6\text{Cl}_2-2p\text{O}_{p+q} \bar{V}_{\text{Cl}} + 3q\text{CaO} + (2p + q)\text{SbCl}_3. \]  
(5.3)

From the antimony and the chlorine content of the reaction product \( p \) and \( q \) can be calculated, so that the relative proportions of chlorine ions, oxygen ions and chlorine vacancies can be deduced.

In the foregoing we have assumed that after the reaction has been finished the Sb is present in the apatite lattice and moreover as \( \text{SbCl}_3 \) and \( \text{Sb}_2\text{O}_3 \). In practice, however, it has been found that calcium oxide may react with antimony trioxide. Under oxidizing conditions calcium antimonates are formed \(^5\)–\(^5\). As these experiments are carried out in a neutral atmosphere, the formation of antimonates can be excluded but not that of the recently discovered calcium antimonites \(^5\)–\(^6\). In this case part of the trivalent antimony found in the analysis would come from the antimonite and the conclusions on the composition of the apatite would be erroneous. However, a separate experiment, in which calcium oxide was heated in gaseous antimony oxide, showed that no antimony was found in the calcium oxide after it had been washed with KOH to remove free \( \text{Sb}_2\text{O}_3 \). Therefore antimonites, if formed, did not interfere in our experiment.

5.3.2. The reaction between chlorapatite and various gaseous antimony compounds carried out in a closed system

The effect of the Sb compound when heated separately with chlorapatite in the closed system follows from the results in table 5-II. Tables 5-III and IV deal with the effects of the vapour pressure of the \( \text{Sb}_2\text{O}_3 \) and the amount of \( \text{Sb}_2\text{O}_3 \) heated, respectively. A sufficient amount of \( \text{Sb}_2\text{O}_3 \) was employed and after the experiment was carried out, part of it was still present in the low-temperature compartment of the closed system.

From the results it follows that in the experiments in the closed system, too, the loss of chlorine is larger than the amount of antimony taken up. From the composition of the samples 3-5 of table 5-II it is clear that the amount of \( \text{Sb}^{3+} \) ions taken up and the loss of \( \text{Cl}^- \) ions decrease if the amount of \( \text{SbCl}_3 \) present in the gaseous phase is larger. When chlorapatite is heated in gaseous \( \text{SbCl}_3 \) neither are \( \text{Sb}^{3+} \) ions incorporated into the apatite lattice nor are \( \text{Cl}^- \) ions
TABLES 5-II, III, IV

Reaction of Ca$_{10}$(PO$_4$)$_6$Cl$_2$ with various gaseous Sb compounds in a closed system

<table>
<thead>
<tr>
<th>TABLE 5-II</th>
<th>TABLE 5-III</th>
<th>TABLE 5-IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>number of the experiment</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Sb compound</td>
<td>Sb$_2$O$_3$</td>
<td>Sb$_4$O$_5$Cl$_2$</td>
</tr>
<tr>
<td>Quantity (mg)</td>
<td>900</td>
<td>426</td>
</tr>
<tr>
<td>Heating temperature (°C)</td>
<td>800</td>
<td>800 ± 230</td>
</tr>
<tr>
<td>Vapour pressure (mm Hg) (approximately)</td>
<td>30</td>
<td>? ± 760</td>
</tr>
</tbody>
</table>

**Final product**

**Chemical analysis**

<table>
<thead>
<tr>
<th></th>
<th>Sb$^{3+}$ (wt %)</th>
<th>Cl$^-$ (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.19</td>
<td>6.40</td>
</tr>
<tr>
<td>4</td>
<td>0.09</td>
<td>6.67</td>
</tr>
<tr>
<td>5</td>
<td>0.01</td>
<td>6.78</td>
</tr>
</tbody>
</table>

**Calculated changes in composition**

<table>
<thead>
<tr>
<th></th>
<th>( \Delta \text{Sb (g)} )</th>
<th>( \Delta \text{Cl (2p + q)} )</th>
<th>( \Delta \text{number of Cl vacancies (p)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.016</td>
<td>-0.116</td>
<td>0.050</td>
</tr>
<tr>
<td>4</td>
<td>0.008</td>
<td>-0.035</td>
<td>0.0135</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>-0.159</td>
<td>0</td>
</tr>
</tbody>
</table>

The Cl percentage of the Ca$_{10}$(PO$_4$)$_6$Cl$_2$ employed was 6.79 wt %. 
lost by it. The result of the latter experiment in which the chlorapatite was heated in antimony-chloride vapour was more or less unexpected, as from factory practice it had been known for a long time that an atmosphere containing some SbCl₃ is favourable to the making of good phosphors and it was thought that possibly the antimony might be incorporated directly into the apatite via the SbCl₃ atmosphere. This has proved to be incorrect. Similar heating experiments with fluorchlorapatites in gaseous antimony trichloride led to the same conclusion: no antimony is incorporated via SbCl₃ and heating a commercial halophosphate in SbCl₃ vapour may even result in a substantial loss of antimony. In the course of our work the favourable effect of antimony chloride in the manufacturing process was found to be connected with an entirely different type of reaction (see chapter 8).

It is evident that reactions (5.1) and (5.2) as assumed can be expected to be dominant where the SbCl₃ can be readily removed. This follows also from the fact that in a closed system the loss of chlorine is less than in the experiments carried out in an open system as reported in table 5-I.

It is also understandable that larger amounts of Sb³⁺ ions and Cl⁻ ions will be present in the final product if the vapour pressure of the antimony oxide is increased by raising the temperature of the Sb₂O₃ from 600 to 1000 °C as set out in table 5-III.

Another point to be considered is the effect of the quantity of antimony trioxide. More antimony and less chlorine are incorporated with an increasing quantity of antimony oxide as may be seen from table 5-IV. These facts may be explained in the following way. Cooke ⁵⁻¹ reported that Sb₂O₅Cl₂ melts at 320 °C. At a somewhat higher temperature it dissociates into Sb₂O₃ and SbCl₃. Cooke's data give evidence that part of the SbCl₃, formed in our heating experiments, can dissolve into the molten Sb₂O₃. It is likely that a lower temperature of the Sb₂O₃ (table 5-III) or a larger amount of Sb₂O₃ (table 5-IV) results in a larger amount of SbCl₃ being dissolved into the Sb₂O₃ present in the low-temperature section of the closed system. This effect gives rise to a decreased $p_{\text{SbCl}_3}$. It follows from eqs (5.1) and (5.2) that a lowering of the partial vapour pressure of the SbCl₃ will promote the incorporation of a larger amount of Sb³⁺ and the formation of more vacancies as actually found in tables 5-III and IV.

5.3.3. The luminescence of the reaction products

The s.e.d. curves of the luminescence (254-nm excitation) are shown in figs 5.3 and 5.4. The numbers written near the curves correspond to the numbers of the experiments. Note that sample 5 did not show any fluorescence.

It was already known that the Sb emission in the mixed fluorchlorapatite consists of two bands, one located at 490 nm and a minor band at 395 nm ⁵⁻¹,⁸).
Kamiya \textsuperscript{5-8}) observed that the minor band (at 395 nm) is more dominating with a small amount of Sb\textsuperscript{3+} ions incorporated into the apatite host lattice.

In our experiments both types of Sb emission bands were observed, as may be seen from fig. 5.3. The short-wavelength emission band dominates with a very low percentage of Sb\textsuperscript{3+} and a high percentage of Cl (curve 4 in fig. 5.3). With increasing amounts of Sb\textsuperscript{3+} ions taken up by the apatite lattice the short-wavelength emission band vanishes and the long-wavelength emission band appears. Its peak shifts slightly towards longer wavelengths both with increasing amounts of trivalent antimony and halogen vacancies.

Neither the chemical data nor the emission curves are sufficient to allow definite conclusions to be drawn as regards the position of the antimony ion and its surroundings. Taking into account the conclusions drawn in chapter 4, the following hypothesis may tentatively be given. The impossibility of incorporating antimony by means of SbCl\textsubscript{3} into calcium chlorapatite and the simultaneous increase in antimony content and decrease in the chlorine content when incor-
porating Sb into chlorapatite, strongly indicate a Ca_{11} position for the antimony with an adjacent oxygen ion, as suggested by Ouweltjes, Prener and Williams. The incorporation of antimony being accompanied by the creation of vacancies, might then be due to an effect identical to what happens when OH\(^-\) is substituted for Cl\(^-\) in the chlorapatite. In the latter case the hydroxyl ions, by a preferential occupancy of the in-plane positions, push out the Cl\(^-\) ions and give rise to vacancies; whereas, when substituting SbO for CaCl, it might well be that the oxygen ions, also preferring the in-plane position, in order to be as close as possible to the antimony ion, push out part of the chlorine ions. With very small amounts of antimony we still have the situation that the accompanying oxygen ion occupies a chlorine position:

$$\text{Cl} \quad \text{Ca} \quad \text{O} \quad \text{Sb}$$

- $z = 0$
- $z = \frac{3}{4}$
- $z = \frac{1}{2}$
- $z = \frac{1}{4}$.
This configuration could then be responsible for the 365-nm emission band, whereas with higher antimony concentrations the in-plane position of the SbO group predominates and gives rise to the 490-nm emission band. This band is slightly shifted when more halogen vacancies are introduced, as might be expected when the nearest-neighbour configuration remains unaltered, but at slightly larger distances chlorine ions are substituted by vacancies and oxygen ions.

REFERENCES

5-6) W. L. Wanmaker, A. H. Hoekstra and J. G. Verriet, to be published.
THE REACTION OF CHLORAPATITE MIXED WITH PYROPHOSPHATE OR ORTHOPHOSPHATE WITH GASEOUS ANTIMONY TRIOXIDE

6.1. Introduction

Wanmaker 6-1) found that the amount of trivalent antimony present in Ca-halophosphate phosphors, prepared by heating a mixture of CaHPO₄, CaCO₃, CaF₂, SrCl₂, MnCO₃ and Sb₂O₃ depends upon the M/P mole ratio (M = Ca + Sr + Mn). In order to incorporate the amount of antimony required for a sufficiently high u.v. absorption, a slight excess of phosphate should be employed. Similar results were obtained by Wachtel 6-2) in preparing antimony- and manganese-activated halophosphate phosphors from flux-grown apatites.

In chapter 4 it was said that when a Ca/P mole ratio smaller than that corresponding to the theoretical ratio of an apatite is employed in preparing chlorapatite, pyrophosphate and orthophosphate are also present in the final product.

The question therefore arises as to how the take-up of trivalent antimony proceeds if mixtures of chlorapatite and either one of the two phosphates are heated in an atmosphere of antimony trioxide.

6.2. Experimental

Equimolar mixtures of calcium chlorapatite and either calcium pyrophosphate or calcium orthophosphate were heated in gaseous Sb₂O₃ both in the open and the closed system as shown in figs 5.1 and 5.2.

The experiments in the open system were carried out with samples of about 5 g heated to 1100 °C for one hour.

In the experiments in the closed system samples of about 5 g present in compartment A were heated to 1100 °C, whereas 900 mg of Sb₂O₃ present in the other compartment was kept at 800 °C corresponding to a vapour pressure of the Sb₂O₃ of 30 mm Hg. The reaction time was three hours. After firing, the reaction products were quickly cooled and leached as usual with a 2 n KOH solution. The final products were analysed for Sb³⁺ and Cl⁻ and an X-ray analysis was carried out, too.

6.3. Results and discussion

The results of these experiments are given in table 6-1. As compared with the corresponding experiment with pure chlorapatite in the closed system (table 5-II), the samples with a smaller Ca/P mole ratio contain considerably more antimony. This is in agreement with the results of Wanmaker 6-1) and Wachtel 6-2).
TABLE 6-1

Heating experiments using equimolar mixtures of chlorapatite and two calcium phosphates in gaseous antimony oxide

<table>
<thead>
<tr>
<th>composition of the firing mixture</th>
<th>0.75 mole of Ca₁₀(PO₄)₆Cl₂</th>
<th>0.75 mole of Ca₁₀(PO₄)₆Cl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.75 mole of β-Ca₃P₂O₇</td>
<td>0.75 mole of β-Ca₃(PO₄)₂</td>
</tr>
<tr>
<td>Ca/P mole ratio</td>
<td>1.500</td>
<td>1.625</td>
</tr>
<tr>
<td>wt% Cl</td>
<td>5.47</td>
<td>5.25</td>
</tr>
<tr>
<td>equipment</td>
<td>open system</td>
<td>closed system</td>
</tr>
<tr>
<td>number of the experiment</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>open system</td>
<td>closed system</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>final product chemical analysis</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>wt% Sb³⁺</td>
<td>0.96</td>
<td>1.14</td>
</tr>
<tr>
<td>wt% Cl⁻</td>
<td>2.06</td>
<td>4.95</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>calculated changes in overall composition (mole/6 moles of P)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>∆Sb</td>
<td>0.075</td>
<td>0.092</td>
</tr>
<tr>
<td>∆Cl</td>
<td>-0.945</td>
<td>-0.124</td>
</tr>
<tr>
<td>∆O</td>
<td>0.585</td>
<td>0.200</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>X-ray-diffraction analysis</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca₁₀(PO₄)₆Cl₂</td>
<td>s-m</td>
<td>s</td>
</tr>
<tr>
<td>β-Ca₃P₂O₇</td>
<td>a-vw?</td>
<td>w</td>
</tr>
<tr>
<td>α-Ca₃(PO₄)₂</td>
<td>m-w</td>
<td>a</td>
</tr>
<tr>
<td>β-Ca₃(PO₄)₂</td>
<td>s-m</td>
<td>a</td>
</tr>
</tbody>
</table>

Relative intensity of the strongest X-ray-diffraction lines: s = strong, m = medium, w = weak, vw = very weak, ? = questionable, a = absent.

When the starting mixture contains pyrophosphate, it may be expected that the calcium oxide formed during the incorporation of antimony will react with pyrophosphate to orthophosphate, facilitating the take up of Sb³⁺. From the figures of table 6-1 (first and second column) it follows that about 0.1 mole of antimony is taken up. Consequently the same amount of calcium oxide should be formed so that an equivalent amount of pyrophosphate could be converted.
into the orthophosphate. The quantities of unreacted $\text{Ca}_2\text{P}_2\text{O}_7$ and formed $\text{Ca}_3(\text{PO}_4)_2$ as calculated from the reaction equation

$$\text{CaO} + \text{Ca}_2\text{P}_2\text{O}_7 \rightarrow \text{Ca}_3(\text{PO}_4)_2,$$  \hspace{1cm} (6.1)

should certainly betray their presence in the X-ray diagrams. It was found, however, that in the experiment in the open system (first column) a larger amount of orthophosphate was formed than expected, whereas no pyrophosphate could be detected. In the experiment in the closed system (second column) just the opposite occurred: orthophosphate was absent and the excess of phosphate was present as pyrophosphate.

When the mixture of chlorapatite and pyrophosphate is heated in the open system in gaseous antimony oxide a considerable loss of chlorine is observed, whereas the X-ray diagram shows that the amount of apatite decreases simultaneously. This is not observed when the mixture is heated in a stream of nitrogen without antimony trioxide. Consequently the loss of chlorine and the formation of orthophosphate are due to a reaction with antimony trioxide. The formation of $\text{Ca}_3(\text{PO}_4)_2$ reminds us of the reaction that occurs when a mixture of chlorapatite and pyrophosphate is heated in water vapour as discussed in chapter 4. The oxygen-vacancy pairs formed reduce the stability of the chlorhydroxyapatite. A similar mechanism is proposed in the experiments carried out in the open system in gaseous antimony oxide. In chapter 5 we have stated in the discussion that when pure chlorapatite is heated in gaseous antimony oxide, two reactions occur simultaneously, viz.

$$3 \text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2 + 2 \text{Sb}_2\text{O}_3 \rightarrow 3 \text{Ca}_9\text{Sb}(\text{PO}_4)_6\text{ClO} + 3 \text{CaO} + \text{SbCl}_3 \hspace{1cm} (6.2)$$

and

$$3 \text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2 + \text{Sb}_2\text{O}_3 \rightarrow 3 \text{Ca}_{10}(\text{PO}_4)_6\text{O} + 2 \text{SbCl}_3. \hspace{1cm} (6.3)$$

These reactions will also occur when a mixture of chlorapatite and pyrophosphate is employed, with the result that an antimony-activated apatite is formed. In this case oxygen-vacancy pairs also reduce the stability of the apatite and it will react with pyrophosphate to orthophosphate. When the incorporation of antimony and oxygen-vacancy pairs is left out of consideration, the overall decomposition can be given by a reaction of the type

$$3 \text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2 + 3 \text{Ca}_2\text{P}_2\text{O}_7 + \text{Sb}_2\text{O}_3 \rightarrow 12 \text{Ca}_3(\text{PO}_4)_2 + 2 \text{SbCl}_3. \hspace{1cm} (6.4)$$

This reaction becomes predominant when the mixture containing pyrophosphate is heated in such a way that the antimony chloride is removed continuously. The high chlorine loss, the low apatite/phosphate mole ratio and the large amount of orthophosphate as found in table 6-1 are thus explained.

When these two decomposition reactions, the one by water vapour and the other by gaseous antimony oxide, are compared, the question arises as to whether the latter reaction is also a reversible one, in other words, whether orthophos-
phate when heated in gaseous antimony trichloride may be converted into chlorapatite and pyrophosphate (the reverse of eq. 6.4). This could explain the absence of orthophosphate in the experiment in the closed system (second column). Moreover, it could explain the smaller loss of chlorine (third and fourth column) as compared with the corresponding experiment without orthophosphate. In chapter 8 it will be shown that the conversion of orthophosphate by SbCl$_3$ into chlorapatite and pyrophosphate indeed occurs.

Now it becomes evident that in the presence of calcium phosphate (either pyro or ortho) a larger amount of antimony is taken up. This can be attributed to a decrease in the vapour pressure of the antimony chloride caused by the reaction with orthophosphate. The decreased $p_{\text{SbCl}_3}$ gives rise to more chlorine vacancies (reaction (6.3)) and this is the reason why a larger amount of antimony can be incorporated into the apatite lattice. The presence of more chlorine vacancies in the activated apatite also follows from the emission spectra of the luminescence (254-nm excitation). These spectra are shown in figs 6.1 and 6.2 (the number written near the curve corresponds to the number of the experiment). As compared with the curve of the corresponding sample obtained by heating pure chlorapatite in gaseous antimony oxide (fig. 5.3, curve 3), these curves

![Emission Spectra](image)

*Fig. 6.1. The emission spectra of some antimony-activated chlorapatite samples prepared by heating in gaseous Sb$_2$O$_3$. Open system. Started from:*

1. a mixture of Ca$_{10}$(PO$_4$)$_6$Cl$_2$ + Ca$_3$P$_2$O$_7$,
2. a mixture of Ca$_{10}$(PO$_4$)$_6$Cl$_2$ + Ca$_3$(PO$_4$)$_2$.
Fig. 6.2. The emission spectra of some antimony-activated chlorapatites prepared by heating in gaseous Sb$_2$O$_3$. Closed system. Started from:

(2) a mixture of Ca$_{10}$(PO$_4$)$_6$Cl$_2$ + Ca$_2$P$_2$O$_7$,
(4) a mixture of Ca$_{10}$(PO$_4$)$_6$Cl$_2$ + Ca$_3$(PO$_4$)$_2$.

show emission maxima all located at longer wavelengths. We ascribe this shift to the presence of more chlorine vacancies, as discussed in chapter 5.

It is also obvious that a mixture of chlorapatite and orthophosphate reacts more readily with gaseous antimony trioxide than a mixture of chlorapatite and pyrophosphate. When orthophosphate is present, the reaction with the antimony trichloride formed can proceed at once whereas pyrophosphate must first be converted into orthophosphate by reacting with liberated calcium oxide. It is conceivable that the latter process may proceed less rapidly.

REFERENCES

7. THE REACTION OF GASEOUS ANTIMONY TRIOXIDE
WITH A MIXTURE OF CALCIUM PYROPHOSPHATE
AND ORTHOPHOSPHATE

7.1. Introduction

In the preceding chapter we dealt with the reaction of \( \text{Sb}_2\text{O}_3 \) with mixtures of \( \text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2 \) and either \( \text{Ca}_2\text{P}_2\text{O}_7 \) or \( \text{Ca}_3(\text{PO}_4)_2 \). We have already discussed the occurrence of a side-reaction, i.e. the reaction between \( \text{Ca}_3(\text{PO}_4)_2 \) and \( \text{SbCl}_3 \), which will be dealt with in chapter 8 in more detail. It is obvious that still other side-reactions are possible, e.g. reactions of \( \text{Ca}_2\text{P}_2\text{O}_7 \) with \( \text{SbCl}_3 \) or of a mixture of \( \text{Ca}_2\text{P}_2\text{O}_7 \) and \( \text{Ca}_3(\text{PO}_4)_2 \) with \( \text{Sb}_2\text{O}_3 \).

From separate experiments carried out by us it was established that the first type of transformation is negligible; conversions of the latter type are quite feasible, however. We shall therefore discuss in this chapter the reaction of mixtures of \( \beta\text{-Ca}_3\text{P}_2\text{O}_7 \) with increasing amounts of \( \beta\text{-Ca}_3(\text{PO}_4)_2 \) added, heated to 1100 °C in gaseous \( \text{Sb}_2\text{O}_3 \).

Kinney \(^7-1\)) found that the incorporation of trivalent antimony into calcium pyrophosphate was stimulated by sodium ions. Neither the amount of antimony nor the amount of sodium affected the spectrum of the luminescence under 254-nm excitation.

No literature references concerning the incorporation of antimony into the calcium-orthophosphate lattice are known. The incorporation of another trivalent ion, viz. \( \text{Ce}^{3+} \) has been reported by Froelich \(^7-2\)).

7.2. Experimental

The evacuated closed system as described in fig. 5.2 was also used for the heating experiments with mixtures of pyro and orthophosphate in gaseous antimony oxide. Phosphate samples weighing 5 g were heated to 1100 °C in one compartment of the system, while 2 g of \( \text{Sb}_2\text{O}_3 \) kept at 800, 950 or 1100 °C, were present in the other one. The vapour pressure of the \( \text{Sb}_2\text{O}_3 \) corresponding to these temperatures amounts to 30, 80 and 150 mm Hg, respectively. In all the experiments the reaction time was three hours. The reaction products were leached as usual with 2n KOH solution. The final products were analysed for \( \text{Sb}^{3+} \) and an X-ray analysis was carried out.

7.3. Results and discussion

7.3.1. The chemical properties of the samples

The antimony percentage of the various samples obtained in these experiments is plotted in fig. 7.1 as a function of the composition of the reaction mixture. Other properties of part of the samples are given in table 7-1.
### TABLE 7-1

Heating experiments using mixtures of $\beta$-Ca$_2$P$_2$O$_7$ and $\beta$-Ca$_3$(PO$_4$)$_2$ in gaseous Sb$_2$O$_3$

<table>
<thead>
<tr>
<th>Molar composition of the firing mixture</th>
<th>Final reaction product</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$p_{\text{Sb}_2\text{O}_3} = 30$ mm Hg</td>
</tr>
<tr>
<td>Ca$_2$P$_2$O$_7$</td>
<td>Ca$_3$(PO$_4$)$_2$ mole ratio</td>
</tr>
<tr>
<td>------------------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>1.00</td>
<td>0.00</td>
</tr>
<tr>
<td>0.84</td>
<td>0.16</td>
</tr>
<tr>
<td>0.67</td>
<td>0.33</td>
</tr>
<tr>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>0.42</td>
<td>0.58</td>
</tr>
<tr>
<td>0.33</td>
<td>0.67</td>
</tr>
<tr>
<td>0.17</td>
<td>0.83</td>
</tr>
<tr>
<td>0.12</td>
<td>0.88</td>
</tr>
<tr>
<td>0.08</td>
<td>0.92</td>
</tr>
<tr>
<td>0.04</td>
<td>0.96</td>
</tr>
<tr>
<td>0.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

The brightness relative to that of a standard blue Ca-halophosphate phosphor, $\lambda_{\text{max}} = 485$ nm is given. Relative intensity of the strongest diffraction lines: s = strong, m = medium, w = weak, vw = very weak, ? = questionable, a = absent.

CP is calcium pyrophosphate, α-C$_3$P$_2$ is α-calcium orthophosphate, β-C$_3$P$_2$ is β-calcium orthophosphate.
Fig. 7.1. The percentage of antimony in samples obtained by heating a mixture of Ca$_2$P$_2$O$_7$ and Ca$_3$(PO$_4$)$_2$ in gaseous Sb$_2$O$_3$.

When the pure components Ca$_2$P$_2$O$_7$ or Ca$_3$(PO$_4$)$_2$ are heated in an atmosphere of Sb$_2$O$_3$, only a small amount of antimony is found in either of them. This is not surprising, as it is general experience in the synthesis of luminescent materials that a slight excess of the anion constituent is required in order to incorporate the activator $^{7-3,4,5,6)}$. It may be seen from fig. 7.1 that a similar picture is found for $\beta$-Ca$_3$(PO$_4$)$_2$, viz. the largest amount of antimony take-up is observed with mixtures containing an excess of phosphate.

In order to test whether the same occurs for Ca$_2$P$_2$O$_7$, some preparations were made of Ca$_2$P$_2$O$_7$ with increasing amounts of Ca(PO$_3$)$_2$ added. It was found, however, that in this case pure Ca$_2$P$_2$O$_7$ can incorporate the largest amount of trivalent antimony. This deviation from the general rule given above is not evident. Possibly this rule only holds good when there is a great difference between the energy required to incorporate a normal cation (Ca) or an activator ion (Sb) into the host lattice.

In the specific case of heating pure calcium pyrophosphate or calcium orthophosphate in an atmosphere of Sb$_2$O$_3$, incorporation of the antimony can only occur if accompanied by segregation of calcium oxide (which is highly improbable) and forming a defect structure or by formation of the next higher, more basic calcium phosphate. The question as to what actually happens can be answered by studying the X-ray diagrams.
When pure pyrophosphate reacts with gaseous antimony oxide and $p_{Sb_2O_3}$ is gradually increased, the amount of antimony taken up increases considerably, whereas X-ray analysis shows that the amount of $\beta$-orthophosphate increases simultaneously. This may be explained by assuming a reaction of the type

$$(1 + 3x)Ca_3P_2O_7 + xSb_2O_3 \rightarrow Ca_{3-3x}Sb_{2x}P_2O_7 + 3xCa_3(PO_4)_2. \quad (7.1)$$

Samples with a Ca/P mole ratio between 1·44 and 1·50 exclusively show the presence of the $\beta$-orthophosphate lattice whereas the $(Ca + \frac{3}{2}Sb)/P$ mole ratio amounts to about 1·50. Apparently a relatively small amount of the pyrophosphate originally present reacted with antimony oxide to calcium-antimony orthophosphate according to the reaction

$$(1 - 3x)Ca_3(PO_4)_2 + 3xCa_3P_2O_7 + xSb_2O_3 \rightarrow \beta-Ca_{3-3x}Sb_{2x}(PO_4)_2. \quad (7.2)$$

The antimony-activated orthophosphate can also be considered to be a range of solid solutions of SbPO$_4$ into $\beta$-Ca$_3$(PO$_4$)$_2$. A mixture of these compounds (the SbPO$_4$ was prepared by a method given by Robbins$^7$) heated to 1100 °C in a closed evacuated tube did indeed form solid solutions with the $\beta$-orthophosphate crystal structure. The amount of SbPO$_4$ that could be dissolved into the orthophosphate was small, however. This finding shows why pyrophosphate and antimony oxide cannot completely react to a calcium-antimony orthophosphate as required by the formula $Ca_6Sb_2(PO_4)_6$. In the range of solid solutions represented by $Ca_{3-3x}Sb_{2x}(PO_4)_2$, $x$ is relatively small and in our experiments no higher values than $\approx 0·05$ were found, whereas $x = 0·33$ would be required for complete conversion of the pyrophosphate.

Entirely different results were obtained by employing pure $\beta$-orthophosphate in these experiments. When $p_{Sb_2O_3}$ is gradually increased, the percentage of antimony hardly increases. Moreover, these samples contain a small amount of the high-temperature or $\alpha$-form of calcium orthophosphate although the transition temperature in the literature is given as 1180 °C.$^7$.

7.3.2. The luminescence of the samples

The s.e.d. curves of the luminescence (254-nm excitation) of Ca$_2$P$_2$O$_7$-Sb prepared by us and of $(Ca,Na)_2P_2O_7$-Sb prepared by Kinney$^7$ are shown in fig. 7.2. The two curves are quite similar and the conclusion may be drawn that by heating pyrophosphate in an atmosphere of antimony oxide the same phosphor has been prepared as the one made by Kinney by heating a mixture of CaHPO$_4$, $(NH_4)_2HPO_4$, Na$_2$CO$_3$ and Sb$_2$O$_3$ to elevated temperatures.

The antimony-containing $\beta$-orthophosphate with a Ca/P mole ratio less than 1·5 is also a luminescent material and the emission spectrum (254-nm excitation) is shown as curve a in fig. 7.3.

The spectrum of Ca$_2$P$_2$O$_7$-Sb shows one emission peak located at 415 nm, whereas the defect $\beta$-Ca$_3$(PO$_4$)$_2$-Sb has two emission bands at 415 nm and
Fig. 7.2. The emission spectrum of Ca$_2$P$_2$O$_7$-Sb.
(a) Ca$_{1.997}$Sb$_{0.003}$P$_2$O$_7$,
(b) (Ca,Na)$_2$P$_2$O$_7$-Sb (Kinney 7-1)).

Fig. 7.3. The emission spectra of samples prepared by heating a mixture of Ca$_2$P$_2$O$_7$ and Ca$_3$(PO$_4$)$_2$ in gaseous Sb$_2$O$_3$; p$_{Sb_2O_3}$ = 150 mm Hg.
(a) $\beta$-Ca$_{2.862}$Sb$_{0.092}$(PO$_4$)$_2$,
(b) $\beta$-Ca$_3$(PO$_4$)$_2$-Sb + Ca$_2$P$_2$O$_7$-Sb Ca/P = 1.33, Sb/P = 0.043,
(c) $\beta$-Ca$_3$(PO$_4$)$_2$-Sb + Ca$_2$P$_2$O$_7$-Sb Ca/P = 1.17, Sb/P = 0.030,
(d) $\beta$-Ca$_3$(PO$_4$)$_2$-Sb + Ca$_2$P$_2$O$_7$-Sb Ca/P = 1.08, Sb/P = 0.016.
590 nm. Thus, from the s.e.d. curves of the luminescence of the samples in which both phosphates are present, conclusions may be drawn concerning the distribution of the antimony between the two kinds of phosphate. From fig. 7.3 it may be seen that in the emission spectra of samples in which pyrophosphate is absent (curve a) or present (curve b-d) the ratio of the intensity of the two emission bands is similar. Therefore it may be concluded that the antimony is not evenly distributed between the Ca$_2$P$_2$O$_7$ and Ca$_3$(PO$_4$)$_2$ phases but mainly present in the latter.

The s.e.d. curve of the luminescence (254-nm excitation) of samples prepared by heating pure β-orthophosphate in gaseous antimony oxide is given in fig. 7.4. In these samples some α-orthophosphate is also present; as the spectrum is quite different from that of the defect β-Ca$_3$(PO$_4$)$_2$-Sb, the question arises as to whether the 495-nm emission band may be attributed to antimony incorporated into α-Ca$_3$(PO$_4$)$_2$. This proved to be incorrect when we heated samples of β-Ca$_3$(PO$_4$)$_2$-Sb to 1400 °C in a nitrogen atmosphere for two hours. The X-ray diagrams show the presence of the α-modification mainly and the emission spectra consist of a single band located at about 580 nm as shown in fig. 7.5. Thus it is evident that the 495-nm emission band as shown in fig. 7.4 cannot be attributed to α-Ca$_3$(PO$_4$)$_2$-Sb. In sec. 7.3.4 we shall put forward a tentative explanation concerning the origin of this emission band.
7.3.3. The effect of orthophosphate and pyrophosphate on the luminous efficiency of calcium-halophosphate phosphors

In the application of luminescent materials visible light originates from the u.v. radiation impinging on phosphor particles and transformed inside them into visible light. It may be clear that the efficiency of this process, given by the ratio

\[
\frac{\text{number of visible quanta emitted}}{\text{number of u.v. quanta absorbed}}
\]

the quantum efficiency, should be as high as possible. When a substance shows a high u.v. absorption, but hardly any visible light is emitted, one speaks of an ineffective u.v. absorption. It is evident that the presence of such materials considerably reduces the efficiency and should therefore be avoided.

An excess of phosphate is employed in preparing halophosphate phosphors and, as discussed in chapter 4, either Ca$_2$P$_2$O$_7$ or Ca$_3$(PO$_4$)$_2$ or a mixture of both phosphates is also present in the final product. The absorption of visible radiation by partially oxidized β-(Ca,Mn)$_3$(PO$_4$)$_2$ was known $^{7-9}$, but so far little was known about the u.v. absorption of the contaminants. Table 7-I gives interesting information on the u.v. absorption of the antimony-containing calcium orthophosphates. In all cases the luminous efficiency is so low compared with that of the halophosphate phosphors, that the excitation energy, absorbed
by the contaminating phase, must be considered as a loss. Just as in the halo-
phosphates, the ultraviolet absorption is due to the antimony and table 7-1
shows that the antimony content, and thus the u.v. absorption, is low as long
as we have Sb\(^{3+}\) incorporated in a pure pyrophosphate or a pure orthophos-
phate lattice. Unfortunately, the conditions prevailing in large-scale halophos-
phate manufacture are such that this is never the case. In view of the fact that
in a mixture of chlorapatite and pyrophosphate apatite is decomposed by traces
of moisture, but also by antimony trioxide, to give orthophosphate, it is obvious
that the presence of both orthophosphate and pyrophosphate is far more likely
to occur and this is exactly the condition for obtaining a \(\beta\)-orthophosphate
phase with high antimony content. As we shall see in chapter 8, the best chances
of reducing the harmful effect of the excess of phosphate necessary for the
incorporation of the antimony are in maintaining an atmosphere of antimony
chloride which transforms calcium-antimony orthophosphate into Ca\(_2\)P\(_2\)O\(_7\) and
Ca\(_{10}\)(PO\(_4\))\(_6\)Cl\(_2\)-Sb.

7.3.4. The analogy of antimony and tin-activated \(\beta\)-calcium orthophosphate

The electronic configurations of a trivalent antimony ion (atomic number of
Sb is 51) and a divalent tin ion (atomic number of Sn is 50) are identical. It is
therefore tempting to suggest a relationship between the spectra of the lumines-
cence of crystal lattices activated by either of these two kinds of ions.

In the spectra of \(\beta\)-(Ca, Mg\){(PO\(_4\))\(_2\)}-Sn\(^{2+}\) phosphors Wanmaker and
Radielović \(^7-10\) observed three emission bands located at about 385 nm,
500 nm and 630 nm. The 385-nm emission band is not found in the
spectrum of \(\beta\)-Ca\(_3\)(PO\(_4\))\(_2\)-Sn\(^{2+}\). Lendvay \(^7-11\) attributed the main emission
band of this phosphor, located at 630 nm, to Sn\(^{2+}\) ions present on calcium
lattice sites and suggested that the sub-band at 500 nm might be caused by
interstitial tin ions.

Three emission bands are also found in the antimony-activated orthophos-
phates prepared by us. Two of them, located at 415 nm and 590 nm, appear in
the emission spectra of samples having a Ca/P mole ratio smaller than 1·50,
whereas the material with the stoichiometrical Ca/P mole ratio shows one
emission band located at 495 nm. Following Lendvay's suggestion, this emission
band might be attributed to interstitial antimony ions. The presence of inter-
stitials in samples having a Ca/P mole ratio smaller than 1·50 is less probable as
a lower ratio implies the presence of some pyrophosphate in the mixture before
heating, and from the foregoing it follows that in this case \(\beta\)-Ca\(_{3-3x}\)Sb\(_{2x}\)(PO\(_4\))\(_2\)
will be formed during the heating process. Therefore we may attribute the
415-nm and the 590-nm emission band in the spectrum of \(\beta\)-Ca\(_3\)(PO\(_4\))\(_2\)-Sb to
antimony ions located on Ca lattice sites. Moreover, the interstitials might be
connected with the presence of a small amount of the high-temperature or
\(\alpha\)-form of Ca\(_3\)(PO\(_4\))\(_2\).
7.3.5. *The ratio of the intensities of the 415-nm and the 590-nm emission band in the spectrum of β-Ca₃(PO₄)₂-Sb*

Luminescent β-Ca₃(PO₄)₂-Sb was also prepared in two other ways, viz. by a direct synthesis and by a conversion of β-Ca₂P₂O₇-Sb into β-Ca₃(PO₄)₂-Sb.

In the direct synthesis samples of 20 g of a mixture of CaHPO₄, CaCO₃ and Sb₂O₃ were heated to 1180 °C in air for two hours. The reaction products were analysed for trivalent antimony and an X-ray analysis was carried out. The results are given in table 7-II. The β-orthophosphate lattice is present exclusively and the (Ca + ³/₅Sb)/P mole ratio amounts to about 1.50. The s.e.d. curve of the luminescence (254-nm excitation) is given in fig. 7.6 (curve a).

![Fig. 7.6. The effect of the position of the activator ion in β-Ca₃(PO₄)₂-Sb.](image)

(a) Sample prepared by direct synthesis,
(b) sample prepared by converting β-Ca₂P₂O₇-Sb.

In the second method β-Ca₂P₂O₇-Sb was prepared according to a slightly modified method given by Kinney ⁷⁻¹). The activated pyrophosphate was mixed with the theoretical amount of calcium carbonate and the mixture was also heated to 1180 °C in air for two hours. X-ray-diffraction analysis confirmed the conversion of the β-pyrophosphate into the β-orthophosphate and chemical analysis revealed the presence of about 1.0 wt.% antimony. The s.e.d. curve of the luminescence of this antimony-activated orthophosphate is also given in fig. 7.6 as curve b. The location of the two emission bands is similar but the
### TABLE 7-II

Direct synthesis of $\beta$-Ca$_3$(PO$_4$)$_2$-Sb

<table>
<thead>
<tr>
<th>molar composition of the firing mixture</th>
<th>properties of the final product</th>
<th>relative intensity of the emission bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaHPO$_4$</td>
<td>CaCO$_3$</td>
<td>Sb$_2$O$_3$</td>
</tr>
<tr>
<td>6.00</td>
<td>2.96</td>
<td>0.6</td>
</tr>
<tr>
<td>6.00</td>
<td>2.56</td>
<td>0.8</td>
</tr>
</tbody>
</table>
ratio of the intensities is quite different. Apparently in the lattice of $\beta$-Ca$_3$(PO$_4$)$_2$ there is a high probability of forming two different kinds of activator centres. This effect may be related to the fact that two different kinds of Ca lattice sites are present in $\beta$-Ca$_3$(PO$_4$)$_2$ and the distribution of the antimony between them probably determines the intensity ratio of the two emission bands. The centres giving rise to the deep-blue emission band may be correlated to those present in Ca$_3$P$_2$O$_7$-Sb as the short-wavelength band is dominant when Ca$_3$P$_2$O$_7$-Sb is transformed into $\beta$-Ca$_3$(PO$_4$)$_2$-Sb by reacting with calcium carbonate.

7.3.6. Energy transfer in Ca$_3$(PO$_4$)$_2$ activated with antimony and manganese

According to Kinney $^7$ energy transfer occurs in (Ca,Na)$_2$P$_2$O$_7$-Sb,Mn. The u.v. is absorbed by the antimony and partly transferred to the manganese. The observed luminescence of this material may vary between blue-white and pink-white depending upon the manganese concentration. The question therefore arises as to whether energy transfer may also occur in the double-activated calcium orthophosphate.

Two series of experiments were carried out as described in sec. 7.2. In one series calcium-manganese orthophosphates with a variable Mn/P ratio were used, in the other series mixtures of calcium-manganese orthophosphates and pyrophosphate with a variable Mn/P and a constant overall (Ca + Mn)/P ratio of 1.42 were heated. Results were obtained similar to those of the corresponding experiments without manganese. The spectra of the luminescence (254-nm excitation) are given in figs 7.7 and 7.8 for a (Ca + Mn)/P ratio of

![Fig. 7.7. The emission spectra of Ca$_3$(PO$_4$)$_2$-Sb,Mn.](image-url)
Fig. 7.8. The emission spectra of defect $\beta$-Ca$_3$(PO$_4$)$_2$-Sb,Mn.

1.50 and 1.42, respectively. From the increase in the intensity of the manganese emission band and the decrease of the intensity of the antimony emission band(s) when the Mn/Sb ratio is increased, it follows that energy transfer takes place from antimony to manganese. The manganese emission band, located at 660 nm, is also found in the emission spectrum of similar double-activated phosphors as Ca$_3$(PO$_4$)$_2$-Ce,Mn$^{7-2}$ and Ca$_3$(PO$_4$)$_2$-Sn,Mn$^{7-12}$).

REFERENCES

8. THE REACTION OF CALCIUM $\beta$-ORTHOPHOSPHATE WITH GASEOUS ANTIMONY TRICHLORIDE

8.1. Introduction

The experiments described in chapter 6, in which the reaction between gaseous antimony trioxide and a mixture of chlorapatite and pyrophosphate was studied under various conditions, led us to suggest that the reaction might be reversible. This is not a purely academic question. In commercial halophosphate phosphors the amount of orthophosphate is always surprisingly small. Even with a considerable phosphate excess (e.g. M/P = 1.60) this excess is nearly always found as pyrophosphate rather than as orthophosphate. In sec. 4.7 we referred to the possibility that orthophosphate, if formed, could be converted by gaseous HCl. According to eq. (8.1) one might expect that when $\text{Ca}_2\text{P}_2\text{O}_7$ and $\text{Sb}_2\text{O}_3$ are present, the apatite already formed is partly decomposed into orthophosphate. Normally this decomposition is not noticeable, however. Apparently reaction (8.1) is a reversible one in which antimony chloride is the active agent. In normal practice an excess of halogen is used, and it is well known that the relative loss of chlorine is much higher than the loss of fluorine. The latter is in fact hardly detectable. Moreover, a considerable amount of the antimony is volatilized during the firing process, probably as $\text{SbCl}_3$. This is the most volatile antimony compound that can be formed from the ingredients in the firing mixture. So it is very likely that there is temporarily an atmosphere of $\text{SbCl}_3$ in the interior of the reaction vessels during the firing process.

It is thus of considerable practical interest to demonstrate that there can be a reaction between orthophosphate and gaseous antimony chloride and it was therefore decided to study that system more closely. In this investigation the effect of the vapour pressure of both the antimony chloride and the antimony oxide was determined and with given vapour pressures of $\text{Sb}_2\text{O}_3$ and $\text{SbCl}_3$ the temperature of the orthophosphate was varied.

8.2. Equipment

In order to keep $p_{\text{SbCl}_3}$ constant, the apparatus as described in chapter 5 was slightly modified. The low-temperature part of the evacuated system was placed in a thermostat filled with oil, as shown in fig. 8.1. The part of the system outside the furnace and the thermostat was wrapped in an electrically heated tape in order to be sure that the temperature in the thermostat is the lowest of the system. The orthophosphate and the antimony chloride were put separately into the tube which was then evacuated and sealed off.
8.3. Experimental

A quantity of 15 mmoles (4.65 g) of $\beta$-orthophosphate was put into compartment A and 4.3 mmoles (1.0 g) of SbCl$_3$ were present in part B of the system. In one series of experiments the orthophosphate was heated to 1100 °C. The antimony chloride was kept at temperatures ranging from 80 to 260 °C, corresponding to $P_{\text{SbCl}_3}$ varying from 3.6 mm Hg to 3 atmospheres. In another series the orthophosphate was heated to various temperatures whereas the SbCl$_3$ was kept at 190 °C, corresponding to $P_{\text{SbCl}_3} = 260$ mm Hg.

The reaction time was three hours for all these experiments. After cooling, the materials were leached as usual with a 2n KOH solution and analysed for chlorine and trivalent antimony. Moreover, an X-ray analysis was carried out.

8.4. Results and discussion

8.4.1. The effect of the SbCl$_3$ vapour pressure

The results of these experiments are shown in table 8-I. These figures indicate clearly that $\beta$-orthophosphate can be converted into chlorapatite and pyrophosphate when it is heated in an atmosphere of antimony trichloride, provided SbCl$_3$ is present in sufficient quantity. For instance, a complete conversion takes place with an antimony-chloride vapour pressure of 260 mm Hg and higher.

Pyrophosphate could not be detected when only a small amount of orthophosphate was converted. It is assumed that the pyrophosphate and the antimony trioxide simultaneously generated in accordance with reaction (8.1), will react with the excess of orthophosphate still present to the defect, antimony-containing, $\beta$-orthophosphate as discussed in chapter 7. The presence of this
TABLE 8-1
Effect of the vapour pressure of the SbCl₃ on the conversion of β-Ca₃(PO₄)₂

<table>
<thead>
<tr>
<th>number of the experiment</th>
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</tr>
<tr>
<td>temperature SbCl₃ (°C)</td>
<td>80</td>
<td>120</td>
<td>150</td>
<td>180</td>
<td>182</td>
<td>185</td>
<td>190</td>
<td>200</td>
<td>210</td>
<td>220</td>
<td>230</td>
<td>±260</td>
</tr>
<tr>
<td>vapour pressure SbCl₃ (mm Hg)</td>
<td>3.6</td>
<td>26</td>
<td>75</td>
<td>190</td>
<td>210</td>
<td>225</td>
<td>260</td>
<td>340</td>
<td>460</td>
<td>610</td>
<td>760</td>
<td>±2500</td>
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<td></td>
<td></td>
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<tr>
<td>Ca₃(PO₄)₂</td>
<td>s</td>
<td>s</td>
<td>s</td>
<td>m</td>
<td>s</td>
<td>m-w</td>
<td>a</td>
<td>a</td>
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<td>a</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>Ca₁₀(PO₄)₆Cl₂</td>
<td>vw</td>
<td>w</td>
<td>w</td>
<td>s</td>
<td>s</td>
<td>s</td>
<td>s</td>
<td>s</td>
<td>s</td>
<td>s</td>
<td>s</td>
<td>s</td>
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<tr>
<td>Ca₂P₂O₇</td>
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<td>a</td>
<td>a</td>
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<td>a</td>
<td>a</td>
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<td>a</td>
<td>a</td>
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</tr>
<tr>
<td>mole ratio Ca₃(PO₄)₂/Ca₁₀(PO₄)₆Cl₂</td>
<td>40</td>
<td>17</td>
<td>17</td>
<td>7</td>
<td>4</td>
<td>0.9</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<td>ratio of the lattice constants of the apatite (c/a)</td>
<td>0.712</td>
<td>0.714</td>
<td>0.708</td>
<td>0.706</td>
<td>0.706</td>
<td>0.706</td>
<td>0.706</td>
<td>0.703</td>
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<tr>
<td>Sb³⁺ (wt%)</td>
<td>0.12</td>
<td>0.93</td>
<td>0.81</td>
<td>1.62</td>
<td>1.89</td>
<td>3.20</td>
<td>3.60</td>
<td>1.36</td>
<td>1.42</td>
<td>0.92</td>
<td>0.86</td>
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<tr>
<td>Cl⁻ (wt%)</td>
<td>0.42</td>
<td>1.01</td>
<td>1.14</td>
<td>2.05</td>
<td>2.42</td>
<td>3.39</td>
<td>4.33</td>
<td>5.15</td>
<td>5.29</td>
<td>5.29</td>
<td>5.31</td>
<td>5.64</td>
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<td>33</td>
<td>33</td>
<td>42</td>
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<td>u.v. absorption</td>
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<td>82</td>
<td>78</td>
<td>92</td>
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<td>98</td>
<td>98</td>
<td>92</td>
<td>91</td>
<td>91</td>
<td>89</td>
<td>86</td>
</tr>
<tr>
<td>λₘₚₜ Ca₁₀(PO₄)₆Cl₂-Sb (nm)</td>
<td>500?</td>
<td>510</td>
<td>515</td>
<td>505</td>
<td>505</td>
<td>505</td>
<td>505</td>
<td>505</td>
<td>495</td>
<td></td>
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</table>

Relative intensities of the strongest X-ray-diffraction lines: s = strong, m = medium, w = weak, vw = very weak, ? = questionable, a = absent. The brightness relative to that of a standard blue Ca-halophosphate phosphor, λₘₚₜ = 485 nm is given.
material follows clearly from the emission curves of these samples as shown in fig. 8.2 (compare with fig. 7.3).

Fig. 8.2. The emission spectra of some samples prepared by heating $\beta$-Ca$_3$(PO$_4$)$_2$ to 1100 °C in gaseous SbCl$_3$ ($p_{SbCl_3} \leq 210$ mm Hg).

Fig. 8.3. The emission spectra of some samples prepared by heating $\beta$-Ca$_3$(PO$_4$)$_2$ to 1100°C in gaseous SbCl$_3$ ($p_{SbCl_3} \geq 225$ mm Hg).
A gradual increase in $p_{\text{SbCl}_3}$ results in a larger amount of orthophosphate being converted. This is also apparent from the emission spectra given in figs 8.2 and 8.3 which show an increasing intensity in the emission band of chlorapatite whereas at the same time the intensity of the orthophosphate band is reduced. The chlorapatite and the antimony oxide formed now react to $\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2\cdot\text{Sb}$ as stated in chapter 5 while, on the other hand, part of the pyrophosphate formed reacts with liberated calcium oxide to orthophosphate, which will in turn react with $\text{SbCl}_3$, and so on.

When $p_{\text{SbCl}_3}$ exceeds 260 mm Hg, orthophosphate is absent; apatite and pyrophosphate are the only phases the presence of which can be detected with certainty. Note that as the chlorine content increases, the antimony content drops. This confirms the thesis that a high chlorine content and a high antimony content are incompatible, and supports the hypothesis on the incorporation of antimony discussed by us in chapter 5. A higher $p_{\text{SbCl}_3}$ results in a smaller number of vacancies, and vacancies are a condition sine qua non for the incorporation of a large amount of antimony into the chlorapatite lattice.

8.4.2. The effect of the temperature of the $\beta$-orthophosphate

The results of the experiments in which $\beta$-orthophosphate was heated to various temperatures in an atmosphere of antimony chloride ($p_{\text{SbCl}_3} = 260$ mm Hg) are given in table 8-II and the spectra of the luminescence of these samples

<table>
<thead>
<tr>
<th>number of the experiment</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
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<td><strong>Experimental conditions</strong></td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>temperature of the $\beta$-$\text{Ca}_3(\text{PO}_4)_2$ ($^\circ$C)</td>
<td>500</td>
<td>600</td>
<td>650</td>
<td>700</td>
<td>750</td>
<td>800</td>
</tr>
<tr>
<td><strong>Final reaction product</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta$-$\text{Ca}_3(\text{PO}_4)_2$</td>
<td>s</td>
<td>s</td>
<td>m-w</td>
<td>a</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>$\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$</td>
<td>vw</td>
<td>w-m</td>
<td>s</td>
<td>s</td>
<td>s</td>
<td>s</td>
</tr>
<tr>
<td>$\beta$-$\text{Ca}_2\text{P}_2\text{O}_7$</td>
<td>a</td>
<td>a</td>
<td>vw</td>
<td>w</td>
<td>m</td>
<td>m-w</td>
</tr>
<tr>
<td>Ratio of the lattice constants of the apatite ($c/a$)</td>
<td></td>
<td></td>
<td></td>
<td>0.706</td>
<td>0.702</td>
<td>0.706</td>
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<tr>
<td><strong>Chemical analysis</strong></td>
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<td></td>
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<tr>
<td>$\text{Sb}^{3+}$ (wt %)</td>
<td>0.58</td>
<td>1.32</td>
<td>1.92</td>
<td>2.06</td>
<td>0.53</td>
<td>1.18</td>
</tr>
<tr>
<td>$\text{Cl}^-$ (wt %)</td>
<td>1.00</td>
<td>1.52</td>
<td>4.82</td>
<td>5.13</td>
<td>5.75</td>
<td>5.44</td>
</tr>
</tbody>
</table>

Relative intensities of the strongest X-ray-diffraction lines: s = strong, m = medium, w = weak, vw = very weak, a = absent.
are shown in fig. 8.4. Under our experimental conditions the transformation of the orthophosphate starts at 500 °C and complete conversion is obtained at 700 °C.

The samples obtained at the lowest reaction temperatures still show the luminescence characteristic of $\beta$-Ca$_3$(PO$_4$)$_2$-Sb, which accords well with the X-ray data. The mechanism of the activation reaction has been discussed in the preceding section.

The most important conclusion to be drawn from this series of experiments is that the conversion of orthophosphate by gaseous SbCl$_3$ into chlorapatite and pyrophosphate proceeds readily. Provided the SbCl$_3$ is not exhausted, the conversion can be expected to be complete in a short time at temperatures of 700 °C and above.

The loss of antimony and chlorine in large-scale halophosphate manufacture occurs at about 800 °C and therefore we can now understand that no orthophosphate will be found in phosphors which have had the proper firing treatment. If orthophosphate were formed at relatively low temperatures, it would be readily converted as long as antimony chloride is present in sufficient amount in the atmosphere. However, when there is no more SbCl$_3$ available, the newly formed orthophosphate can no longer be converted and must remain in the phosphor as a contaminating phase. In factory-scale production of halophos-
phosphate phosphors this may easily occur during the last stage of the firing process (overfiring). For instance, the halophosphate already formed may be partially hydrolysed by moisture from the air to hydroxyapatite; this will react with the excess of pyrophosphate to orthophosphate, as described in chapter 4. The interaction with moisture is not an essential condition for the decomposition of the apatite, however. Commercial halophosphates nearly always contain small amounts of calcium antimonates, such as CaSb₂O₆ and Ca₂Sb₂O₇ [8]. In the last stage of the firing process these antimonates react with the excess of pyrophosphate. This may lead directly to the formation of an antimony-containing orthophosphate, but as may be seen from the equation

\[ \text{Ca}_2\text{P}_2\text{O}_7 + \text{CaSb}_2\text{O}_6 \rightarrow \text{Ca}_3(\text{PO}_4)_2 + \text{Sb}_2\text{O}_3 + \text{O}_2, \]  

the amount of \( \text{Sb}_2\text{O}_3 \) generated is far too great to be incorporated completely into the newly formed orthophosphate. The remainder may react according to eq. (8.1), viz.

\[ 3 \text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2 + 3 \text{Ca}_2\text{P}_2\text{O}_7 + \text{Sb}_2\text{O}_3 \rightarrow 12 \text{Ca}_3(\text{PO}_4)_2 + 2 \text{SbCl}_3, \]

as discussed in chapter 6.

When halophosphates are fired in open trays in a flow of dry nitrogen as described in the U.S.A. Patent 3,093,594 [8], a similar mechanism may be responsible for the formation of some \( \beta-\text{Ca}_3(\text{PO}_4)_2 \). In spite of the nitrogen atmosphere, some antimonate may be formed by oxidizing action of carbon dioxide at the firing temperature [8].

It is reported in this patent that the trays should not be filled completely and in this way a blanket of \( \text{SbCl}_3 \) will protect the surface layer of the phosphor against discolouration. It is not so likely, however, that the conditions reported will bring about a \( p_{\text{SbCl}_3}/p_{\text{Sb}_2\text{O}_3} \) ratio high enough to prevent the decomposition. Probably a small amount of orthophosphate will be formed and this phase may contain both \( \text{Sb}^{3+} \) and \( \text{Mn}^{2+} \). The nitrogen atmosphere prevents the manganese from being oxidized and in this way no discoloration betrays the presence of an orthophosphate phase.

8.4.3. The conversion of orthophosphate by mixtures of gaseous \( \text{SbCl}_3 \) and \( \text{Sb}_2\text{O}_3 \)

It follows from reaction equation (8.1) that probably the conversion of \( \beta-\text{Ca}_3(\text{PO}_4)_2 \) into chlorapatite, due to \( \text{SbCl}_3 \), will be retarded in the presence of gaseous \( \text{Sb}_2\text{O}_3 \). In the experiments discussed in sec. 8.4.1 the vapour pressure of the \( \text{Sb}_2\text{O}_3 \) could be neglected, as the remaining antimony oxide, neither incorporated in the apatite nor in the pyrophosphate, condensed in the low-temperature section of the apparatus.

During normal halophosphate preparation, however, the vapour pressure of the \( \text{Sb}_2\text{O}_3 \) cannot be neglected, as we start with a firing mixture containing
antimony trioxide. It is therefore interesting to investigate how the conversion will proceed when orthophosphate is heated in a mixture of gaseous SbCl$_3$ and Sb$_2$O$_3$. The following experiment was carried out in the closed system as shown in fig. 5.2. The high-temperature section contained 15 mmoles of $\beta$-Ca$_3$(PO$_4$)$_2$, kept at 1100 °C, while a mixture of 1·67 mmoles of Sb$_2$O$_3$ and 2·07 mmoles of SbCl$_3$, kept at 800 °C, was present in the low-temperature section. The amount of SbCl$_3$ had to be limited to about two mmoles as with larger quantities the vapour pressure rose so high as to blow up the apparatus. The quantity of Sb$_2$O$_3$ (1·67 mmoles) was taken large enough to ensure that the final atmosphere was saturated with gaseous Sb$_2$O$_3$. When the temperature was 800 °C, the final $p_{\text{Sb}_2\text{O}_3}$ amounted to 30 mm Hg. After a reaction time of three hours the final product was analysed. The sample contained 4·10 wt% of Sb$^{3+}$ and 3·69 wt% of Cl$^-$. X-ray analysis showed an incomplete conversion of the $\beta$-Ca$_3$(PO$_4$)$_2$.

It is interesting to compare the results of the above-mentioned experiment with previous experiments reported in sec. 8.4.1. This comparison is given in table 8-III. The vapour pressure of the SbCl$_3$ in this experiment is not a

| TABLE 8-III |
|-------------------|-----------------|-----------------|-----------------|-----------------|
| final vapour | conversion of | location of the | discussed |
| pressure (mm Hg) | the ortho- | emission band of | in section |
| Sb$_2$O$_3$ | phosphate | Ca$_{10}$(PO$_4$)$_6$Cl$_2$-Sb | |
| about 0 | 260 | just complete | 515 | 8.4.1 exp 7 |
| about 0 | about 500 | complete | 505 | 8.4.1 exp 9/10 |
| 30 | about 500 | incomplete | 520 | 8.4.3 |

"saturated" one but it can be calculated from the amount of unreacted SbCl$_3$ and the volume of the system, assuming that the gaseous SbCl$_3$ obeys the ideal-gas law and that it is present in the gaseous state. The latter does not quite hold good, as is stated in chapter 5, but so long as the amount of Sb$_2$O$_3$ added is relatively small, the error in $p_{\text{SbCl}_3}$ can be neglected.

It follows clearly from the figures in table 8-III that the conversion of $\beta$-Ca$_3$(PO$_4$)$_2$, due to SbCl$_3$, is incomplete in the presence of gaseous Sb$_2$O$_3$, showing that reaction (8.1) is reversible and strongly depending upon the partial vapour pressures of the gaseous participants.

It is interesting to consider the location of the emission band of the antimony-activated chlorapatite. A gradual decrease in the final $p_{\text{SbCl}_3}$ or a gradual increase in the final $p_{\text{Sb}_2\text{O}_3}$ brings about a shift of the emission peak to longer wavelengths.
Both changes in the final vapour pressures cause the formation of more oxygen-vacancy pairs in the apatite lattice. The observed shifts in luminescence and the amount of antimony incorporated are in accord with the effects discussed in chapter 5.

From the foregoing it may be concluded that the absence of Sb$_2$O$_3$ and the presence of some SbCl$_3$ during the last stages of the firing process is an essential point in making high-efficiency halophosphate phosphors.

8.4.4. *The conversion of β-(Ca,Mn)$_3$(PO$_4$)$_2$ with gaseous SbCl$_3*

In the preparation of manganese-containing halophosphates the orthophosphate that may be formed in the various stages of the firing process will also contain some manganese. A few experiments were made to find out what happens to β-(Ca,Mn)$_3$(PO$_4$)$_2$ when heated in gaseous SbCl$_3$.

Experiments identical with those discussed in sec. 8.4.1 (exp. 2 and 7) were carried out. The results of these experiments are quite similar to those of the corresponding experiments given in table 8-I. When $p_{\text{SbCl}_3}$ is low, incomplete conversion of the orthophosphate occurs. An increase in $p_{\text{SbCl}_3}$ to 260 mm Hg gives rise to complete transformation of the orthophosphate into chlorapatite and pyrophosphate. The spectra of the luminescence of the final products as shown in fig. 8.5 are in accord with these results. It follows that curve a

![Fig. 8.5. The emission spectra of some samples prepared by heating β-Ca$_{2.94}$Mn$_{0.06}$(PO$_4$)$_2$ in gaseous SbCl$_3$.](image)

(a) $p_{\text{SbCl}_3} = 26$ mm Hg.  (b) $p_{\text{SbCl}_3} = 260$ mm Hg.
\( p_{\text{SbCl}_3} = 26 \text{ mm Hg} \) is typical of orthophosphate activated with antimony and manganese, but curve b \( (p_{\text{SbCl}_3} = 260 \text{ mm Hg}) \) is characteristic of a double-activated apatite.

REFERENCES

8-3) W. L. Wanmaker, A. H. Hoekstra and J. G. Verriet, to be published.
9. GENERAL CONCLUSIONS

The enormous number of compounds with apatite crystal structure indicates that an arrangement of suitable ions in this type of lattice is very advantageous as regards energy. Beevers and McIntyre \(^{9~1)}\) attributed this to the arrangement of the metal and phosphate ions whereas the halogen ions have to find positions within this skeleton.

In principle the halogen ions may be found either in the planes at \(z = \frac{1}{2}\) and \(z = \frac{3}{2}\) (also called “mirror” planes), e.g. fluorine ions in calcium fluorapatite as proposed by Náray Szabó \(^{9~2)}\) or in planes at \(z = 0\) and \(z = \frac{1}{2}\), e.g. in the structure suggested by Mehmel \(^{9~3)}\). Hendricks et al. \(^{9~4)}\) accepted the positions of the fluorine ions as proposed by Náray Szabó and applied the Mehmel-type structure (also called the pyromorphite structure) to calcium chlorapatite.

Let us now have a closer look at both kinds of structures. When the halogen ions are located in the mirror planes in which the Ca\(_n\) ions have their positions, too, the distance between a Ca\(_n\) site and a halogen site is about 2·3 Å. From the ionic radii of Ca\(^{2+}\) = 1·06 Å, F\(^-\) = 1·33 Å, Cl\(^-\) = 1·81 Å, Br\(^-\) = 1·96 Å and I\(^-\) = 2·20 Å it follows that \(r_{\text{Ca}} + r_{\text{F}} \approx 2·4\) Å whereas \(r_{\text{Ca}} + r_{\text{Z}}\) is much longer than the distance between a Ca\(_n\) and a neighbouring halogen site located in the mirror planes if \(Z\) stands for Cl\(^-\), Br\(^-\) or I\(^-\). A fluorine ion just fits into the triangle formed by three Ca\(_n\) sites in a horizontal plane. These sites are too small, however, for the other halogen ions. If these ions are located in the planes at \(z = 0\) and \(z = \frac{1}{2}\) the distance between a Ca\(_n\) site and a halogen site is about 3·0 Å. In that case a chlorine, and apparently a bromine ion, too, fit into these positions; the iodine ion is actually too big for these sites. Consequently alkaline-earth apatites containing iodine do not exist.

The marked effect of the halogen ion on the lattice constants of the alkaline-earth–halogen apatites may be attributed to the position of the halogen ions. It follows from the work of Akhavan Niaki \(^{9~5)}\) that there is a linear relation between the lattice constant \(a\) and the radius of the alkaline-earth ion. These relations are similar for the chlorapatites and bromapatites, but differ for the fluorapatites. When in either of the alkaline-earth fluorapatites the fluorine ions are replaced by chlorine or by bromine ions, the lattice constant \(a\) also increases, but not linearly with the radius of the halogen ions. The behaviour of the lattice constant \(c\) is quite different from that of the constant \(a\). When in either of the calcium-halogen apatites the calcium ions are replaced by the bigger strontium or barium ions, \(c\) increases, but not linearly with the radii of the metal ions. When the fluorine ions are replaced by the bigger chlorine or bromine ions in either of these alkaline-earth fluorapatites \(c\) decreases!

The different relation between the lattice constant \(a\) and the radius of the alkaline-earth ion as found by Akhavan Niaki for the fluorapatites as compared
with the chlorapatites and bromapatites, points to a difference in crystal structure. Apparently the alkaline-earth fluorapatites have the apatite structure but the halogen ions in the chlorapatites and bromapatites must be sought in the (000) and (00\frac{1}{2}) sites. Moreover, in the structure of fluorapatite there is little interaction between the alkaline-earth ions located on $M_{II}$ sites in adjacent planes. The opposite applies for these ions in the Mehlm-type structure. The alkaline-earth ions involved are now attracted by the halogen ions located between the mirror planes, resulting in a decrease in the distance between these planes and hence the lattice constant $c$ decreases as compared with the corresponding fluorapatite.

When we restrict ourselves to the calcium-halogen apatites, $Ca_{10}(PO_4)_6Z_2$, where $Z$ stands for $F$, $Cl$ or $Br$, still another stereometrical consideration can be put forward. In both structures the halogen ions are located on the threefold axis ($c$-axis). From table 9-1 it follows that for calcium fluorapatite $c > 4r_F$, the opposite holds good for chlorapatite and bromapatite. With respect to the neighbouring halogen ion, the chlorine and the bromine ion must fit into the (000) and (00\frac{1}{2}) positions in spite of the fact that $4r > c$. Apparently these halogen ions are strongly polarized by the six surrounding $Ca_{II}$ ions.

From both stereometrical considerations above it follows that, with respect to its radius, the fluorine ion in calcium fluorapatite might be found either in the (000) and (00\frac{1}{2}) or in the (00\frac{1}{2}) and (00\frac{3}{2}) positions. The fact that they are actually found in the latter is probably due to energy. If these ions would be removed to the (000) and (00\frac{1}{2}) sites, the energy content of the apatite would increase. Thus, as soon as the halogen ion fits into both kinds of position, the configuration with the lowest energy content is preferred. Chlorapatite with chlorine ions further removed from the $Ca_{II}$ sites has probably a higher energy content and is therefore less stable than fluorapatite.

It might well be that the apatites with the pyromorphite structure tend to exchange their halogen ions for others which fit into the (00\frac{1}{2}) and (00\frac{3}{2}) sites, hence determining the stability of the calcium-halogen apatites by the radius

<table>
<thead>
<tr>
<th>halogen ($Z$)</th>
<th>$c$ (Å)</th>
<th>$r$ (Å)</th>
<th>$4r$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>fluorine</td>
<td>6·88</td>
<td>1·33</td>
<td>5·32</td>
</tr>
<tr>
<td>chlorine</td>
<td>6·77</td>
<td>1·81</td>
<td>7·24</td>
</tr>
<tr>
<td>bromine</td>
<td>6·76</td>
<td>1·96</td>
<td>7·84</td>
</tr>
</tbody>
</table>
of the halogen ion. This is clearly reflected both in the formation and in the pyrohydrolysis of these apatites.

Fluorapatite may be formed in aqueous solution; Baudrienghien and Bras- 
seur 9-6) succeeded in precipitating a non-stoichiometrical hydroxychlorapatite 
under special reaction conditions. However, no such references have been found 
concerning the formation of an apatite containing bromine.

As for pyrohydrolysis, calcium fluorapatite has to be heated to elevated 
temperatures in water vapour for a long time for the fluorine ions to be replaced 
by hydroxyl ions. Chlorapatite and bromapatite (the latter in particular) pyro-
hydrolyse when heated in air at a temperature of about 700-800 °C.

It is understandable that when in calcium chlorapatite only a small proportion 
of the chlorine ions are replaced by hydroxyl ions, the latter are still on chlorine 
lattice sites in spite of their preferential positions in the mirror planes. The 
remaining chlorine ions force them to occupy these sites. This may be seen as a 
kind of steric hindrance. When the hydroxychlorapatite formed loses water, 
giving rise to the formation of oxygen-vacancy pairs, this hindrance is removed 
and the remaining hydroxyl ions can occupy their normal sites in the mirror 
planes.

Probably a similar picture applies to chlorapatite containing antimony. An 
antimony and an oxygen ion are substituted for a calcium ion and a chlorine 
ion but simultaneously two chlorine ions are replaced by an oxygen-vacancy 
pair. The foregoing raises the question whether a gradual change of the crystal 
structure will occur.

An accurate determination of the lattice constants of our antimony-contain-
ing samples was scarcely possible; with Brasseur's method 9-7), however, we 
were able to determine the c/a ratio.

When the experimental conditions in preparing the samples were chosen such 
that only a very small amount of antimony is incorporated, the c/a ratio is found 
to be about 0·702 (identical to that of chlorapatite), the number of oxygen-
vacancy pairs is very small and the emission band is located at about 365 nm. 
When the amount of antimony taken up increases from 0.1 to 0.2 wt %, the 
c/a ratio and the number of oxygen-vacancy pairs increase, the 365-nm emission 
band vanishes, but a new one, located at 490 nm, appears. A further increase 
in the antimony content (up to about 3·5 %) gives rise to a c/a ratio of 0·714 
and the emission band is gradually shifted from 490 nm to 515 nm. The increase 
in the c/a ratio may be caused either by a decrease in the constant a or by an 
increase in the constant c. From Akhavan Niaki's results it is hard to believe 
that the substitution involved would result in a noticeable decrease in the lattice 
constants. Probably a picture similar to that given in the explanation of the 
expansion of the lattice constant c of the apatite as compared with the constant 
of the corresponding pyromorphite also holds good for this problem. In other 
words, the oxygen ion of the SbO group prefers to occupy a (00\frac{1}{2}) or a (00\frac{3}{2}) site
as in this way the energy content of the activated apatite is lowered. The oxygen ion involved can only occupy one or other of these sites when oxygen-vacancy pairs are formed. We therefore attribute the driving force of the formation of these pairs to a decrease in the energy content of the apatite.

A similar picture cannot explain the formation of these pairs in calcium hydroxyapatite. According to Posner et al. the structure of this apatite is identical to that of calcium fluorapatite. The hydroxyl ions have already occupied the sites giving rise to the lowest energy content.

Kay, Young and Posner made a refinement of the structure of this apatite by using X-ray and neutron-diffraction data. These authors concluded that the O-H-bond direction is parallel to the c-axis, that the oxygen of the hydroxyl ion is displaced about 0.3 Å from the mirror planes and that the O-H bond does not straddle these planes. From stereometrical considerations it follows that only one hydroxyl ion can be located “between” adjacent mirror planes giving rise to an ordered arrangement of the direction of the O-H bonds. This direction may be reversed by special structural circumstances, e.g. when a hydroxyl ion is replaced by a fluorine ion or when oxygen-vacancy pairs are present.

The suggestion that an increase in temperature will give rise to a disordered arrangement of the O-H-bond direction is by no means unlikely and in this case the driving force of the formation of oxygen-vacancy pairs is indeed attributed to the preferential disordered arrangement of the O-H-bond direction at elevated temperatures.

When a mixture of chlorapatite and calcium pyrophosphate is heated, no reaction occurs if water vapour is absent. A decomposition to orthophosphate occurs, however, in the presence of water vapour or gaseous antimony oxide, provided that the HCl or SbCl₃ formed is continuously removed. These conditions give rise to the formation of oxygen-vacancy pairs in the chlorapatite. We therefore attribute the decomposition to a reduced stability of the apatite in the presence of pyrophosphate due to the presence of these pairs. On the other hand, we found that when calcium orthophosphate is heated either in gaseous HCl or SbCl₃ such that the water or antimony oxide formed is continuously removed, it is completely converted into calcium chlorapatite and calcium pyrophosphate. Apparently the difference between the energy content of 3 moles of Ca₁₀(PO₄)₆Cl₂ + 3 moles of Ca₃P₂O₇ + 3 moles of H₂O (or one mole of Sb₂O₃) and 12 moles of Ca₃(PO₄)₂ + 6 moles HCl (or 2 moles of SbCl₃) is small at the reaction temperature.

A similar picture probably applies to the reaction between hydroxyapatite and pyrophosphate. The apatite reacts with pyrophosphate at elevated temperatures when vacancies have been formed. On the other hand, Schleede et al. found that when calcium orthophosphate is suspended in boiling water, it is gradually converted into hydroxyapatite.
The decomposition of the apatite and the conversion of orthophosphate are very important reactions in the manufacture of halophosphate phosphors. A high $P_{3b\text{Cl}_3}/P_{3b\text{O}_3}$ ratio during the last stage of the firing process gives rise to the absence of a calcium-orthophosphate phase, but results in a relatively small amount of antimony activator being incorporated. Just the opposite occurs when the $P_{3b\text{Cl}_3}/P_{3b\text{O}_3}$ ratio is relatively low. These conditions easily result in the formation of a $\beta$-calcium-orthophosphate phase which contains antimony and manganese, giving rise to a highly ineffective u.v. absorption and, under oxidizing conditions, to discoulouration of the final product.

REFERENCES

9-1) C. A. Beevers and D. B. McIntyre, Mineral Mag. 27, 254-257, 1946.
Samenvatting

In dit proefschrift worden de eigenschappen van zuiver en van met antimoon geactiveerd calcium-chloorapatiet en van antimoonhoudende calciumfosfaten samengevat. Dit onderzoek werd opgezet om een beter inzicht te krijgen in de ingewikkelde reacties die bij de bereiding van calciumhalofosfaat-fosforen optreden. In een korte inleiding worden de problemen uiteengezet, die zich bij de bereiding van deze fosfor voordoen. In hoofdstuk 2 wordt de literatuur van verbindingen met de kristalstructuur van apatiet gerecenseerd en in hoofdstuk 3 wordt een overzicht gegeven van de gebruikte grondstoffen en de toegepaste methodieken. Het experimentele deel wordt in de hoofdstukken 4 t/m 8 behandeld en algemene conclusies worden in hoofdstuk 9 vermeld.

Het niet geactiveerde calcium-chloorapatiet wordt in hoofdstuk 4 besproken. Dit apatiet wordt gemakkelijk gepyrohydrolyseerd tot calcium-hydroxyapatiet. Wanneer de pyrohydrolyse plaats vindt in aanwezigheid van pyrofosfaat treedt tevens ontleding op in orthofosfaat. Wanneer chloorapatiet met een overmaat fosfaat gemaakt wordt dan verklaart deze reactie het voorkomen van \( \text{Ca}_3(\text{PO}_4)_2 \) en \( \text{Ca}_3\text{P}_2\text{O}_7 \) als tweede fase. De pyrohydrolyse en de ontleding van chloorapatiet zijn omkeerbare reacties en de bestudering van de eerste reactie heeft een verbeterde bereidingsmethode voor zuiver calcium-chloorapatiet opgeleverd, die in § 4.5 besproken wordt. Ondanks een verschil in structuur bestaat er een ononderbroken reeks mengkristallen tussen calcium-chloorapatiet en calcium-hydroxyapatiet, die aan het vervangen van chloor- of hydroxyl-ionen door zuurstof-vacature paren wordt toegeschreven.

In de hoofdstukken 5, 6 en 8 wordt het met antimoon geactiveerde calcium-chloorapatiet behandeld. Uit de samenstelling van de monsters verkregen door \( \text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2 \) in de damp van \( \text{Sb}_2\text{O}_3 \) te verhitten volgt, dat naast het vervangen van Ca-Cl door Sb-O paren een extra chloorverlies optreedt, dat aan de vorming van zuurstof-vacature paren wordt toegeschreven. De hierop gebaseerde hypothese, die betrekking heeft op de plaats en de omringing van het Sb\(^{3+}\) ion in het chloorapatiet rooster, wordt ondersteund door het verschil in de emissiespectra. De aanwezigheid van zuurstof-vacature paren vermindert de stabilitéit van het met antimoon geactiveerde apatiet en in aanwezigheid van \( \text{Ca}_3\text{P}_2\text{O}_7 \) kan het ontleden in \( \text{Ca}_3(\text{PO}_4)_2 \). Deze ontleding is een omkeerbare reactie; orthofosfaat kan door verhitting in gasvormig SbCl\(_3\) in chloorapatiet en pyrofosfaat worden omgezet.

In hoofdstuk 7 worden calciumfosfaten, die antimoon bevatten, besproken. Bij het activeren van \( \text{Ca}_3\text{P}_2\text{O}_7 \) of \( \text{Ca}_3(\text{PO}_4)_2 \) wordt zeer weinig Sb\(^{3+}\) ingebouwd, zodat deze stoffen nauwelijks luminesceren. Calcium-antimoon-orthofosfaat van de samenstelling \( \text{Ca}_{3-x}\text{Sb}_{2x}(\text{PO}_4)_2 \) (\( x \approx 0.05 \)) ontstaat echter gemakkelijk. In vergelijking tot de halofosfaten vertoont dit materiaal geringe luminescentie maar een hoge u.v. absorptie en de energie, die door deze verbinding geabsorbeerd wordt, kan als verloren worden beschouwd.
In hoofdstuk 9 wordt de stabiliteit van chloorapatiet in verband gebracht met de grootte van de straal van het chloor-ion. Calcium-chloorapatiet toont de pyromorfiet-structuur met chloor-ioniën op de (000) en (00\(\frac{1}{2}\)) plaatsen. Zowel bij de reactie met water als bij de reactie met Sb\(_2\)O\(_3\) zullen de resterende chloor-ioniën trachten de substituenten te dwingen om chloorplaatsen te bezetten ondanks de voorkeur van deze substituenten voor de (00\(\frac{1}{2}\)) en (00\(\frac{3}{2}\)) plaatsen. Zodra echter zuurstof-vacature paren aanwezig zijn, kunnen de betreffende substituenten hun voorkeursplaatsen wel innemen.
Dankwoord

De in dit proefschrift beschreven onderzoekingen werden verricht op het Fluorescentie Laboratorium van de H.I.G. Licht van de N.V. Philips' Gloeilampenfabrieken te Eindhoven. Gaarne betuig ik de directie van deze H.I.G. mijn dank voor de mij verleende vrijheid dit onderzoek te verrichten en in het bijzonder Dr. J. L. Ouweltjes voor zijn voortdurende aanmoedigingen om de resultaten in een proefschrift samen te vatten.

Veel dank ben ik verschuldigd aan verschillende collega's voor hun steeds opbouwende kritiek. De uitgebreide steun van Dr. J. L. Ouweltjes en Dr. W. L. Wanmaker heeft een grote bijdrage geleverd tot de uiteindelijke vormgeving van dit proefschrift.


Curriculum vitae

STELLINGEN

I
De door Berak uitgesproken veronderstelling dat calciumfluorapatiet geen oxyapatiet kan bevatten, is onjuist.


II
De argumenten die Johnson aanvoert voor zijn veronderstelling dat Sb$^{3+}$ in Ca$_{10}$(PO$_4$)$_6$Cl$_2$ op Ca$_4$ plaatsen aanwezig is, zijn onvoldoende en tendeel onjuist.


III
De methode van Tachoire c.s. tot bepaling van het optisch rendement van verbrandingsprocessen leidt door onjuiste veronderstellingen tot foutieve resultaten.


IV
De hoge intensiteitsverhouding van de oranje tot de rode emissie lijnen in het spectrum van LaVO$_4$-Eu schrijven Palilla, Levine en Rinkevics ten onrechte toe aan een grotere waarschijnlijkheid van de toegestane magnetische dipoolovergang $^5$D$_0$ $\rightarrow$ $^7$F$_1$ tengevolge van de relatief lage symmetrie van het monokline moederrooster.


V
Ten onrechte schrijven Dieke en Hall de korte decaytijd en het lagere rendement van de fluorescentie van zouten van andere zeldzame aarden dan Gd toe aan een grotere interactie van deze ionen met het rooster.

VI
De door Cerrai en Ghersini beschreven methoden om Fe$^{III}$ te bepalen via extractie met behulp van een oplossing van di-(2-ethylhexyl) orthofosforzuur in cyclohexaan biedt geen specifieke voordelen ten opzichte van overige extractiemethoden o.a. met behulp van methyl isobutyl keton.


VII
De experimentele gegevens die Nitschmann tot de conclusie geleid hebben dat de omzetting van $\gamma$-FeOOH in $\alpha$-FeOOH een topochemische en pseudomorfse vaststoff-reactie is, zijn onvoldoende.


VIII
De regeneratieve wolfraam-jodium cyclus die in gloeilampen met een jodium bevattend vulgas optreedt, schrijven Zubler en Mosby ten onrechte toe aan de omkeerbare reactie $W + 2J \leftrightarrow W_2J$.


IX
Het is onwaarschijnlijk dat de chromatische adaptatie van het oog op bevredigende wijze met liniaire Von Kries transformaties beschreven kan worden.


X
Uit de experimenten van Metson en Macartney kan niet afgeleid worden dat de lage temperatuurgeleiding van oxide kathoden een oppervlakteverschijnsel is, veroorzaakt door geadsorbeerd Ba. Evenmin is het experimentele werk van Dubova en medewerkers een bewijs voor de opvatting dat geadsorbeerd Ba geen rol speelt bij de emissie van deze kathoden.


XI
Het is gewenst dat de snelheid van verkeersdeelnemers, die krachtens het Wegenverkeersreglement een rood stoplicht mogen passeren, ter plaatse van de kruising de daar geldende maximum snelheid niet mag overschrijden.

A. H. Hoekstra 6 juni 1967