Cation distribution in calcium-strontium-hydroxyapatites

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Published in: Journal of Inorganic and Nuclear Chemistry

DOI: 10.1016/0022-1902(79)80375-9

Published: 01/01/1979

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

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Table 1. Eigenvalues and eigenvectors of $^{3}H_{4}$ term in the crystal field of $C_{2}$, symmetry calculated with values listed in Fig. 2. $(J_{r})$ represents $[-J_{r}]$.

<table>
<thead>
<tr>
<th>Eigenvalue (cm$^{-1}$)</th>
<th>Eigen vector</th>
</tr>
</thead>
<tbody>
<tr>
<td>4784</td>
<td>0.0171$(4&gt;0) - 0.4092(12&gt;0) + 0.8153i0)$</td>
</tr>
<tr>
<td>4780</td>
<td>-0.1454$(13&gt;0) + 0.6920(11&gt;0)$</td>
</tr>
<tr>
<td>1578</td>
<td>-0.1267$(14&gt;0) + 0.6957(12&gt;0)$</td>
</tr>
<tr>
<td>1560</td>
<td>-0.4466$(13&gt;0) + 0.5482(11&gt;0)$</td>
</tr>
<tr>
<td>-1135</td>
<td>-0.1804$(4&gt;0) + 0.5551(12&gt;0) + 0.56460)$</td>
</tr>
<tr>
<td>-1107</td>
<td>0.6920$(13&gt;0) + 0.1454(11&gt;0)$</td>
</tr>
<tr>
<td>-2162</td>
<td>0.5482$(3&gt;0) + 0.4466(11&gt;0)$</td>
</tr>
<tr>
<td>-4040</td>
<td>0.6957$(4&gt;0) + 0.1267(12&gt;0)$</td>
</tr>
<tr>
<td>-4056</td>
<td>0.6835$(4&gt;0) + 0.1567(12&gt;0) + 0.12870)$</td>
</tr>
</tbody>
</table>

The calculation of the magnetic susceptibility from the energy splitting behavior thus obtained has been done with use of the Van Vleck formula to the first excited state, including an additional open variable $Q$ introduced by Amberger et al.[10]. As shown in Fig. 1, a good agreement with the experimental result up to 170 K is obtained, when $R_{4}$ and $Q$ are taken to be 2.35 Å and 0.829, respectively ($\theta_{4} = 67.2^\circ$). The eigenvalues and the eigenvectors are listed in Table 1. The value of $Q$ is intermediate between that of uranocene ($Q=0.94$)[11] and that of $\text{CsH}_{0.4}\text{U(IV)}$ ($Q = 0.707$)[10]. The distance $R_{4}$ and the angle $\theta_{4}$ seems to be reasonable values considering that the U-N distance of $\text{U(NCS)}_{6.4}(\text{C}_{2}\text{H}_{8}\text{N}$ is 2.38 Å[12] and the angle of $\theta$ in $\text{C}_{2}$ is 67.2$^\circ$[5]. The small deviation from the experimental value above about 170°K may be explained by taking into account higher excited states.

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Pergamon Press Ltd. 1979 Printed in Great Britain
pure end-members CaOHA and SrOHA were also subjected to this heat treatment prior to X-ray diffraction. Both the Philips Guinier XDC-700 and the Nonius Guinier-de Wolff camera were used, either with CrKα or CuKα. The cell parameters were determined by measuring the position of at least 28 reflections for each sample. The accuracy of the cell parameters a and c of the hexagonal cell which were calculated by using a least squares procedure is estimated to be better than ±0.003 and ±0.002 respectively. The results with both cameras were the same and are represented in Fig. 1. They confirm the linear variation with composition found earlier [3, 4].

In the apatite structure two sublattices occur for the cations. Position I is fourfold (Wyckoff notation f) and position II is six-fold (denoted by h). The structure formula of solid solutions of CaOHA and SrOHA can thus be written as

$$Ca_{4-x}Sr_x(Ca_{6-(1-x)}Sr_{(1-x)})(PO_4)_6(OH)_2.$$  

As the cation distributions were not known, we derived them from a comparison of the experimental values of the intensity ratios 210/002, 300/002, 220/002, 002/202, 321/202, 321/410 and 213/312 with their theoretical values depending on α. In the calculation of the theoretical values Lorentz-polarisation and multiplicity factor were taken into account, absorption correction and temperature factor were neglected. Both peak heights and peak areas were taken as a measure for the intensities of reflections.

In this way two sets of seven α values were obtained for each composition x. The average per set was independent of the fact whether peak heights or peak areas were taken. A distribution coefficient K was defined as

$$K = \frac{[6-(1-\alpha)x][\alpha x]}{[4-\alpha x][(1-\alpha)x]}$$  

and its value and standard deviation were calculated from the two sets of α values at a given x. A constant value for K was found throughout the range 1 ≤ x ≤ 9 within the limits of experimental error. Its overall weighted mean was 0.841 ± 0.065. This means (a) that apparently an equilibrium is reached according to

$$Ca(I) + Sr(II) \rightleftharpoons Ca(II) + Sr(I)$$  

at the temperature of preparation and (b) that the solid solutions are close to ideal in the thermodynamical sense [9]. The latter conclusion enables the quantitative estimation of the effect of Sr²⁺ ion incorporation on the solubility product of CaOHA from knowledge about the solubility products of both CaOHA and SrOHA [7].

N.B. The individual values of α and K derived from the intensity ratios are available on request.

Acknowledgement—The authors are indebted to Mr. F. C. Kruger for carrying out the X-ray diffraction experiments.

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