Electrical transport and defect properties of Ca- and Mg-doped yttrium aluminum garnet ceramics

Citation for published version (APA):

Schuh, L. H., Metselaar, R., & With, de, G. (1989). Electrical transport and defect properties of Ca- and Mg-doped yttrium aluminum garnet ceramics. *Journal of Applied Physics*, 66(6), 2627-2632.
<https://doi.org/10.1063/1.344485>

DOI:

[10.1063/1.344485](https://doi.org/10.1063/1.344485)

Document status and date:

Published: 01/01/1989

Document Version:

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

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Electrical transport and defect properties of Ca- and Mg-doped yttrium aluminum garnet ceramics

L. Schuh,^{a)} R. Metselaar, and G. de With^{b)}

Eindhoven University of Technology, Department of Physical Chemistry and Centre for Technical Ceramics, 5600 MB Eindhoven, The Netherlands

(Received 8 December 1988; accepted for publication 5 June 1989)

Electrical transport properties of a sintered yttrium aluminum garnet (YAG) doped with Ca or Mg have been investigated as a function of temperature and partial pressure of oxygen. Conductivity and ionic transport measurements show Ca- and Mg-doped YAG to be mixed ionic-electronic *p*-type conductors exhibiting an activation energy of about 2 eV. Thermally stable inclusions of alumina, which were found to be present in sintered YAG powders, act as a source of Al vacancies. Al vacancies are dominating the defect chemistry at high oxygen partial pressure. The electronic contribution to total conductivity becomes more pronounced when the temperature increases. At low *p*O₂ a hole-release from O_i[•] centers (trapped holes) influences the transport behavior. We developed a possible defect model which explains the experimental data qualitatively. This model considers the influence of dispersed particles of constant activity over a *p*O₂ regime ranging from 10⁵ to 10⁻¹² Pa and their influence on the defect chemistry.

I. INTRODUCTION

YAG (yttrium aluminum garnet or Y₃Al₅O₁₂) is widely used as a host for metal ions in lasers¹ and phosphorescent sources.²⁻⁴ The defect properties of single-crystalline YAG doped with different ions were investigated in the past by means of optical absorption,⁵⁻¹² paramagnetic resonance,¹³⁻¹⁶ and electrochemical methods.¹⁷⁻²² All workers come to the same conclusion that the predominant defects in YAG are oxygen vacancies. These are the most mobile ionic defects in the garnet structure. Therefore, diffusion has to be described in terms of the anti-Wagner mechanism.²³

Besides single-crystalline material, sintered YAG gained some interest in recent years. It has been shown that YAG powders can be sintered to optical transiucency.²⁴⁻²⁸ Moreover, some physical properties are better than those of the most common Lucalox²⁸ (translucent Al₂O₃), e.g., corrosion resistance, optical transmittance, or some mechanical properties. This makes YAG ceramics a candidate material for high-temperature applications. A particular problem concerning YAG ceramics is that after sintering up to 5 vol % Al₂O₃ inclusions (dimensions about 0.25–0.5 μm) are present.^{29,30}

Translucent ceramics have a low porosity.³¹ Until now nearly no experimental data about the influence of sinter additives on densification, grain growth, and mechanical and physical properties have been published. It is remarkable that no effect of grain-boundary pinning by the inclusions was found in YAG; Rhodes³² showed that such a pinning effect should lead to a remarkable reduction in grain growth.

In one of our earlier papers²² we discussed the influence of hydrogen on high-temperature properties of Zr-doped YAG ceramics. The present paper gives a defect model for

Ca- and Mg-doped YAG ceramics with alumina inclusions. The inclusions are considered to be a source of Al vacancies governing the transport properties.

II. EXPERIMENTAL TECHNIQUES

A. Sample preparation and characterization

Ca- and Mg-doped YAG powders were prepared by spray drying sulfate solutions. After calcination, milling, and sieving, the powder was isostatically pressed into pellets and presintered in air. The final sintering took place in wet hydrogen at 2070 K. The resultant samples were optically translucent. Impurity and dopant concentrations were determined by optical emission spectroscopy on specimens designated as YAG: 70 Ca, YAG:400 Ca, and YAG: 60 Mg in Table I. About 80% of the MgO evaporates under the sintering conditions, while the concentration of CaO does not change markedly. Both dopants acted as strong grain growth inhibitors, with Ca being the most effective.³³

TABLE I. Dopant and impurity concentrations in the sintered samples determined by optical emission spectroscopy.

Element	Sample name: YAG: 70 Ca YAG: 400 Ca YAG: 60 Mg		
	Concentration in at. ppm		
Ca	70	400	< 35
Mg	12	12	60
Si	15	11	11
Fe	4	3	3
Ga	1	1	1
Cr	6	6	6
Ti	2	1	2
Na	< 65	< 65	< 65
Ni	< 5	< 5	< 5
Mo	< 3	< 3	< 3

^{a)} Now at the Asea Brown Boveri Corporate Research Centre, 6900 Heidelberg, Federal Republic of Germany.

^{b)} Also affiliated with Philips Research Laboratories, Eindhoven.

On the basis of crystal-chemical considerations it is assumed that Ca enters the dodecahedral site and substitutes for Y. Mg ions should enter the dodecahedral as well as the octahedral sites.^{34,35} The solubility of Ca in YAG is low; it has been shown that Ca concentrations of 300–400 ppm tend to form precipitates.³³ As described by Mulder and de With,³⁰ YAG samples sintered in vacuum contain Al-rich inclusions in spite of the fact that the stoichiometry of the starting powder is 3:5. Inclusions in YAG sintered in vacuum were observed by scanning electron microscopy/energy-dispersive x rays (SEM/EDX) and transmission electron microscopy (TEM).³⁰ Our own high-resolution TEM studies show these inclusions to be crystalline, presumably Al_2O_3 .³³ Firing in hydrogen instead of vacuum diminishes these inclusions, but they are still present.

B. Electrical conductivity and emf measurements

The electrical conductivity was determined using a Solartron 1174 Frequency Response Analyser interfaced to a HP-86 computer. The high-temperature conductivity cell was described previously in Ref. 36. The impedance was measured in the complex $Z'-Z''$ plane as a function of T and $p\text{O}_2$, which allowed bulk, grain-boundary, and electrode effects to be separated from each other. Electrode effects (i.e., the capacitance of the electrode-electrolyte interface) were minimized by first sputtering a Pt layer followed by the application of a Pt paste. The samples were disk shaped with a diameter of about 10 mm and a thickness of 0.7 mm. The oxygen pressure was controlled by using O_2/N_2 , CO/CO_2 , and $\text{H}_2/\text{H}_2\text{O}$ mixtures.

emf data were measured using a three-terminal technique with a volume guard. This technique is described in Ref. 37. A gas-tight connection between the guard tube and the sample was established by a high-temperature treatment using a Pt seal ring. This allows different $p\text{O}_2$'s to be maintained on each side of the sample. The ionic transference numbers t_i were determined by differentiating the emf of the concentration cell.

III. RESULTS

Figures 1(a)–1(c) show the isotherms $\log \sigma$ vs $\log p\text{O}_2$ for YAG: 70 Ca, YAG: 400 Ca, and YAG: 60 Mg. The ionic transport numbers for all three samples are given in Fig. 2. Analyses of complex impedance diagrams in the $Z'-Z''$ plane revealed that the grain-boundary resistance was not a function of $p\text{O}_2$, so the conductivity data are attributed to the grain interior. Transport numbers t_i were calculated from

$$t_i = \left(\frac{d(4FE/2.3 RT)}{d \log p\text{O}_2'} \right)_{p\text{O}_2' = \text{const (air)}}, \quad (1)$$

where $p\text{O}_2'$ and $p\text{O}_2''$ denote the oxygen pressures on each side of the sample in the concentration cell, E is the emf, and the other symbols have their usual meaning.

Using the relations $\sigma_{\text{ion}} = \sigma_{\text{tot}} t_i$ and $\sigma_{\text{el}} = \sigma_{\text{tot}} (1 - t_i)$ allows the separation of the ionic from the electronic conductivity. The fact that σ_{el} increases with $p\text{O}_2$ indicates that we are dealing with holes: $\sigma_{\text{el}} = \sigma_{\text{hole}}$. Ionic and hole conductivity for YAG: 70 Ca and YAG: 60 Mg are drawn in Figs. 1(a) and 1(c). At higher $p\text{O}_2$'s the hole conductivity

FIG. 1. $p\text{O}_2$ dependence of the conductivity for (a) YAG: 70 Ca, (b) YAG: 400 Ca, (c) YAG: 60 Mg. Besides total conductivity (σ_{tot}), (a) and (c) give the ionic and hole conductivities (σ_{ion} , σ_{hole}).

changes proportional $p\text{O}_2^{3/16}$. In heavily acceptor-doped YAG: 400 Ca we detected ionic conductivity over nearly the entire $p\text{O}_2$ regime. t_i was found to decrease with increasing temperature.

Figure 3 illustrates σ as $f(T)$ measured at different oxygen partial pressures. The activation energies E_a (Table II) were calculated using an Arrhenius relationship. Analyses of complex impedance data allowed us to separate the grain boundary from bulk (grain interior) effects.

E_a in oxygen is about 2 eV for bulk conduction for all three samples. The grain-boundary conductivity has a considerably higher activation energy: 2.4 eV was a typical value we found in our samples. This difference indicates that the grains are covered by a continuous intergranular film, with no easy-path conduction via direct grain-grain contacts, as

FIG. 2. Ionic transport numbers as $f(pO_2)$ for (a) YAG:70 Ca, (b) YAG:400 Ca, and (c) YAG:60 Mg.

FIG. 3. Temperature dependence of the conductivities of YAG:70 Ca, YAG:400 Ca, and YAG:60 Mg. The numbers denoting the lines are specified in Table II.

TABLE II. The activation energies for conduction processes in different acceptor-doped YAG ceramics (the numbers refer to the lines in Fig. 3).

Line	Sample	pO_2 (Pa)	Specification	E_a (eV)
1	YAG: 70 Ca	10^5	bulk (<i>p</i> -type)	2.0
2	YAG: 70 Ca	10^5	grain boundary	2.4
3	YAG: 70 Ca	10^{-9}	bulk (ionic)	2.7
4	YAG: 400 Ca	10^5	bulk (mixed)	1.07
5	YAG: 60 Mg	10^5	bulk (<i>p</i> -type)	2.2

described, e.g., for zirconia.^{38,39} For the conductivity at a pO_2 as low as 10^{-9} Pa the activation energy was 2.7 eV.

IV. THEORY

To fix the defect concentration in the ternary YAG system we use as variables the temperature T , the partial oxygen pressure pO_2 , and the activity of alumina. The latter activity is fixed during our measurements, because the garnet is always saturated with alumina. However, before we apply the theory of classical defect chemistry,⁴⁰ we have to assure that the alumina precipitates do not influence our results in other ways. Specifically we verify that electrical double layers do not affect our measurements. Examples of such effects have been described in several ionic conductors with dispersed second phases, e.g., TiO_2/SiO_2 ,⁴¹ $CuCl/Al_2O_3$,⁴² and LiI/Al_2O_3 .⁴³

According to the formalism worked out by Crosby,⁴¹ the ratio of conductivity in the double layer near the dispersoid interface σ_{disp} to that of the bulk matrix σ_{bulk} can be expressed by

$$\sigma_{disp}/\sigma_{bulk} = 1 + 0.83g|Z|V_v(L_D^2/r_l^2), \quad (2)$$

where g is a factor depending on the surface potential ($g \approx 20$).⁴¹ Z is the defect charge, V_v is the volume fraction of the dispersoid, L_D is the Debye length, and r_l is the radius of the dispersoid. For our experimental conditions we derived a Debye length of 1.2 nm. In YAG containing 5 vol % dispersed Al_2O_3 particles with a radius of $0.25 \mu m$, no considerable change in conductivity behavior due to space-charge effects is expected ($\sigma_{disp}/\sigma_{bulk} = 1.00004$), so this effect should not be important for our system. Furthermore, we verified experimentally the absence of nonlinear current-voltage effects.

To explain the dependence of conductivity on partial oxygen pressure we consider the effect of isolated vacancies and interstitials in YAG. Use will be made of the Kröger-Vink notation.⁴⁰ Discussions of the nonstoichiometry in YAG by Neiman *et al.*¹⁷ and Osiko *et al.*⁴⁴ point out that the oxygen and aluminum sublattices show the highest disorder.

TABLE III. Defect formation energies calculated by computer simulation. (Ref. 45).

Equation	(3)	(5)	(6)
Defect formation energy per single defect	≈ 8 eV	≈ 10 eV	≈ 5 eV

TABLE IV. The electroneutrality conditions which govern the different regimes. pO_2 decreases from regime I to regime IV.

Regime I	$[h'] = 3[V_{Al}''']$
Regime II	$[Ca_Y'] = [h']$
Regime IIIa	$2[V_O''] = [Ca_Y'] < [Ca_{tot}]^a$
Regime IIIb	$2[V_O''] = [Ca_Y'] \approx [Ca_{tot}]^a$
Regime IV	$[e'] = 2[V_O'']$

^a The Mg-doped YAG is treated in a comparable way.

We have calculated energies for the Frenkel and Schottky reactions:

Table III shows the results of these calculations. Schottky defects have a lower formation energy than Frenkel defects. O_i' was not considered as a possible defect since the largest interstitial site in YAG (the empty b site) cannot accommodate the large oxygen ions. We therefore base our defect calculations on the following native defects: V_O'' , V_{Al}''' , e' , and h' . Furthermore, we have Ca (or Mg) as extrinsic defects. These ions lead to the following ionization reaction:

There are experimental indications that part of the impurity ions are associated with neighboring oxygen ions. In our acceptor-doped samples we observed a red-brown color after annealing in oxygen at 1870 K followed by quenching to room temperature. Samples quenched after annealing in a reducing atmosphere are colorless. Similar results are reported for single-crystalline YAG,⁹ alumina,⁴⁶⁻⁴⁸ and others. Cox and co-workers⁴⁶⁻⁴⁸ proved by means of electron-spin-resonance (ESR) measurements in Mg-doped alumina that the brownish color centers present after quenching in oxygen are paramagnetic. These authors identified the paramagnetic centers as holes trapped near Mg_{Al}' centers. The holes are localized on oxygen ions, giving O_O^x centers. Thus

and

The occurrence of $O_O^{\cdot}$ centers in YAG has been proved by optical absorption and ESR measurements.^{12,13} In our calculations of defect concentration diagrams at high temperatures the association reactions are not taken into account.

We have to determine the concentration of the following defects as a function of oxygen partial pressure: V_O'' , V_{Al}''' , V_Y''' , Ca_Y' , Ca_Y^x , e' , and h' . These can be derived from the seven defect relations specified below:

Atomic disorder:

with

$$K_s = [V_Y'']^3 [V_{Al}''']^5 [V_O'']^{12}; \quad (9b)$$

electronic disorder:

with

$$K_i = [e'] [h']; \quad (10b)$$

impurity ionization:

with

$$K_{Ca} = [Ca_Y'] [h'] / [Ca_Y^x]; \quad (11b)$$

interphase reactions:

with

$$K_{Al} = [V_{Al}''']^2 [V_O'']^3 a_{Al_2O_3}, \quad (12b)$$

and

with

$$K_O = [V_O''] [e']^2 pO_2^{1/2}; \quad (13b)$$

electroneutrality condition:

$$3[V_Y''] + 3[V_{Al}'''] + [Ca_Y'] + [e'] = 2[V_O''] + [h']; \quad (14)$$

constant impurity content:

$$[Ca]_{tot} = [Ca_Y'] + [Ca_Y^x] \quad (15)$$

(analogous relations can be written by replacing Ca by Mg.)

Since we always have Al_2O_3 inclusions in our material, the activity $a_{Al_2O_3}$ is constant during the experiments. The

TABLE V. Exponents n in $[defect] \propto pO_2^n$ assuming a pO_2 -dependent concentration of acceptors.

Regime	← hole released hole trapped →				
	$2[V_O''] = [e']$	$[Ca_Y'] = 2[V_O'']$		$[Ca_Y'] = [h']$	$[h'] = 3[V_{Al}''']$
	IV	IIIb	IIIa	II	I
V_O''	-1/6	0	-1/6	-1/2	-1/8
e'	-1/6	-1/4	-1/6	0	-3/16
h'	1/6	1/4	1/6	0	3/16
V_{Al}'''	1/4	0	1/4	3/4	3/16
Ca_Y'	0	0	-1/6	0	0
Ca_Y^x	0	1/4	0	0	0

FIG. 4. Defect diagram for Ca-doped YAG. The Roman letters denote the neutrality regimes defined in Table IV.

defect concentrations can be obtained easily by using the Brouwer approximation.⁴⁹ At the highest partial oxygen pressures one expects holes and aluminum vacancies to be the dominating defects, i.e., the electroneutrality condition can be simplified to $[h] = 3[V_{Al}^{''}]$. The conditions for the whole pO_2 regime we investigated is given in Table IV.

Using the usual procedure (see, e.g., Ref. 40) expressions are obtained for defect concentrations as a function of pO_2 . Results are given in Table V. At lower values of pO_2 we enter regions with different neutrality regimes. The defect concentrations corresponding to the different regimes are shown schematically in Fig. 4. The actual widths of regions I–IV depend on the concentration of acceptors in the crystal and on the magnitude of the equilibrium constants.

Taking into account that electronic charge carriers have a much higher mobility than ionic defects we can qualitatively derive the conductivity isotherms given in Fig. 5; they are in good accordance with the experimental curves.

V. DISCUSSION

Our Mg- and Ca-doped YAG samples are acceptor dominated. Referring to the model developed in the previous section we find well-defined pO_2 regimes. At high oxygen partial pressure Al vacancies $V_{Al}^{''}$ are balanced by holes. Al vacancies are liberated while the formation of Al_2O_3 inclusions progresses under sintering conditions. The p -type conductivity changes proportional to $pO_2^{3/16}$ for YAG: 70 Ca as well as for YAG: 60 Mg. This process is characterized by an

FIG. 5. Predicted pO_2 dependence of σ for samples doped at a low and high level of acceptors according to our defect model.

activation energy E_a of about 2 eV (see Table II); Rotman reported for single-crystalline, acceptor-dominated YAG $E_a = 2.2$ eV for p -type conductivity.²⁰

As shown in Figs. 1(a)–1(c) the high-pressure region I is followed by a region with constant p -type conductivity and increasing ionic contribution, as predicted for region II. At still lower pO_2 -values we enter region III. For the samples with low acceptor concentrations the conductivity passes through a minimum as expected when the electron concentration becomes higher than the hole concentration.

VI. CONCLUSION

High-temperature measurements of electronic and ionic conductivity of YAG doped with 70 ppm Ca, 400 ppm Ca, and 60 ppm Mg as $f(pO_2, T)$ can be interpreted assuming $V_O^{''}$, $V_{Al}^{''}$, $Ca_V^{''}$, $Ca_V^{''}$, h^+ , and e^- defects. Al_2O_3 precipitates observed in the sintered material keep the alumina activity at a constant value. The inclusions are responsible for the formation of Al vacancies, leading to a $pO_2^{3/16}$ dependence of the hole conductivity at high oxygen partial pressures.

Ionic transference measurements show that the samples are mixed ionic-electronic conductors. The ionic contribution to the total conduction increases with increasing acceptor concentration and decreasing temperature. At the highest temperature the material should become a p -type electronic conductor.

The defect model presented here explains the conductivity curve over the entire pO_2 regime we could investigate, ranging from 10^5 to 10^{-12} Pa.

ACKNOWLEDGMENTS

The authors wish to thank J. Vreeswijk, J. J. C. Oomen, B. E. M. M. vd. Broek, M. M. Dedding, L. V. Ijzendoorn, and J. P. Sneijders from the Philips Lighting Division (Eindhoven, The Netherlands) for their help in performing this study. Further we want to thank Professor C. R. A. Catlow, who made it possible for me to perform a detailed computer simulation on YAG at the University of Keele (England).

¹A. A. Kaminskii, *Lasernie Kristally* (Izd. Nauka, Moscow, 1975) [translation: *Laser Crystals* (Springer, Berlin, 1983)].

²J. M. Robertson, M. W. van Tol, J. P. H. Heynen, and W. M. Smits, *Philips J. Res.* **35**, 354 (1980).

³M. F. Yan, T. C. D. Huo, and H. C. Ling, *J. Electrochem. Soc.* **134**, 493 (1987).

⁴G. Blasse and A. Bril, *Philips Tech. Rev.* **31**, 304 (1970).

⁵G. A. Slack, D. W. Oliver, R. M. Chrenko, and S. Roberts, *Phys. Rev.* **177**, 1308 (1969).

⁶S. R. Rotman and H. L. Tuller, *Mater. Res. Soc. Symp. Proc.* **60**, 413 (1986).

⁷T. Masumoto and Y. Kuwano, *Jpn. J. Appl. Phys.* **24**, 413 (1985).

⁸M. Bass and A. E. Paladino, *J. Appl. Phys.* **38**, 2706 (1967).

⁹J. Kvapil, J. Kvapil, B. Perner, and B. Manek, *Krist. Tech.* **10**, 529 (1975).

¹⁰J. Kvapil, J. Kvapil, and B. Perner, *Krist. Tech.* **10**, 161 (1975).

¹¹H. J. Bernhardt, *Phys. Status Solidi B* **87**, 213 (1978).

¹²H. J. Bernhardt, *Phys. Status Solidi A* **37**, 445 (1976).

¹³K. Mori, *Phys. Status Solidi A* **42**, 375 (1977).

¹⁴R. A. Serway, F. H. Yang, and S. A. Marshall, *Phys. Status Solidi B* **89**, 267 (1978).

¹⁵H. R. Asatryan, A. S. Kuzanyan, A. G. Petrosyan, A. K. Pertosyan, and E. G. Sharoyan, *Phys. Status Solidi B* **135**, 343 (1986).

- ¹⁶T. Yosida, Y. Chiba, and M. Date, *J. Magn. Magn. Mater.* **31-34**, 689 (1983).
- ¹⁷A. Yu. Neiman, E. V. Tkachenko, and V. M. Zhukovshii, *Dokl. Akad. Nauk. SSSR* **240**, 876 (1978).
- ¹⁸J. L. Bates and J. E. Garnier, *J. Am. Ceram. Soc. Commun.* **64**, C-138 (1981).
- ¹⁹A. P. Andreev, S. F. Akhmetov, G. L. Akhmetova, and S. V. Davydchenko, *Acta Crystallogr. A* **40** (Suppl.), C-330 (1984).
- ²⁰S. R. Rotman, R. P. Tandon, and H. L. Tuller, *J. Appl. Phys.* **57**, 1951 (1985).
- ²¹S. R. Rotman and H. L. Tuller, *J. Appl. Phys.* **62**, 1305 (1987).
- ²²L. Schuh, R. Metselaar, and G. de With, *Sci. Ceram.* **14**, 973 (1988).
- ²³H. Schmalzried, *Festkörper-Reaktionen* (Verlag Chemie, Weinheim, 1971).
- ²⁴G. E. Gazza and S. K. Dutta, U.S. Patent 37 677 45 (1973).
- ²⁵G. E. Gazza and S. K. Dutta, U.S. Patent 40 297 55 (1977).
- ²⁶A. V. Belayakov, E. S. Lukin, A. S. Vlasov, and V. P. Tarosovskii, *Tr. Mosk. Khim. Tekhnol. Inst.* **118**, 78 (1981).
- ²⁷G. de With and H. J. A. van Dijk, *Mater. Res. Bull.* **19**, 1669 (1984).
- ²⁸G. de With, *Philips J. Res.* **42**, 119 (1987).
- ²⁹F. J. C. Toolenaar and G. de With, *Proc. Brit. Ceram. Soc.* **37**, 241 (1986).
- ³⁰C. A. M. Mulder and G. de With, *Solid State Ionics* **16**, 87 (1985).
- ³¹W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, *Introduction to Ceramics* (Wiley, New York, 1972).
- ³²W. H. Rhodes, *J. Am. Ceram. Soc.* **64**, 13 (1981).
- ³³L. Schuh, R. Metselaar, and G. de With (unpublished).
- ³⁴S. Geller, *Z. Kristallogr.* **125**, 1 (1967).
- ³⁵W. Tolksdorf and U. H. Wolfmeier, in *Landolt-Börnstein 12/III a (Neue Serie)*, edited by K.-H. Hellwege (Springer, Berlin, 1978).
- ³⁶R. Metselaar and P. K. Larsen, *J. Phys. Chem. Solids* **37**, 599 (1976).
- ³⁷A. M. Hoefsloot, P. H. F. Thijssen, and R. Metselaar, *Silicates Ind.* **3-4**, 35 (1985).
- ³⁸J. Bauerle, *J. Phys. Chem. Solids* **30**, 2657 (1969).
- ³⁹M. Miyayama, H. Inoue, and H. Yanagida, *J. Am. Ceram. Soc.* **66**, C-164 (1983).
- ⁴⁰F. A. Kröger, *The Chemistry of Imperfect Crystals* (North-Holland, Amsterdam, 1974).
- ⁴¹G. M. Crosby, *J. Solid State Chem.* **25**, 367 (1978).
- ⁴²T. Jow and J. B. Wagner, Jr., *J. Electrochem. Soc.* **126**, 1963 (1979).
- ⁴³C. C. Liang, *J. Electrochem. Soc.* **120**, 1289 (1973).
- ⁴⁴V. V. Osiko, Yu. K. Voron'ko and A. A. Sobal, *Crystal Growth Properties and Applications 10 (Growth and Defect Structures)* (Springer, Heidelberg, 1984).
- ⁴⁵L. Schuh and C. R. A. Catlow (to be published).
- ⁴⁶R. T. Cox, *Solid State Commun.* **9**, 1989 (1971).
- ⁴⁷R. T. Cox, *J. Phys. (Paris) Colloq.* **11-12**, C9-333 (1973).
- ⁴⁸H. A. Wang, C. H. Lee, F. A. Kröger, and R. T. Cox, *Phys. Rev. B* **27**, 3821 (1983).
- ⁴⁹G. Brouwer, *Philips Res. Rep.* **9**, 366 (1954).