

Surface Degradation of Fluoride Conducting Crystals $MF_2 : UF_4 : CeF_3$ ($M = Ca, Sr, Ba$)

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The ac electrical response of cell systems composed of single crystals of the concentrated solid solutions $M_{1-x-y}U_xCe_yF_{2+2x+y}$ ($M = Ca, Sr, Ba$ and $2.7 < 2x + y < 26.5$ m/o), and ionically blocking electrodes has been studied as a function of frequency and temperature. At elevated temperatures the crystals react with traces of oxygen or water vapor. Complex admittance analysis reveals the formation of low-conducting surface layers, contrary to diluted solid solutions which under similar conditions react to form high-conducting surface layers (2). The activation enthalpy for the layer conductivity is substantially larger than that for the bulk conductivity, and equals that for interstitial fluoride ion motion in dilute solid solutions. A mechanism of charge compensation in the layers is presented. After reaction the solid solutions based on CaF_2 show also a surface electronic conductivity. Scanning electron micrographs clearly reveal the surface degradation.

1. Introduction

At elevated temperatures water vapor or oxygen reacts readily with the alkaline earth metal fluorides CaF_2 , SrF_2 , and BaF_2 (1-6). Highly conductive coatings result from the reactions, whereby either HF or F_2 evolves from the crystal surfaces (3). To date, it is well established that oxide ions enter the lattice substitutionally and replace fluoride ions, while charge neutrality is preserved by fluoride ion vacancies.

Ure (2) observed an increase of the ionic conductivity of undoped CaF_2 and $CaF_2 : YF_3$ crystals, and ascribed this increase to oxide contamination, even though the crystals were heated in a purified He atmosphere. In addition to an enhanced ionic conductivity Ure observed after heating to $\sim 930^\circ K$ on some $CaF_2 : NaF$ and $CaF_2 : YF_3$ crystals a high surface conductivity, which appeared to be electronic in nature.

Franklin *et al.* (4) oxidized $CaF_2 : GdF_3$ crystals provided with platinum paste electrodes by thermal treatments at $\sim 975^\circ K$ in air. Oxide-rich layers thus formed produced a relaxation dispersion in the dielectric spectrum with characteristics of orienting point defect pairs.

Levitskii *et al.* (5, 6) showed the ionic conductivity of CaF_2 (5) and BaF_2 (6) to increase with the partial oxygen pressure. These authors evaluated intrinsic, extrinsic, and defect association domains as a function of the oxygen partial pressure.

Recently, we have started an investigation of the electrical properties of some fluoride conducting solid solutions of composition $M_{1-x-y}U_xCe_yF_{2+2x+y}$, with $M = Ca, Sr, Ba$, and $2x + y$ in the range 2.7 to 26.5 mole per cent (m/o). The solid solutions exhibit at moderate temperatures interesting solid electrolyte properties (8). We observed that thermal treatments in nitrogen cause surfaces

of these solid-solution crystals to degradate to some extent due to reaction with traces of water vapor and/or oxygen. This influences markedly the frequency dispersion observed commonly for solid electrolytes provided with ionically blocking electrodes.

In this paper we present a complex admittance analysis (9–11) of this frequency dispersion. It will be shown that due to the interphase reactions surface layers acquire ionic conductivity properties, representative for the low-conducting diluted solid solutions. In addition the solid solutions based on CaF_2 show also a surface electronic conductivity. The crystal surfaces were studied in a scanning electron microscope during several stages of the investigation.

2. Experimental Aspects

The melt-growth and description of single crystals with composition $M_{1-x-y}\text{U}_x\text{Ce}_y\text{F}_{2+2x+y}$ ($M = \text{Ca}, \text{Sr}$ and Ba , and $2.7 < 2x + y < 26.5$ m/o) have been reported by Catalano and Wrenn (12). The single crystals used in the present study were kindly put at our disposal by Dr. E. Catalano of the Lawrence Livermore Laboratory, University of California, who has studied optical properties of these solid solutions. The crystals had polished surfaces, were transparent, and had a green color. The admittance parameters were studied in the temperature region 300–500°K and over a frequency range 0.2 Hz–30 kHz. Details of the conductivity equipment will be published elsewhere (8).

As electrode contact material a platinum paint (Leitplatin 308A, Degussa) was used. Crystals with a surface area of about 0.5 cm², and about 0.2 cm thick were studied, both "as received" and after a 2-hr anneal at ~975°K. Throughout all thermal treatments and conductivity experiments a nitrogen ambient obtained from boiling liquid nitrogen was employed. This nitrogen ambient contained about 25 ppm O₂ and 40 ppm H₂O.¹

¹ AGA-GAS, supplier of the liquid nitrogen, carried out the analyses.

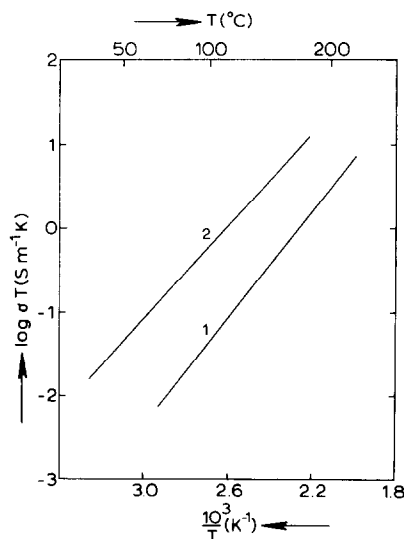


FIG. 1. The temperature dependence of the frequency independent conductivity, plotted as $\log \sigma T$ vs $10^3/T$, of $\text{Ba}_{0.835}\text{U}_{0.100}\text{Ce}_{0.065}\text{F}_{2.265}$. (1) As received; (2) after thermal treatment.

The crystal surface studies were made in a Stereoscan S4 scanning electron microscope.

3. Results

All crystals examined exhibited an increased conductivity after thermal treatment. The temperature dependence of the frequency-independent conductivity of an "as received" solid solution based on BaF_2 is, together with this dependence after thermal treatment, presented in Fig. 1.

Generally two types of complex admittance plots were obtained for all solid solutions, the difference being due to the thermal treatment. In Fig. 2 we have gathered a series of complex admittance plots for $\text{Ba}_{0.882}\text{U}_{0.113}\text{Ce}_{0.005}\text{F}_{2.231}$. Similar results were obtained for other solid solutions based on BaF_2 and those based on SrF_2 . The "as received" crystals provided with platinum paint electrodes reveal one circular arc with its center below the real axis (Fig. 2a). The thermally treated crystals reveal two circular arcs. The low-frequency arc increases at the expense of the second arc upon increasing the temperature (Fig. 2b, c). After repolishing the electrode surfaces of the crystal

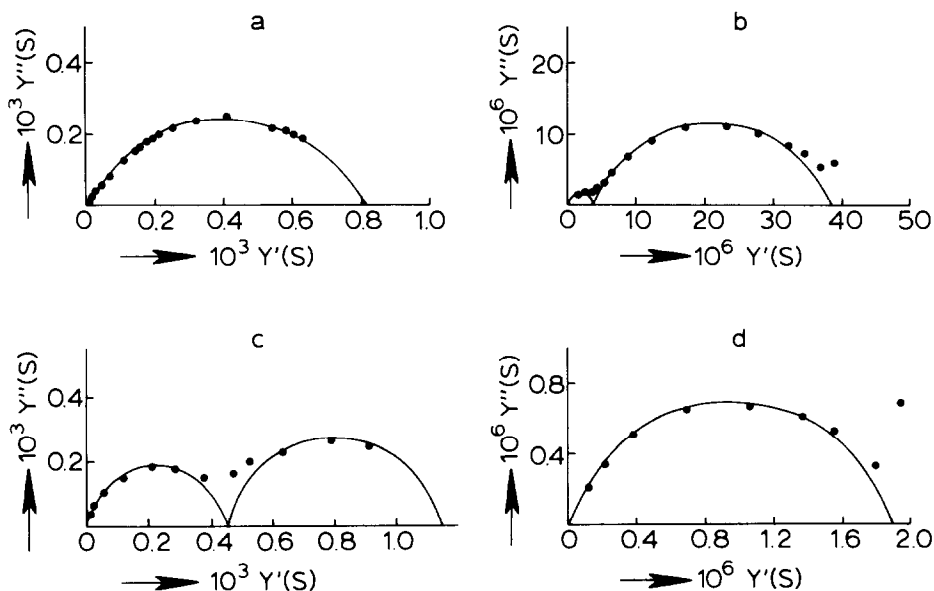


FIG. 2. Complex admittance plots for $Ba_{0.882}U_{0.113}Ce_{0.005}F_{2.231}$ with platinum paint electrodes. (a) $T = 475^\circ K$, as received (1 Hz–20 kHz); (b) $T = 351^\circ K$, thermally treated (1 Hz–20 kHz); (c) $T = 441^\circ K$, thermally treated (5 Hz–40 kHz); (d) $T = 338^\circ K$, after repolishing (5 Hz–20 kHz).

one circular arc results on the complex admittance plot (Fig. 2d). If the extrapolated high-frequency conductances are used to calculate specific bulk conductivities, then, the data obtained from Fig. 2a lead to a dependence as depicted by line 1 in Fig. 1, while the data obtained from Figs. 2b to d all lead to one line like line 2 in Fig. 1. This strongly suggests that the appearance of two circular arcs after thermal treatments is related to surface effects, and that the thermally induced jump in the conductivity is a bulk phenomenon. This latter feature will be dealt with in more detail in a forthcoming paper (8).

For solid solutions based on CaF_2 the complex admittance plots do not pass through the origin of the complex plane after a thermal treatment (see Fig. 3). Application of small dc voltages across a thermally treated solid solution provided with ionically blocking electrodes causes dc currents to decay to steady-state values which behave ohmic. The linear current voltage curves lead to dc conductances which coincide with the extrapolated zero-frequency conductances in the

complex admittance plots indicating an electronic contribution to the conductivity.

By grinding off the surface regions of these crystals, however, this electronic contribution is strongly suppressed. Also in this case, the complex admittance plot reveals one circular arc (see Fig. 3c).

Scanning electron micrographs of surfaces of investigated crystals are presented in Fig. 4. The micrographs clearly reveal a thermally induced surface degradation. In several crystals cracks, which are located in the surface regions, show up. Cracking occurs presumably along the (111) direction (13).

4. Discussion

In undoped CaF_2 (5), in $CaF_2:YF_3$ (0.16 m/o) (2), and in $CaF_2:GdF_3$ (0.1 m/o) (4) the influence of a reaction with oxygen and/or water vapor is to increase the ionic conductivity in the surface regions by increasing the concentration of fluoride ion vacancies. The conductivity activation enthalpies in the extrin-

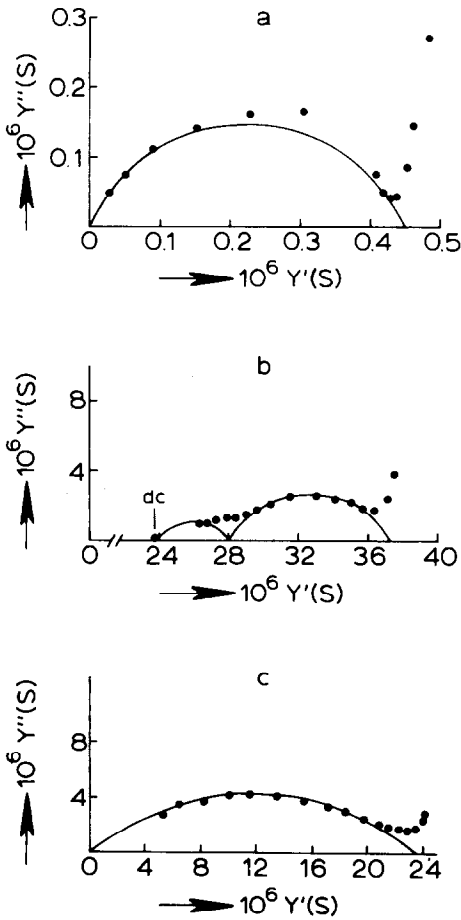
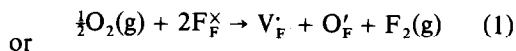


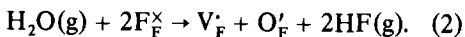
FIG. 3. Complex admittance plots for $\text{Ca}_{0.903}\text{U}_{0.092}\text{Ce}_{0.005}\text{F}_{2.189}$. (a) $T = 398^\circ\text{K}$, as received (0.6 Hz–30 kHz); (b) $T = 486^\circ\text{K}$, thermally treated. This figure includes a dc measurement (0.6 Hz–30 kHz); (c) $T = 500^\circ\text{K}$, after repolishing (0.8 Hz–30 kHz).

sic regions equal that observed for $\text{CaF}_2:\text{NaF}$ (2).

It is evident that in these dilute solid solutions first O'_{F} will replace F'_{I} for charge compensation of M'_{Ca} , and that subsequently the concentration of fluoride ion vacancies is increased via



or

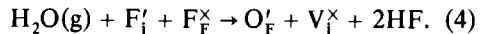
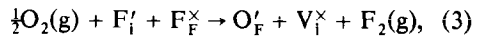


If interstitial fluoride ions carry the current in the bulk a decrease of the conductivity

activation enthalpy will result, since the migration enthalpy for V'_{F} motion is smaller than that for F'_{I} motion.

An enhanced surface conductivity may well account for the occurrence of a second arc in the complex admittance plots (5). The (extrapolated) high-frequency conductance would then represent the sum of the bulk and of the surface conductance, while the intercept of the low-frequency arc with the real axis would represent the bulk conductance. Removal of the surface regions would yield a smaller frequency-independent conductance.

In the concentrated solid solutions $\text{M}_{1-x-y}\text{U}_x\text{Ce}_y\text{F}_{2+2x+y}$ interstitial fluoride ions will be consumed by the reaction with oxygen or water vapor as well, i.e.,



For these solid solutions the frequency-independent conductivities of a thermally treated, and subsequently repolished crystal are the same. This precludes a model wherein enhanced surface conduction results from the reaction with oxygen. Instead, the second arc can be ascribed to the presence of a thin layer with reduced conductivity $(R_{\text{L}})^{-1}$ at the interface electrode–electrolyte. The layer at the sides goes then unnoticed. The layer at the interface can be modeled as a parallel RC combination in series with the bulk resistance (R_{b}) and an interfacial capacitance. In such an equivalent circuit the frequency-independent conductance represents the bulk conductance $(R_{\text{b}})^{-1}$. The intercept of the first arc with the real axis then represents $(R_{\text{b}} + R_{\text{L}})^{-1}$, with R_{L} the resistance of the layer. In Fig. 5 we have plotted the layer conductance and the bulk conductance for $\text{Ba}_{0.882}\text{U}_{0.113}\text{Ce}_{0.005}\text{F}_{2.231}$ as $\log (R_{\text{b}})^{-1} T$ and $\log (R_{\text{L}})^{-1} T$ vs T^{-1} , respectively. Since R_{b} and R_{L} are of the same order of magnitude, while the crystal thickness is large as compared to the layer thickness, the specific conductivity of the layer appears to be much lower than the specific bulk conduc-

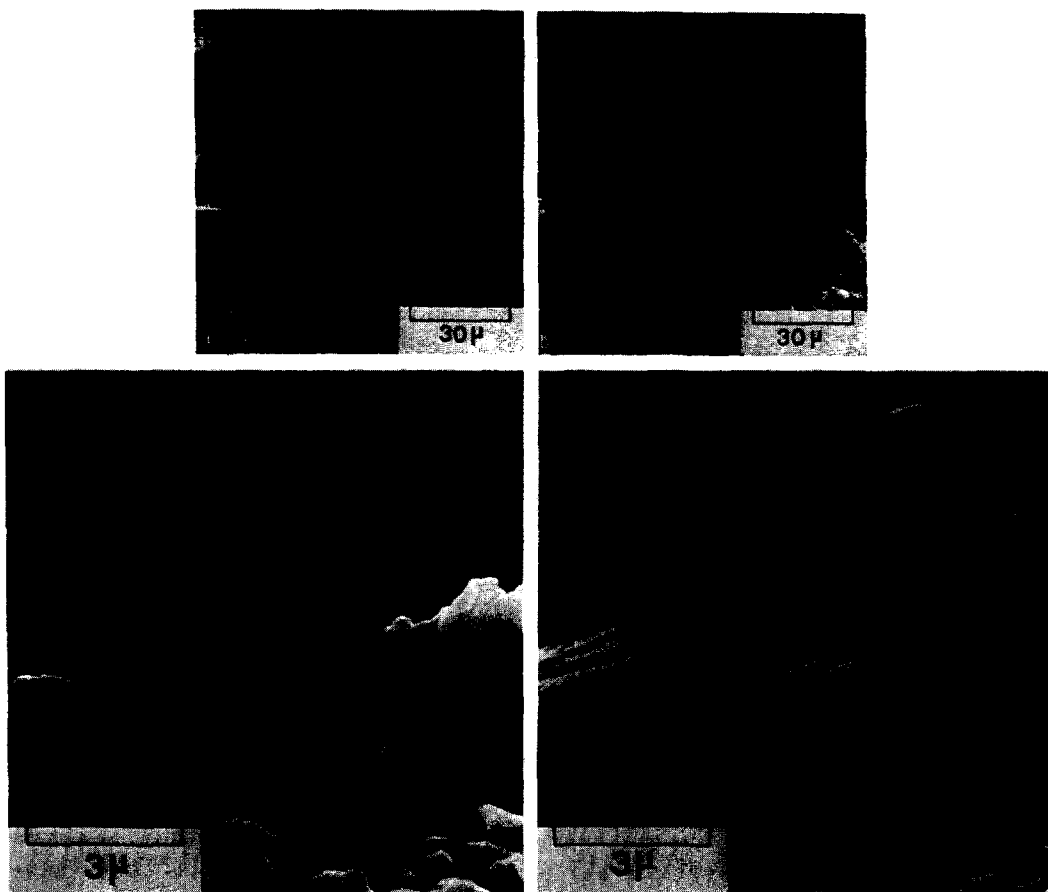


FIG. 4. Scanning electron micrographs of several crystal surfaces. (a) Polished surface of "as received" $Ca_{0.903}U_{0.092}Ce_{0.005}F_{2.189}$. The crystal surfaces of solid solutions based on SrF_2 were very similar. (b) Same surface as in (a) after thermal treatment. (c) Polished surface of $Ba_{0.899}U_{0.100}Ce_{0.001}F_{2.201}$ before a thermal treatment. White grains are remaining parts of the painted platinum electrode. (d) Same crystal as in (c) after thermal treatment. In addition to surface roughening, cracking has occurred. Cracks are located in the surface regions only.

tivity. For the bulk conductivity the activation enthalpy ΔH_m is calculated to be (0.502 ± 0.004) eV. This value is dependent on the amounts of UF_4 and CeF_3 present in the solid solutions, in that it decreases with increasing amounts of dopant (8).

The temperature dependence of the layer conductance leads to the much larger value (0.83 ± 0.03) eV for ΔH_m . The ionic conductivity of BaF_2 doped with small amounts of MF_3 has been studied extensively (7, 14, 15). In dilute systems the interstitial fluoride ions require a migration enthalpy of 0.79–0.83 eV (14, 15). These values strongly suggest that by

reaction with oxygen or water vapor the surface regions of the present concentrated solid solutions acquire conducting properties which are representative for dilute systems in which interstitial fluoride ions carry the current.

It has been recognized for some time that in alkaline earth fluorides heavily doped with MF_3 , both interstitial fluoride ions and fluoride ion vacancies are present (16, 17). This observation has been accounted for by the formation of clusters (18). If two nearest-neighbor M^{3+} substitutional- F^- interstitial pairs dimerize, the aggregate is stabilized by a

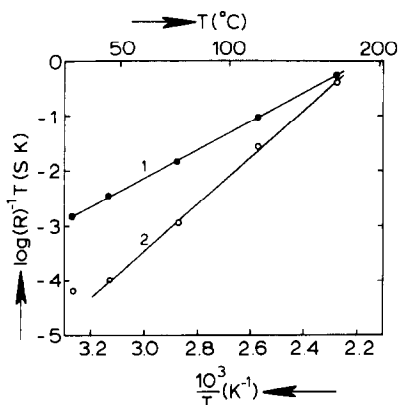


FIG. 5. The temperature dependence of the bulk conductance and layer conductance of thermally treated $\text{Ba}_{0.882}\text{U}_{0.113}\text{Ce}_{0.005}\text{F}_{2.231}$ plotted as $\log(R)^{-1}T$ and $\log(R)^{-1}T$ vs $10^3/T$, respectively. (1) R_b ; (2) R_L .

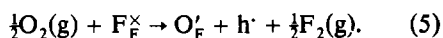
coupled lattice–interstitial relaxation. As a result a stable 2:2:2 cluster is formed, which contains two anion vacancies and four anion interstitials. The cluster stage following dimer formation involves four pairs. This extension of interstitial aggregation leads to a 4:3:2 cluster in which three vacancies and six interstitials are present. Réau *et al.* ascribe the more rapidly than linearly increase in conductivity of $\text{Ca}_{1-x}\text{Y}_x\text{F}_{2+x}$ (19) and $\text{Pb}_{1-x}\text{Bi}_x\text{F}_{2+x}$ (20) solid solutions with x entirely to the rapid growth of the number of vacancies caused by the cluster formation. It is, however, questionable whether the anion vacancies, or more generally, the defects composing the clusters would be mobile at all.

The stable clusters mentioned so far contain terminal interstitials, which means that lattice ions neighboring these terminal interstitials can easily go into an interstitial position (18). This leaves the cluster unaltered, but means that the cluster provides a permanent easy conduction path for migrating interstitials via the interstitialcy mechanism commonly employed to describe F_i' motion in dilute solid solutions (21, 22). The observation that ΔH_m decreases with increasing amounts of dopant (19, 20) is compatible with this model.

In the solid solutions $\text{M}_{1-x-y}\text{U}_x\text{Ce}_y\text{F}_{2+2x+y}$ similar cluster stages may be visualized (8).

The observed decrease of ΔH_m is also related to the influence of clusters on the mobility of interstitial fluoride ions. That the surface layers acquire conducting properties representative for diluted systems, then means that as a consequence of reactions (3) and (4) the number of clusters in the layers is strongly reduced.

In the solid solutions based on CaF_2 the reaction with traces of oxygen or water vapor lead not only to a layer with a low ionic conductivity, but to an electronic contribution as well. This electronic conductivity is also located in the surface region, and may arise from the incorporation reaction (5)



All admittance plots reveal circular arcs with their centers below the real axis. It has been emphasized that surface roughness at the interface electrode–electrolyte contributes to this phenomenon (10). In addition, it has been shown (23) that such data cannot be modeled by an equivalent circuit composed entirely of frequency-independent components. This especially counts for the interfacial capacitance and the layer capacitance introduced parallel to R_L in the equivalent circuit. Although the scanning electron micrographs clearly reveal a reaction-induced surface roughness, the values of R_b and R_L will not be influenced. A detailed analysis of the frequency dispersion is presently under study.

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References

1. D. C. STOCKBARGER, *J. Opt. Soc. Amer.* **39**, 731 (1949).

2. R. W. URE, JR., *J. Chem. Phys.* **26**, 1363 (1957).
3. H. BONTINCK, *Physica* **24**, 650 (1958).
4. A. D. FRANKLIN, S. MARZULLO, AND J. WACHMANN, JR., *J. Res. Nat. Bur. Stand. Sect. A* **71**, 355 (1967).
5. V. A. LEVITSKII, A. HAMMOU, M. DUCLOT, AND C. DEPORTES, *J. Chim. Phys.* **73**, 305 (1976).
6. V. A. LEVITSKII, A. HAMMOU, AND M. DUCLOT, *J. Solid State Chem.* **21**, 13 (1977).
7. V. M. CARR, A. V. CHADWICK, AND D. R. FIGUEROA, Ionic conductivity measurements of barium fluoride single crystals. Presented at the Second Europhysical Topical Conference on Lattice Defects in Ionic Crystals, Berlin (1976).
8. K. E. D. WAPENAAR AND J. SCHOONMAN, to be published.
9. J. E. BAUERLE, *J. Phys. Chem. Solids* **30**, 2657 (1969).
10. R. D. ARMSTRONG AND R. A. BURNHAM, *J. Electroanal. Chem.* **72**, 257 (1976).
11. P. H. BOTTELBERGHS AND G. H. J. BROERS, *J. Electroanal. Chem.* **73**, 21 (1976).
12. E. CATALANO AND W. WRENN, *J. Cryst. Growth* **30**, 54 (1975).
13. E. CATALANO, private communication (1977).
14. E. BARSIS AND A. TAYLOR, *J. Chem. Phys.* **48**, 4362 (1968).
15. W. BOLLMANN, *Phys. Status Solidi A* **18**, 313 (1973).
16. A. K. CHEETHAM, B. E. F. FENDER, AND M. J. COOPER, *J. Phys. C* **4**, 3107 (1971).
17. D. STEELE, P. E. CHILDS, AND B. E. F. FENDER, *J. Phys. C* **5**, 2677 (1972).
18. C. R. A. CATLOW, *J. Phys. C* **9**, 1859 (1976).
19. J. M. RÉAU, C. LUCAT, G. CAMPET, J. PORTIER, AND A. HAMMOU, *J. Solid State Chem.* **17**, 123 (1976).
20. C. LUCAT, G. CAMPET, J. CLAVERIE, J. PORTIER, J. M. RÉAU, AND P. HAGENMULLER, *Mater. Res. Bull.* **11**, 167 (1976).
21. C. R. A. CATLOW, *J. Phys. C* **9**, 1845 (1976).
22. S. KH. BATYGOV AND V. V. OSIKO, *Sov. Phys. Solid State* **13**, 8, 1886 (1972).
23. I. D. RAISTRICK, CHUN HO, AND R. A. HUGGINS, *J. Electrochem. Soc.* **123**, 1469 (1976).