

Self-Compensation in Lanthanum-Doped Strontium Titanate

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Gravimetric measurements on pure and lanthanum-doped SrTiO₃ have shown that the reversible change of oxygen content, between specified states of oxidation and reduction, is proportional to the dopant concentration. These measurements indicate that the donor dopants are electronically compensated by additional oxygen uptake in the oxidized state. The range of this reversible change in oxygen stoichiometry is up to more than an order of magnitude larger than the oxygen nonstoichiometry of the undoped SrTiO₃. A single-phase region from La_{0.2}Sr_{0.8}Ti_{0.8}Ti_{0.2}O₃ to La_{0.2}Sr_{0.8}Ti⁴⁺O_{3.10} has been confirmed for lanthanum-doped SrTiO₃. The gravimetric measurements can be explained by a model involving a shear structure.

Introduction

In addition to the extensive family of stoichiometric perovskites of general formula ABO₃, many such compounds exhibit nonstoichiometry on one or more sublattices (1). The literature concerning the effect of dopant ions on the physical properties of SrTiO₃ is limited. Little of the work has been concerned with establishing phase diagrams or structure data, although we have noted the study of La³⁺-doped PbTiO₃ (2, 3). Eror and Smyth have reported (4) that in BaTiO₃ up to 20 at.% barium may be substituted by lanthanum to retain a single-phase fully oxidized material. They did not observe any second phase either by optical means or by X-ray diffraction studies. Tofield and Scott have reported (5) that La³⁺-doped SrTiO₃ has no significant range of nonstoichiometry. They reached this conclusion based on their estimation of slight solubility of La³⁺ in SrTiO₃. We have

observed that up to 40 at.% of lanthanum is soluble in strontium titanate (6).

The disorder created by La³⁺ as a donor dopant in SrTiO₃ should lend itself to description by Verwey's controlled valency model (7). By this model, there would be compensation for the La³⁺ on Sr sites by the creation of equal numbers of Ti³⁺ ions. The Ti³⁺ ions are then responsible for the increase in electrical conductivity. In this case the donor dopant dominates the positive side of the electroneutrality equation and as a consequence the negative defect concentration would be independent of equilibrium oxygen activity. This compensation mechanism has also been referred to as controlled electronic imperfection (8). Similarly, the donor dopant may be compensated by the formation of charged point defects that would also be independent of equilibrium oxygen activity. This compensation mechanism has been referred to as controlled atomic imperfection (8), self-compensation (4, 9-14), and stoichiometric compensation (4).

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For BaTiO_3 with high concentrations of donor dopants, the theories that have been offered for the self-compensation range from the creation of compensating barium vacancies (15–17) to a change of the cation site occupied by the donor dopant (18). In considering these theories for the donor-doped SrTiO_3 , it must be kept in mind that SrTiO_3 is a ternary compound and that the Sr/Ti ratio is fixed. For the case of the creation of strontium vacancies at higher donor-dopant concentrations there should be an irreversible loss of strontium or precipitation of a strontium-rich phase. For the case of different site occupancy it would be possible to have compensation if some of the donor dopant substituted for Sr^{2+} were to shift to Ti^{4+} sites and vice versa. For the case of a +3 valent dopant substituted for Sr^{2+} only one-sixth of the dopant would have to shift from +2 to +4 valent sites for complete compensation to occur. The factor $\frac{1}{6}$ arises from the fact that the +3 valent dopant removes itself as a donor when it shifts site, becomes an acceptor on a Ti^{4+} site, and results in two strontium vacancies which may become doubly ionized (one vacancy from the site it left behind and another since it now occupies and, therefore, creates a new Ti site). For the case of +5 ion donor dopant substituted for Ti^{4+} shifting to Sr^{2+} sites, one-sixth of the dopant would have to occupy Sr^{2+} sites for complete compensation to occur. From a crystal chemistry point of view, some of these schemes involve some very unlikely site assignments and would require significant concentrations of titanium vacancies which are structurally unsound for the perovskite structure.

Experimental

The donor doped SrTiO_3 was prepared by the liquid mix technique (4, 19). Required amounts of strontium carbonate (Johnson-Mathey Corp., Spec. Pure), lan-

thanum carbonate (Rare-Earth division, Spec. Pure), and tetraisopropyl titanate solution (Dupont Co., Tyzor) were dissolved in an ethylene glycol-citric acid solution. There was no evidence of any precipitation in the solutions as they were evaporated to a rigid, transparent, uniformly colored polymeric glass. The samples were then calcined at 700–900°C—there was no evidence of a second phase in any of the as-calcined samples. The various calcined compositions were then pressed at 50,000 psi and sintered in air at 1350°C. For gravimetric measurements the samples were equilibrated in oxygen or carbon dioxide-carbon monoxide mixture at 1050°C for the oxidized and reduced states, respectively, and quenched in the ambient gas. The CO/CO_2 mixture was adjusted to provide oxygen partial pressure of 10^{-15} atm at the equilibration temperature. All gravimetric measurements were made at room temperature on at-least-duplicate samples on a Cahn model 4100 electrobalance. All the oxidized samples are bright yellow and insulating, whereas the reduced samples are dark and semiconducting.

Results and Discussion

Gravimetric measurements on pure SrTiO_3 and on samples doped with up to 20 at.% La^{3+} substituted for Sr^{2+} have shown that the reversible change of oxygen content, between specified states of high and low oxygen activity, is proportional to the dopant concentration. If it is assumed that each added oxygen will neutralize two La^{3+} dopant ions, there is a correlation of 95% or better between the measured increase in weight on oxidation of a sample that had been equilibrated in an atmosphere of low oxygen activity and the calculated amount of oxygen required to neutralize the dopant.

The driving force for additional uptake of oxygen is the compensation of the elec-

tronic disorder introduced by the donor dopant. Such charge compensation has been described for the case of doped elemental semiconductors (20) where the solid solubility of impurities is found to be proportional to the concentration of electronic disorder. The increase in energy that is required to introduce an ion into the host lattice is more than compensated by the decrease in electronic disorder. The amount of energy gained by the compensation of the electronic disorder is determined by its ionization energy and may be of the order of an electron volt.

It is possible to increase the amount of electronic disorder created by a given donor-dopant concentration by substituting a +4 valent dopant of the appropriate ionic size for Sr^{2+} or a +6 valent dopant for Ti^{4+} . Such dopants would require twice as much reversible oxygen weight change for electronic compensation as would an equal atomic concentration of La^{3+} on Sr^{2+} site or Ta^{5+} on Ti^{4+} site. Self-compensation of BaTiO_3 with up to 1 at.% Th^{4+} substituted for Ba^{2+} or up to 2 at.% Mn^{6+} substituted for Ti^{4+} has been measured by Eror and Smyth, (4) and found to agree with the assumption that each added oxygen ion will neutralize one donor-dopant ion. Their results established that Mn^{6+} substitutes for Ti^{4+} in BaTiO_3 when equilibrated with an atmosphere of high oxygen activity and that Th^{4+} does substitute for Ba^{2+} .

La^{3+} was chosen as a dopant in order to understand the mechanism by which the "self-compensation" by oxygen occurs because we found its extensive range of solid solution (up to 40 at.%) (6). As can be seen in Fig. 1 there is excellent agreement between the calculated amount of oxygen necessary to compensate the La^{3+} dopant and the measured reversible oxygen weight change between the oxidized state at one atmosphere oxygen and the reduced state of equilibration in a CO/CO_2 mixture. For the 10 at.% La^{3+} concentration this

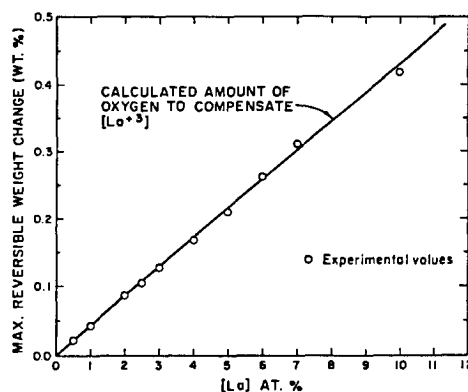


FIG. 1. Maximum reversible weight change observed for SrTiO_3 , between oxygen partial pressures established by CO/CO_2 mixture, or oxygen, as a function of La^{3+} dopant concentration (at 1050°C).

amounts to a 40-fold increase in oxygen nonstoichiometry compared with that of undoped SrTiO_3 . For a La^{3+} concentration of 20 at.%, the oxidation kinetics became extremely slow so that good quantitative results were difficult to obtain. However, there is self-compensation at this concentration also with at least an 85% correlation with the predicted weight change.

A Kröger-Vink diagram (21) is a useful representation to consider when discussing the defects in ternary oxides of the type ABO_3 . Figure 2 illustrates the variation of defect concentrations as a function of oxygen partial pressure (P_{O_2}) for the case of fully ionized atomic defects and the elec-

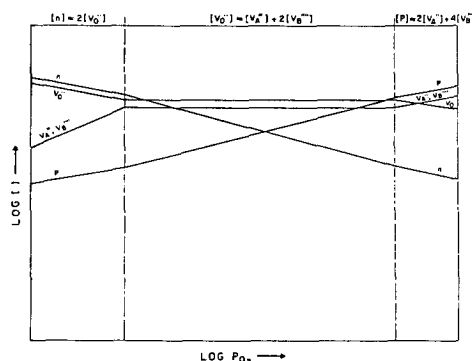


FIG. 2. Defect concentrations vs the oxygen partial pressure in pure ternary oxide ABO_3 .

trons $[n]$, and electron holes $[p]$. It is assumed that the A and B content of the oxide ABO_3 is constant. The familiar $[n] \propto P_{O_2}^{-1/8}$ in the region with electrical neutrality condition $[n] \cong 2[V_0^{\bullet}]$ is illustrated in Fig. 2. Figure 3 is for the case of a ternary oxide ABO_3 with a donor dopant, I_m , that is fully ionized, I_m^+ . It is seen from Fig. 3, that for sufficient departures from stoichiometry, the electrical conductivity is controlled by $[n] \cong 2[V_0^{\bullet}]$ and the effect of the donor dopant is not seen. When a donor element is added, the n to p transition is shifted to higher P_{O_2} while the metal excess to metal deficit transition is moved to lower P_{O_2} [see Fig. 3]. This means that with the shift of the transition of metal excess to metal deficit disorder to lower P_{O_2} values, there may be significantly larger concentrations of atomic disorder than for the undoped oxide. The possibility of self-compensation is built into the random defect model of nonstoichiometry if the oxide is stable over a sufficiently wide range of oxygen partial pressure.

The observation that highly donor-doped $SrTiO_3$ is self-compensated is unequivocally explained by the measured reversible change in oxygen stoichiometry, the question of how the extra oxygen is accommodated remains to be answered. The obser-

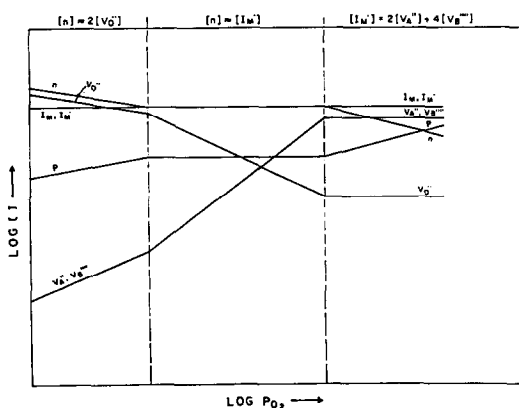


FIG. 3. Concentrations of charged defects as a function of P_{O_2} for donor-doped ABO_3 .

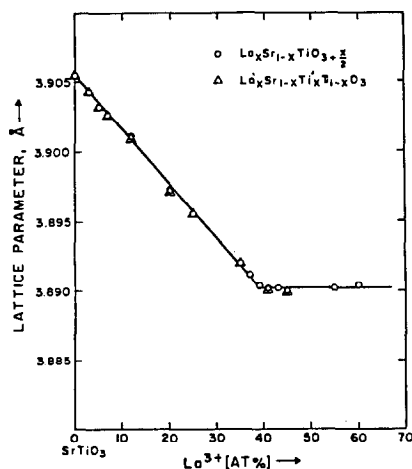


FIG. 4. Lattice parameters of solid solutions in lanthanum-doped strontium titanate.

vation of self-compensation at a La^{3+} concentration as high as 20 at. % eliminates the following possibilities:

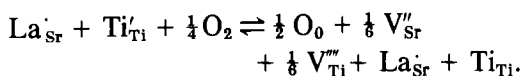
- Additional oxygen uptake at grain boundaries;
- A discrete second phase that is stable only in the fully oxidized state (no second phase observed optically, by X-ray diffraction or by Raman laser spectroscopy, which is a more sensitive technique than the first two);
- Irreversible loss of Sr resulting in both V_{Sr} and V_0 in the reduced state (none observed);

(d) Interstitial oxygen (presence of interstitials is unrealistic in this close packed structure with all lattice sites occupied—also no significant lattice parameter change between the oxidized and reduced states is observed, as can be seen in Fig. 4).

Even though the La^{3+} deficit compounds like $La_{2/3}TiO_3$ (22), and $La_{(2/3+x)}TiO_3$ (23), $0 < x < \frac{1}{3}$, would be a possible compensating mechanism, a second Sr-rich phase would have to be exsolved to provide the Sr-site vacancies required for compensation, since the $(Sr + La)/Ti$ ratio is unity.

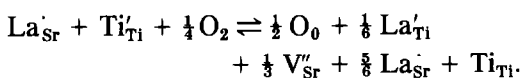
The observation of self-compensation could be explained by the following ways:

(a) The addition of oxygen on oxygen sites creating both strontium and titanium vacancies (although the latter is unlikely structurally)



The presence of *B*-site vacancies in perovskites has been reported for lanthana-substituted PbTiO_3 by Hennings and Rosenstein (2), and for lanthanum manganite by Tofield and Scott (5). Rauser and Kemmler-Sack (24) have reported the ordered perovskites with *B*-site vacancies for a new series of composition $\text{Ba}_2^{2+}\text{B}^{3+}\text{U}_{3/6}^{\text{6+}}\square_{1/6}\text{O}_6$ for $\text{B}^{3+} = \text{Sm-Lu, Sc, and Y}$. Kemmler-Sack *et al.* (25–28) have shown the presence of octahedral vacancies in hexagonal perovskites by structure factor analysis and vibrational spectroscopic investigations. The existence of vacancies on both *A* and *B* sites in SrTiO_3 or in the structural analogs BaTiO_3 and CaTiO_3 are not reported in the literature.

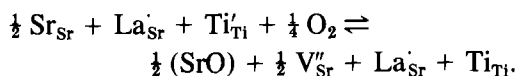
(b) A shift in the cation site occupied by the donor dopant when the samples are oxidized,



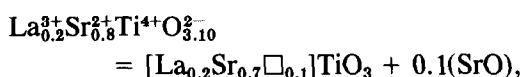
Kwestroo and Paping (29) found evidence that Ca^{2+} ions can be incorporated at titanium sites in the perovskite phase in the system BaO-CaO-TiO_2 . From the luminescence measurements on Sm-substituted BaTiO_3 Murakami *et al.* (30) concluded that Sm^{3+} ions were present at Ti-sites as well as at Ba sites. But neither paper proves that a significant number of such large ions (Ca, Sm) enters Ti sites. Lanthanum ions occupying octahedral sites in perovskites with the general formula $\text{A}^{2+}(\text{B}_1^{3+})_{0.5}(\text{B}_2^{5+})_{0.5}\text{O}_3$ have been found by Brixner (31–32) and Galasso and Darby (33). Takeda and Watanabe (34) have reported evidence of La^{3+} on Ti^{4+} sites. They

obtained an EPR signal characteristic of an F-center equivalent to the acceptor, La'_{Ti} . This signal was present only for the case of a Ba/Ti ratio of 1.02 plus an additional 1.0 at.% La (Ba/Ti ratios of 1.01 and 1.03 had little or no signal). In the present investigation, the large cations to small cation ratio is maintained at unity with a variation of 15–25 ppm. From the results of Takeda and Watanabe's (34) work and the cation ratios used in this experiment, one can assume that La^{3+} ions mainly occupy the Sr^{2+} sites. Also, by careful structure factor analysis Hennings and Rosenstein (2) eliminated the possibility of La^{3+} ions occupying the titanium sites in lanthanum-modified lead titanate. Further, the possibility of a change in cation site occupied by the donor dopant can be discounted because of the unlikely possibility of the creation of titanium vacancies in the perovskite structure that are required to compensate donor dopants substituted for Ti^{4+} . Careful X-ray diffraction intensity measurements should be performed before completely discarding this possibility as well as the possibility of the addition of oxygen on oxygen sites creating both strontium and titanium vacancies.

(c) A reversible change from a classic, randomly distributed, point defect model in the reduced state to a compensated structure with ordered defects in the oxidized state.



For a La^{3+} concentration of 20 at.% it will be,



where \square represents the vacancy on an *A* site.

The existence of a perovskite phase of composition $\text{Sr}_{1-1.5x}\text{La}_x\text{TiO}_3$ has been reported by Tien and Hummel (35). (SrO)

does not represent a separate phase but a structural accommodation in an ordered fashion, perhaps in the way that Ruddlesden-Popper phases (36); i.e., $n\text{SrTiO}_3 \cdot \text{SrO}$ are formed by ordered layers of SrO between perovskite type SrTiO_3 layers of various thickness. Figure 5 shows the $\text{Sr}_3\text{Ti}_2\text{O}_7$ structure where double SrTiO_3 perovskite layers are interleaved with SrO layers. McCarthy *et al.* (37) and White *et al.* (38) have prepared and identified by X-ray diffraction and Raman spectroscopy the first three members of the series $n\text{SrTiO}_3 \cdot \text{SrO}$. Tilley (39) was only able to prepare Sr_2TiO_4 and $\text{Sr}_3\text{Ti}_2\text{O}_7$ but was able to demonstrate the presence of crystallographic shear by a lattice imaging technique using transmission electron microscopy. The present authors have prepared the first six members of the series $n\text{SrTiO}_3 \cdot \text{SrO}$ by employing the liquid-mix technique and identified them by Raman laser spectroscopy (40).

By this type of proposed model, the compensation of donor-doped SrTiO_3 is by the strontium vacancy model, but since we have a ternary oxide the additional strontium that results from the strontium vacancies combines with oxygen, accounting for the gravimetric observations, to form (SrO), which is built into the lattice in a reasonably ordered fashion. It should be noted that the perovskite layers may still contain a random distribution of dopant ions and strontium vacancies even in the fully compensated oxidized state. The interlayer ordering might not be detected by conventional X-ray powder pattern techniques, because only 1 (SrO) layer would be required for each 10 perovskite SrTiO_3 layers for the case of 20 at. % La^{3+} substitution for Sr^{2+} . For 20 at. % La^{3+} -doped samples, the lattice parameters of oxidized and reduced materials are 3.8972 and 3.8968 Å. As expected the lattice parameter of lanthanum-doped sample is less than that of the undoped SrTiO_3 (3.9054 Å).

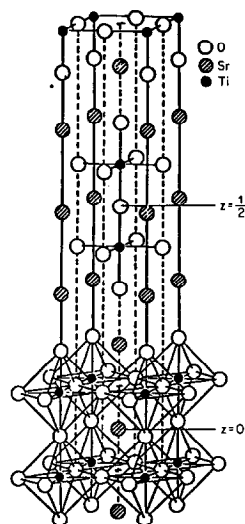


FIG. 5. The structure of $\text{Sr}_3\text{Ti}_2\text{O}_7$.

This work suggests a bridge between the two separate schools of thought on nonstoichiometry: The case of random point defects in which aliovalent cations are incorporated into the host lattice without a change in either structure or cation-anion ratio, and the case of extended defect structures in which all cations retain their normal oxidation states and the resulting change in cation-anion ratio is accommodated by subtle structural changes (41-45).

Acknowledgment

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References

1. J. B. GOODENOUGH AND J. M. LONGO, in "Landolt-Bornstein, Numerical Data in Science and Technology," New Series (K. H. Hellwege, Ed.), Group III, Vol. 4a, p. 131. Springer-Verlag, New York (1970).
2. D. HENNINGS AND G. ROSENSTEIN, *Mater. Res. Bull.* 7, 1505 (1972).
3. D. HENNINGS AND K. H. HÄRDTL, *Phys. Status Solidi (A)* 3, 465 (1970).

4. N. G. EROR AND D. M. SMYTH, "The Chemistry of Extended Defects in Nonmetallic Solids" (L. Eyring and M. O'Keefe, Eds.), pp. 62-74. North-Holland, Amsterdam (1970).
5. B. C. TOFIELD AND W. R. SCOTT, *J. Solid State Chem.* **10**, 183 (1974).
6. U. BALACHANDRAN AND N. G. EROR, *Commun. Amer. Ceram. Soc. C* **64**, 75 (1981).
7. E. J. W. VERWEY, P. W. HAAYMAN, F. C. ROMEYN, AND G. W. VAN OOSTERHOUT, *Philips Res. Rep.* **5**, 173 (1950).
8. F. A. KRÖGER AND J. J. VINK, "Solid State Physics" (F. Seitz and D. Turnbull, Eds.), Vol. III, pp. 307-435. Academic Press, New York (1956).
9. R. F. BREBRICK, "Progress in Solid State Chemistry," Vol. III. Pergamon, Oxford/New York (1966).
10. G. MANDEL, *Phys. Rev. A* **134**, 1073 (1964).
11. G. MANDEL, *Phys. Rev. A* **136**, 826 (1964).
12. F. A. KRÖGER, "Physical Chemistry, An Advanced Treatise" (H. Eyring, Ed.), Vol. X, pp. 229-259. Academic Press, New York (1970).
13. R. S. ROTH AND L. W. COUGHANOUR, *J. Res. Nat. Bur. Stand.* **55**, 209 (1955).
14. M. ITAKURA, N. NIIZEKI, H. TOYODA, AND H. IWASAKI, *Japan J. Appl. Phys.* **6**, 311 (1967).
15. E. C. SUBBARAO AND G. SHIRANE, *J. Amer. Ceram. Soc.* **42**, 279 (1959).
16. J. B. MACCHESNEY, P. K. GALLAGHER, AND F. V. D. MARCELLO, *J. Amer. Ceram. Soc.* **46**, 197 (1963).
17. G. H. JONKER, *Solid State Electron.* **7**, 895 (1964).
18. O. SABURI, *J. Phys. Soc. Japan* **14**, 1159 (1959).
19. M. PECHINI, U.S. Patent 3,330,697, July 11, 1967.
20. H. REISS, C. S. FULLER, AND A. J. PIETRUSZKIEWICZ, *J. Chem. Phys.* **25**, 650 (1956).
21. F. A. KRÖGER AND H. J. VINK, *Solid State Phys.* **3**, 307 (1956).
22. M. ABE AND K. UCHINO, *Mater. Res. Bull.* **9**, 147 (1974).
23. M. KESTIGIAN AND R. WARD, *J. Amer. Chem. Soc.* **77**, 6199 (1955).
24. G. RAUSER AND S. KEMMLER-SACK, *J. Solid State Chem.* **33**, 135 (1980).
25. S. KEMMLER-SACK, *Z. Anorg. Allg. Chem.* **442**, 213 (1978).
26. S. KEMMLER-SACK, U. TREIBER, AND A. FADINI, *Z. Anorg. Allg. Chem.* **453**, 157 (1979).
27. S. KEMMLER-SACK, *Z. Anorg. Allg. Chem.* **454**, 63 (1979).
28. M. HERRMANN AND S. KEMMLER-SACK, *Z. Anorg. Allg. Chem.* **469**, 51 (1980).
29. W. KWESTROO AND H. A. M. PAPIING, *J. Amer. Ceram. Soc.* **42**, 292 (1959).
30. T. MURAKAMI, T. MIYASHITA, M. NAKAHARA, AND E. SEKINE, *J. Amer. Ceram. Soc.* **56**, 294 (1973).
31. L. BRIXNER, *J. Amer. Chem. Soc.* **80**, 3214 (1958).
32. L. BRIXNER, *J. Inorg. Nucl. Chem.* **15**, 352 (1960).
33. F. GALASSO AND W. DARBY, *J. Phys. Chem.* **66**, 131 (1962).
34. T. TAKEDA AND A. WATANABE, *Japan. J. Appl. Phys.* **7**, 232 (1968).
35. T. Y. TIEN AND F. A. HUMMEL, *Trans. Brit. Ceram. Soc.* **66**, 233 (1967).
36. S. N. RUDDLESDEN AND P. POPPER, *Acta Crystallogr.* **11**, 54 (1958).
37. G. J. MCCARTHY, W. B. WHITE, AND R. ROY, *J. Amer. Ceram. Soc.* **52**, 463 (1969).
38. W. B. WHITE AND V. G. KERAMIDAS, "Solid State Chemistry," pp. 113-126. NBS Special Publication 364, (1972).
39. R. J. D. TILLEY, *J. Solid State Chem.* **21**, 293 (1977).
40. U. BALACHANDRAN AND N. G. EROR, in "Extended Abstracts, 158th Meeting of the Electrochemical Society, Vol. 80-2, pp. 914-915 (1980).
41. A. MAGNELI, *Ark. Kemi* **1**, 513 (1950).
42. A. D. WADSLEY, *Acta Crystallogr.* **14**, 660 (1961).
43. J. S. ANDERSON, "Advances in Chemistry," Vol. 39. American Chem. Soc., Washington, D.C. (1963).
44. N. G. EROR, *J. Solid State Chem.*, **38**, 281 (1981).
45. A. D. WADSLEY, "Advances in Chemistry," Vol. 39. American Chem. Soc., Washington, D.C. (1963).