

Oxide ion and electron mixed conduction in sintered oxides of the system $\text{Bi}_2\text{O}_3\text{-Pr}_6\text{O}_{11}$

T. ESAKA, H. IWAHARA, H. KUNIEDA

Department of Environmental Chemistry and Technology, Faculty of Engineering, Tottori University, Minami 4-101, Koyama-cho, Tottori 680, Japan

Received 6 July 1981

Oxide ion and electron conduction in sintered oxides of the system $\text{Bi}_2\text{O}_3\text{-Pr}_6\text{O}_{11}$ have been studied. Two types of rhombohedral phase are formed in this system. Oxide ion conduction is predominant in the rhombohedral β -phase present in the composition range less than 35 mol % $\text{Pr}_2\text{O}_{11/3}$. Electronic (hole) conduction appeared in addition to oxide ion conduction in another rhombohedral phase containing more than 40 mol % $\text{Pr}_2\text{O}_{11/3}$. This phase is of the LaOF-type which is a distorted defect fluorite-type structure. Electronic conduction in the LaOF-type phase is considered to be due to the change of oxidation state of praseodymium at high temperatures.

1. Introduction

Oxide ion conducting solids are potential electrolyte materials for high temperature fuel cells [1, 2]. Electronic conduction coexists with oxide ion conduction but is generally undesirable, because it causes a wastage of fuel [3]. However, a highly conducting solid in which oxide ions and electrons transport electricity (that is, a mixed conductor), would have a potential use as an electrode material for fuel cells [4, 5] and as a diaphragm for the extraction of pure oxygen gas from air.

Several Bi_2O_3 -based fcc oxides are reported to be amongst the best oxide ion conductors known [6-8]. The electronic conductivities of these oxides are low at comparatively high oxygen pressure ($> 10^{-5}$ atm) [9]. This is considered to be due to the fact that the host oxide (Bi_2O_3) as well as the dopant oxide are stable and maintain stoichiometric compositions under ordinary atmospheres. If a high oxide ion conducting phase could be stabilized in the Bi_2O_3 -based oxide systems by adding some electron conducting oxide, oxide ion and electron mixed conductor might be obtained. We considered Pr_6O_{11} to be suitable for the dopant, since it varies its oxygen content and exhibits electronic conduction at high temperatures [10-13]. Furthermore Bi_2O_3 -based oxides doped with the other rare earth oxides show high

oxide ion conduction in the stabilized fcc phases [6-8, 14].

From this point of view, the authors investigated the crystal phases and the electrical conduction of the sintered oxides of the system $\text{Bi}_2\text{O}_3\text{-Pr}_6\text{O}_{11}$ under various conditions.

2. Experimental procedure

Samples were prepared by firing a mixed powder containing defined quantities of Bi_2O_3 and Pr_6O_{11} above 900°C in air for 10 h. The firing temperature was raised to 1200°C with increasing Pr_6O_{11} content. The fired samples were ground thoroughly, pressed into a disc or cylindrical shape under a hydrostatic pressure of 2 ton cm^{-2} and sintered again in air at the same temperatures. Heat treatments were carried out to determine the high and low temperature phases for the representative samples. Quenching was carried out by cooling the samples in a few minutes from the sintering temperatures to room temperature. They were annealed by cooling the samples slowly at a rate of about 2°C min^{-1} .

Electrical conductivity measurements were carried out in air by a two-probe a.c. method using cylindrical samples (5 mm diameter by 5-10 mm length). The frequency used was 10 kHz. Both faces of the samples were smeared with silver

paste to contact the silver wires electrically. For some samples, the measurements were also made under various oxygen atmospheres. The oxygen partial pressures were regulated by mixing air and nitrogen gas.

In order to determine the ionic transport number, an oxygen gas concentration cell was constructed using the disc-shaped samples (10 mm diameter by 2–3 mm thick) as the electrolyte of the cell. Air and oxygen (1 atm) were introduced into the anode and cathode compartments, respectively, and the cell emf was measured. If the conduction in the specimen is predominantly ionic, the emf of the cell (E_0) is given theoretically by Equation 1,

$$E_0 = (RT/4F) \ln (P_{O_2,c}/P_{O_2,a}) \quad (1)$$

where R , T and F have their usual meanings, and $P_{O_2,c}$ and $P_{O_2,a}$ are the oxygen partial pressures at anode and cathode, respectively. If the specimen has some electronic conduction as well as ionic conduction, the emf (E) will be lower than E_0 because of the discharge of the cell due to electronic conduction. The ionic transport number (t_i) is given by the following equation if the electrode reaction is sufficiently reversible,

$$t_i = \frac{\sigma_i}{\sigma_t} = \frac{\sigma_i}{\sigma_i + \sigma_e} = \frac{E}{E_0} \quad (2)$$

where σ_t , σ_i and σ_e are the total, ionic and electronic conductivities, respectively.

3. Results and discussion

The X-ray diffraction patterns of representative annealed samples are shown in Fig. 1, where praseodymium oxide is indicated not by Pr_6O_{11} but by $\text{Pr}_2\text{O}_{11/3}$ to match the cation number of Bi_2O_3 . Pure Bi_2O_3 belongs to the monoclinic system and pure $\text{Pr}_2\text{O}_{11/3}$ to the fluorite-type fcc system. The samples containing 20 and 50 mol% $\text{Pr}_2\text{O}_{11/3}$ show rhombohedral phases, which, however, differ from each other in their crystal structures; one type corresponded to the β -phase in the Bi_2O_3 -SrO system studied by Sillen and Aurivillius [15] and Boivin *et al.* [16, 17], and another to the LaOF-type studied by Zachariassen [18]. Judging from the splitting of the diffraction lines, the latter phase is considered to be somewhat distorted fcc. Each phase has a certain solid solution form-

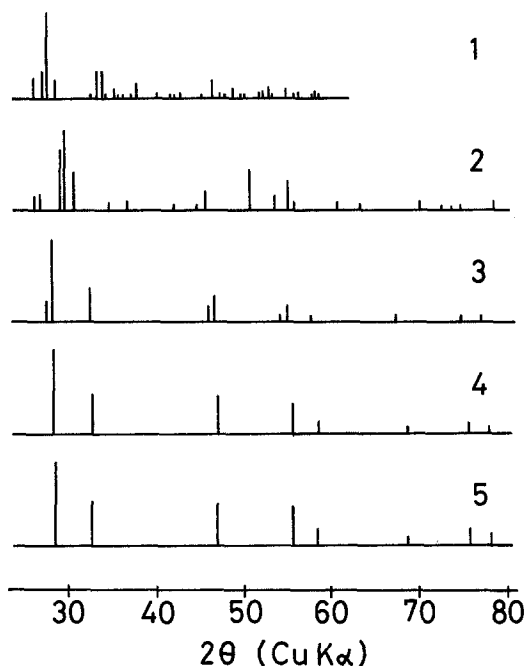


Fig. 1. X-ray diffraction patterns of $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Pr}_2\text{O}_{11/3})_x$. 1: $x = 0$; 2: $x = 0.2$ (0.10–0.35); 3: $x = 0.5$ (0.40–0.70); 4: $x = 0.8$ (0.8–1.0); 5: $x = 1.0$.

ation range, which is shown in parentheses in the figure caption. The samples having more than 80 mol% $\text{Pr}_2\text{O}_{11/3}$ gives fcc X-ray diffraction patterns. X-ray diffraction of the quenched samples showed the presence of the high temperature fcc phase in the composition range corresponding to that of the β -type rhombohedral phase at low temperatures.

Representative examples of the temperature dependence of conductivity are shown in Fig. 2. Pure Bi_2O_3 reveals a conductivity jump which starts at 730°C corresponding to the phase transition from the monoclinic to the fcc system. Similar conductivity jumps were observed in specimens containing 10 and 20 mol% $\text{Pr}_2\text{O}_{11/3}$. However, samples containing more than 40 mol% $\text{Pr}_2\text{O}_{11/3}$ show an almost linear relationship over a wide range of temperatures. The X-ray diffraction and differential thermal analysis (DTA) results (below) indicate that the conductivity jump is due to a phase transition from a low temperature phase to a high temperature phase.

In order to determine the charge carriers in these conductors, the emf of the oxygen gas concentration cell was measured. Fig. 3 shows the E/E_0 versus temperature relationships. As shown

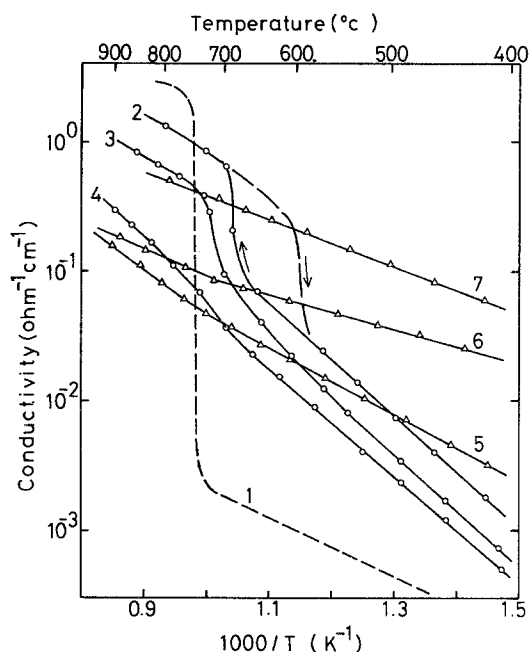


Fig. 2. Temperature dependence of conductivity in air for $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Pr}_2\text{O}_{11/3})_x$. 1: $x = 0$; 2: $x = 0.1$; 3: $x = 0.2$; 4: $x = 0.4$; 5: $x = 0.5$; 6: $x = 0.6$; 7: $x = 0.7$.

in the case of $x = 0.2$, the samples containing less than 30 mol % $\text{Pr}_2\text{O}_{11/3}$ show values close to unity. Steady and stable current could be drawn from these cells, indicating that the conduction in these oxides can be ascribed to oxide ions. However, E/E_0 values decreased with increasing $\text{Pr}_2\text{O}_{11/3}$

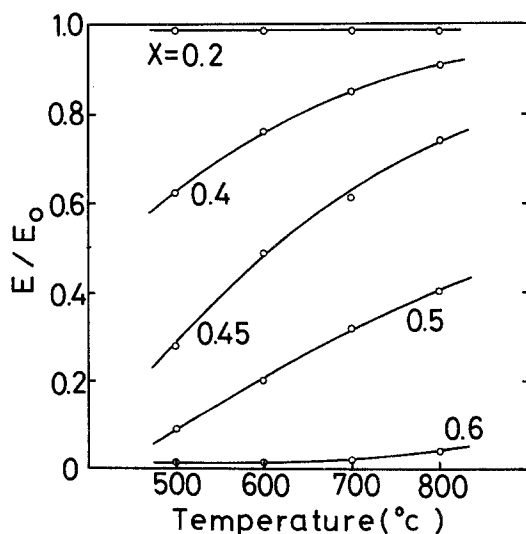


Fig. 3. E/E_0 versus temperature for the cell, $P_{\text{O}_2, \text{a}}, \text{Ag}/(\text{Bi}_2\text{O}_3)_{1-x}(\text{Pr}_2\text{O}_{11/3})_x/\text{Ag}, P_{\text{O}_2, \text{c}}$ where $P_{\text{O}_2, \text{a}} = 0.21 \text{ atm}$ and $P_{\text{O}_2, \text{c}} = 1.0 \text{ atm}$.

Table 1. Comparison of ionic transport numbers measured by two different methods

Specimen*	Temperature ($^{\circ}\text{C}$)	E/E_0	$1 - (I_e/G_t E_0)$
$x = 0.20$	600	0.99	0.97
	700	0.98	0.97
	800	0.98	0.97
$x = 0.45$	600	0.49	0.49
	700	0.61	0.60
	800	0.74	0.72
$x = 0.50$	600	0.20	0.23
	700	0.32	0.39
	800	0.40	0.43

* Specimen: $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Pr}_2\text{O}_{11/3})_x$.

content, and for $x = 0.60$ they almost reached zero. These results mean that electrons, in addition to oxide ions, obviously participate in the conduction in the samples containing more than 40 mol % $\text{Pr}_2\text{O}_{11/3}$, and that electronic conduction is predominant in 60 mol % $\text{Pr}_2\text{O}_{11/3}$ samples.

When electronic conductivity is higher than oxide ion conductivity, E/E_0 values often give incorrect transport numbers because of polarization at the electrode. In Table 1, we compare ionic transport numbers obtained by two different methods. The values of E/E_0 are those determined from the results obtained using the oxygen gas concentration cell. The values of $1 - I_e/G_t E_0$ are those calculated from total conductance (G_t) and electronic current (I_e) which were measured by applying the theoretical voltage (E_0) of the concentration cell to stop the ionic current [19]. These show similar values, independent of the measurement methods, indicating that the effect of polarization is small in these cases.

When the oxygen partial pressure in each electrode gas was changed, keeping the ratio $P_{\text{O}_2, \text{c}}/P_{\text{O}_2, \text{a}}$ constant, the measured E/E_0 and the total conductance (G_t) of the electrolyte altered as shown in Table 2. However, it is clear from this table that the ionic conductance (G_i) of the electrolyte calculated from Equation 2 ($G_i = G_t E/E_0$ in this case) remains almost unchanged. This indicates that the oxide ion conductivity in this mixed conductor is independent of the oxygen partial pressure.

Figure 4 represents the relationship between the total and oxide ion conductivities and the

Table 2. E/E_0 , total conductance (G_t) and ionic conductance (G_i) for oxygen concentration cells constructed under the different conditions using

$(\text{Bi}_2\text{O}_3)_{0.5}(\text{Pr}_2\text{O}_{11/3})_{0.5}$.

Cell I: $P_{\text{O}_2, \text{a}} = 2.1 \times 10^{-1}$ atm, $P_{\text{O}_2, \text{c}} = 1.0$ atm.

Cell II: $P_{\text{O}_2, \text{a}} = 4.5 \times 10^{-2}$ atm, $P_{\text{O}_2, \text{c}} = 2.1 \times 10^{-1}$ atm.

	Temperature ($^{\circ}\text{C}$)	Cell I	Cell II
E/E_0	600	0.20	0.33
	800	0.40	0.59
$G_t(\Omega^{-1})$	600	5.8×10^{-2}	3.4×10^{-2}
	800	2.0×10^{-1}	1.3×10^{-1}
$G_i(\Omega^{-1})$	600	1.1×10^{-2}	1.1×10^{-2}
	800	8.0×10^{-2}	7.8×10^{-2}

$\text{Pr}_2\text{O}_{11/3}$ content. The oxide ion conductivity (closed circles) was calculated by multiplying the total conductivity (open circles) by E/E_0 obtained from an air-oxygen cell. It is obvious that the β -type rhombohedral phase shows ionic conduction and that the LaOF-type rhombohedral phase has mixed oxide ion and electronic conduction. The oxide ion conductivity decreases with increasing $\text{Pr}_2\text{O}_{11/3}$ content, but the total conductivity shows rising curves in the composition range 40–50 mol% $\text{Pr}_2\text{O}_{11/3}$ due to the appearance of electronic conduction.

The conductivity of a mixed oxide ion and electron conductor is, in general, given by

$$\sigma = \sigma_0 + \sigma_p^{\circ} P_{\text{O}_2}^{1/n} + \sigma_n^{\circ} P_{\text{O}_2}^{-1/n} \quad (3)$$

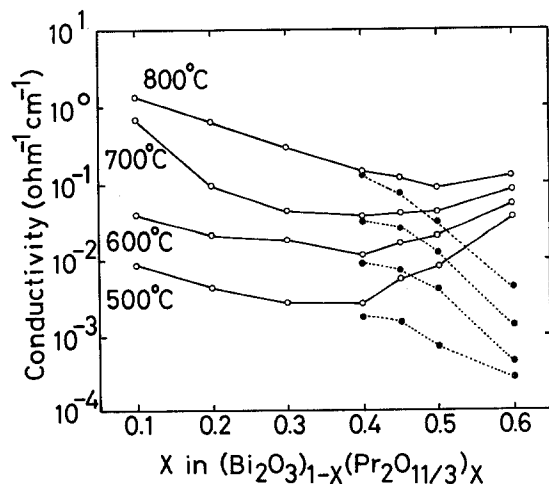


Fig. 4. Conductivity versus $\text{Pr}_2\text{O}_{11/3}$ content. Solid circles are the partial oxide ion conductivity in the composition range showing remarkable electronic conduction.

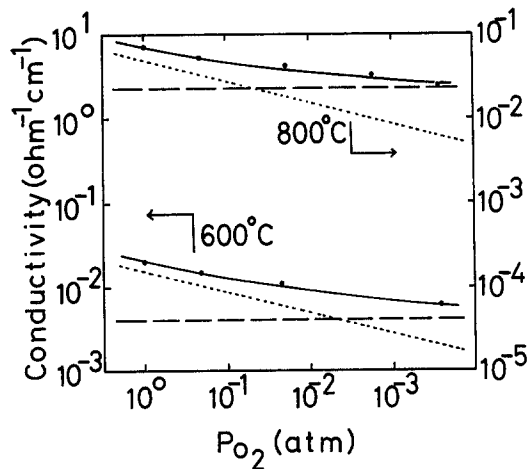


Fig. 5. Dependence of the conductivities of $(\text{Bi}_2\text{O}_3)_{0.5}(\text{Pr}_2\text{O}_{11/3})_{0.5}$ on oxygen partial pressure P_{O_2} at different temperatures.

where σ_0 is the oxide ion conductivity, σ_p° and σ_n° are constants related to hole and excess electron conductivities, respectively, and P_{O_2} is the partial pressure of the oxygen equilibrated with the oxide specimen at any given temperature [20]. When σ_0 is independent of P_{O_2} , the type of electronic conduction is presumed from the dependence of conductivity on P_{O_2} ; the conduction is due to electron holes if the conductivity increases with increasing P_{O_2} and the conduction is due to excess electrons if the situation is the reverse.

Figure 5 shows the dependence of conductivity on oxygen partial pressure in the case of $(\text{Bi}_2\text{O}_3)_{0.5}(\text{Pr}_2\text{O}_{11/3})_{0.5}$. The conductivity decreases with decreasing P_{O_2} indicating that electronic conduction in this specimen can be ascribed to electron holes. Since the oxide ion conductivity of this material is independent of P_{O_2} , it is reasonable to adopt the values shown in Fig. 4 (closed circles at $x = 0.5$) as σ_0 values in Equation 2. Then, the dependence of hole conductivity on P_{O_2} can be expressed by the dotted lines in Fig. 5. The gradient of these lines is $1/4$ ($n = 4$ in Equation 3), which is the same value as that for pure Bi_2O_3 [21] and the Bi_2O_3 - Y_2O_3 system [8]. This result indicates the presence of a number of oxygen vacancies in the LaOF-type phase as well as in the fluorite-type crystal.

As praseodymium may contribute to the formation of electron holes which conduct electricity,

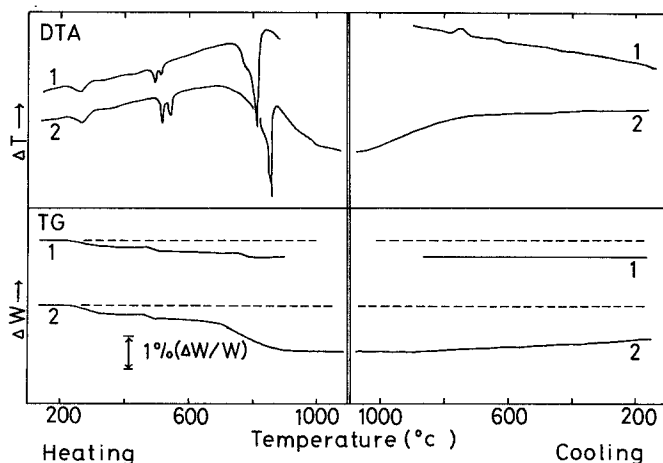


Fig. 6. DTA and TG results of $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Pr}_2\text{O}_{11/3})_x$. 1: $x = 0.2$; 2: $x = 0.5$.

we investigated the valence of Pr by means of DTA and thermogravimetry (TG). Figure 6 shows typical DTA and TG results. The mixed powders of starting materials showed endothermic peaks for every composition during heating and correspondingly the samples lost weight in a stepwise manner. Quantitative analysis of the change in weight showed that Pr finally became trivalent at high temperatures. As pure praseodymium oxide ($\text{PrO}_{1.86}$) is not reduced to $\text{PrO}_{1.5}$ in air but only to $\text{PrO}_{1.66}$, Bi_2O_3 seems to have the role of stabilizing the trivalent state of Pr at high temperatures. This stabilization effect increases as the Bi_2O_3 content increases; in the sample having a high Bi_2O_3 content (for example, $x = 0.2$ in Fig. 6), the sample weight is held constant during cooling, keeping the trivalent oxidation state of Pr even at low temperatures. The exothermic peak observed on the DTA chart is due to the phase transition from the high temperature fcc form to the low temperature rhombohedral one. In the case of $x = 0.5$, however, the sample weight gradually increases during cooling, showing Pr in a higher valency state than three. Considering these results together with the conduction behaviour, we can conclude that the oxidation state of Pr plays an important role in the electronic conduction of sintered oxides in the system $\text{Bi}_2\text{O}_3\text{-Pr}_2\text{O}_{11/3}$; that is, electronic conduction is rarely observed in samples with a constant oxygen content over the temperature ranges examined and hole conduction appears in samples showing a change in oxygen content during heating and cooling.

4. Conclusion

The sintered oxides of Bi_2O_3 doped with $\text{Pr}_2\text{O}_{11/3}$ form two kinds of rhombohedral single phases. One is a β -type in 10–35 mol% $\text{Pr}_2\text{O}_{11/3}$ and the other is the LaOF-type in 40–70 mol% $\text{Pr}_2\text{O}_{11/3}$. In the former phase, high oxide ion conduction is predominant and electronic conductivity is negligibly low at ordinary oxygen pressures. In the latter phase, electronic conduction is observed in addition to oxide ion conduction and the proportion of electronic conductivity increases with increasing $\text{Pr}_2\text{O}_{11/3}$ content. Oxide ion conduction is considered to be due to migration of oxygen vacancies present in the crystal and electronic conduction to electron holes. As the valence states of Pr and the concentration of oxygen vacancies are readily varied in the LaOF-type phase, hole conductivity is considered to appear at comparatively high oxygen pressures. The specimen containing about 50 mol% $\text{Pr}_2\text{O}_{11/3}$ is a mixed conductor, in which oxide ions and electron holes take part to the same degree.

References

- [1] T. Takahashi, in 'Physics of Electrolytes', Vol. 2 (edited by J. Hladik) Academic Press, London (1972) p. 999.
- [2] F. J. Rohr, in 'Solid Electrolytes' (edited by P. Hagenmuller and W. van Gool) Academic Press, London, New York (1978) p. 431.
- [3] T. Takahashi and H. Iwahara, *Energy Conversion* **11** (1971) 105.
- [4] C. S. Tedmon Jr, H. S. Spacil and S. P. Mitoff, *J. Electrochem. Soc.* **116** (1969) 1170.

- [5] T. H. Etsell and S. N. Flengas, *Chem. Rev.* **70** (1970) 339.
- [6] T. Takahashi, H. Iwahara and T. Arao, *J. Appl. Electrochem.* **5** (1975) 187.
- [7] T. Takahashi, T. Esaka and H. Iwahara, *J. Appl. Electrochem.* **5** (1975) 197.
- [8] M. J. Verkerk, K. Keizer and A. J. Burggraaf, *J. Appl. Electrochem.* **10** (1980) 81.
- [9] T. Takahashi, T. Esaka and H. Iwahara, *J. Appl. Electrochem.* **7** (1977) 303.
- [10] R. E. Ferguson, E. Daniel Guth and L. Eyring, *J. Amer. Chem. Soc.* **76** (1954) 3890.
- [11] E. Daniel Guth, J. R. Holden, N. C. Baenziger and L. Eyring, *J. Amer. Chem. Soc.* **76** (1954) 5239.
- [12] G. V. Chandrashekhar, P. N. Mehrotra, G. V. Subba Rao, E. C. Subbarao and C. N. R. Rao, *Trans. Faraday Soc.* **63** (1967) 1295.
- [13] H. B. Lal and B. K. Verma, *Ind. J. Pure Appl. Phys.* **15** (1977) 400.
- [14] H. Iwahara, T. Esaka, T. Soto and T. Takahashi, *J. Sol. Stat. Chem.* **3/4** (1981) 359.
- [15] L. S. Sillen and B. Aurivillius, *Z. Crist.* **101** (1939) 483.
- [16] J. C. Boivin and D. J. Thomas, *Sol. Stat. Ionics* **3/4** (1981) 457.
- [17] P. Conflant, J. C. Boivin and D. Thomas, *J. Sol. Stat. Chem.* **35** (1980) 192.
- [18] W. H. Zachariasen, *Acta Cryst.* **4** (1951) 231.
- [19] T. Takahashi, T. Esaka and H. Iwahara, *J. Sol. Stat. Chem.* **16** (1976) 317.
- [20] H. Schmalzried, *Z. Phys. Chem. NF* **38** (1963) 87.
- [21] C. N. R. Rao, G. V. Subba Rao and S. Ramdas, *J. Phys. Chem.* **73** (1969) 672.