# Heterogeneous doping effects in KCl–Al$_2$O$_3$ composites

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**Abstract.** The composite solid electrolyte systems KCl–Al$_2$O$_3$ have been synthesized by conventional as well as by solution casting methods and have been characterized by means of complex impedance analysis, XRD and DTA techniques. The samples prepared by solution casting method show about an order of magnitude higher conductivity than those prepared by the conventional method. The enhanced conductivity is attributed to the excess cation vacancies generated in the space charge region of the matrix phase surrounding the Al$_2$O$_3$ particles as a consequence of stabilization of cations at the dispersoid surface due to internal adsorption. The XRD and DTA analyses show that no new phase is present. Macroscopically, the compositional and particle size dependence of the conductivity are adequately explained on the basis of random resistor network percolation model.

**Keywords.** Composite solid electrolytes; space charge layer; random resistor network percolation model.

## 1. Introduction

It is widely accepted that in heterogeneously doped two-phase mixtures, increase in conductivity occurs due to formation of high-conducting space charge layer in the matrix phase in the vicinity of the dispersoid (Jow and Wagner 1979; Wagner Jr 1980; Shahi and Wagner 1981; Maier 1984, 1985; Maier and Reichert 1986). The conduction in such electrolytes is different from that in the conventional homogeneously doped ones in the sense that the fulfilment of local electroneutrality is decisive in the latter whereas in the case of the former the deviations from local electroneutrality are important (Maier 1985).

A number of models (Jow and Wagner 1979; Stoneham et al 1979; Roman et al 1986; Wang and Dudney 1986; Roman and Youssouff 1987) have been proposed to explain heterogeneous doping effects. Almost all the models presume formation of high-conducting space charge layer along the matrix–insulator interface, though they differ regarding the origin of the space charge layer. It could be due to enhanced carrier concentration in the space charge layer (Maier 1984, 1985), enhanced carrier concentration at the core of the interface (Phipps et al 1981; Phipps and Whitemore 1983), or interfacial phase formation (Pack et al 1980). The random resistor network (RRN) percolation model (Bunde et al 1986; Roman and Youssouff 1987) macroscopically explains the compositional and particle size dependence of the conductivity quite well.

Though composite solid electrolytes are extensively studied (Liang 1973; Shahi and Wagner 1981; Nakamura and Goodenough 1982; Chang et al 1984; Fujitsu et al 1986; Vaidehi et al 1986; Slade and Thompson 1988), the alkali halide-based composites, with the exception of lithium salts, have not been studied. The alkali halides are the most suitable matrix materials for studying the effect of a second insoluble phase on the ionic conductivity of normal ionic conductors as they do not

exhibit any solid–solid transformation. Besides, they are well understood with regard to their defect and conduction mechanisms. This paper reports the synthesis of $KCl-Al_2O_3$ composites by the conventional and solution casting methods and their structural and electrical characterization studies.

## 2.  Experimental

High-purity polycrystalline KCl was obtained from Aldrich (USA) and the deagglomerated alumina powder of three different particle sizes (0·05, 0·3 and 1·0 $\mu$m) from Buehler Micropolish II (USA). The various compositions of $KCl-Al_2O_3$ were mixed and milled thoroughly in acetone medium in a ball mill (Fritsch Puloeristte Type 0·05 0·202, Germany) for 6–8 h. The solid chunk so obtained was heated above the melting point of the salt in a porcelain crucible. The fused chunk so obtained was thoroughly ground using a pestle and mortar and finally pelletized in a die of 9 mm dia. at a pressure of $\sim$ 5 ton/cm$^2$. The pellets were subsequently sintered at 50°C below the melting point of the salt followed by electroding the faces of the pellets by platinum paint and curing at 160°C for 1 h. In the solution casting method the requisite salt was first ionized in deionized water. The appropriate amount of $Al_2O_3$ was added in the solution containing the ionized salt. This solution was magnetically stirred and simultaneously evaporated by heating the solution. The solid chunk so obtained was processed as in the first method.

The d.c. electrical conductivities of various composite systems are obtained at each temperature from the complex impedance analysis. The impedance measurements were carried out using an HP 4192A impedance analyser over the temperature range 600–200°C during the cooling cycle at steps of 25–30°C. To analyse the a.c. impedance data $|Z|$ and $\theta$, an integrated software package developed in our laboratory (Bhatnagar *et al* 1988) was used which also provides for automatic data entry, acquisition and analysis. The plots of $|Z|\sin\theta$ vs $|Z|\cos\theta$ were found to be semicircles. Thus the impedance spectra could be expressed as a parallel combination of a pure resistor and a capacitor. The diameter of the semicircular plot yielded the d.c. resistance of the sample which was used to calculate the conductivity. The temperature of the furnace was controlled to within $\pm$ 1°C by using a PID temperature controller (Indotherm model 401-D).

The X-ray diffraction (XRD) patterns were recorded at room temperature by using a Rich–Seifert (Iso-Debyeflex 2002D) counter diffractogram employing $CuK_\alpha$ radiation. The DTA measurements were carried out using mini DTA (Linseis model L62) with a heating/cooling rate of 5°C/min. A JEOL model 840A scanning electron microscope was used to examine the distribution of $Al_2O_3$ particles in KCl matrix.

The particle sizes of $Al_2O_3$ were measured by Coulter counter model $Z_B$ and B, and found to have values of 1·2, 2·9 and 5·7 $\mu$m even though the initial particle sizes quoted by the manufacturer were 0·05, 0·3 and 1·0 $\mu$m respectively. The specific surface area of the particles obtained by BET technique was 11·38, 3·35 and 2·74 m$^2$/g respectively.

## 3.  Results and discussion

XRD patterns of sintered KCl–40 mol% $Al_2O_3$ samples revealed that the samples were biphasic and no additional peak was observed which could be attributed to a

new phase formed. As shown in figure 1, no difference is discernible in the XRD patterns between pre-heated and post-heated (600°C, 2 h) mixtures of KCl–40 mol% $Al_2O_3$ samples indicating that the heat treatment merely affected the densification of the mixtures.

DTA curves for the same samples also show no evidence of any chemical reaction between KCl and $Al_2O_3$ (figure 2). The peaks corresponding to the melting point of the alkali salt are unaffected due to dispersion of alumina which suggests that there is no solubility of the latter in the former even at the elevated temperatures near the melting point of the salt.
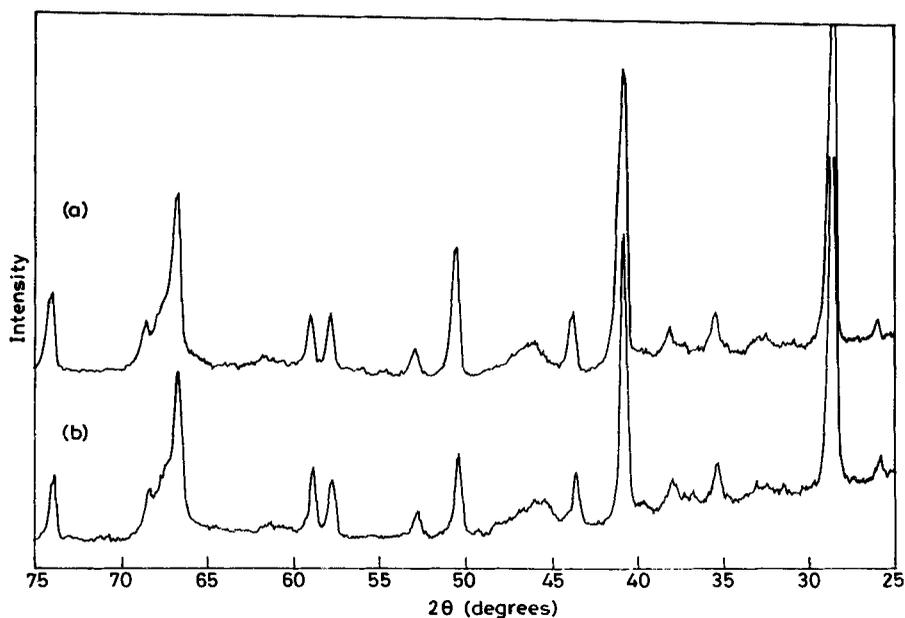


**Figure 1.** The X-ray diffraction patterns for (a) preheated and (b) post-heated KCl–40 mol% $Al_2O_3$ composite sintered at 600°C.
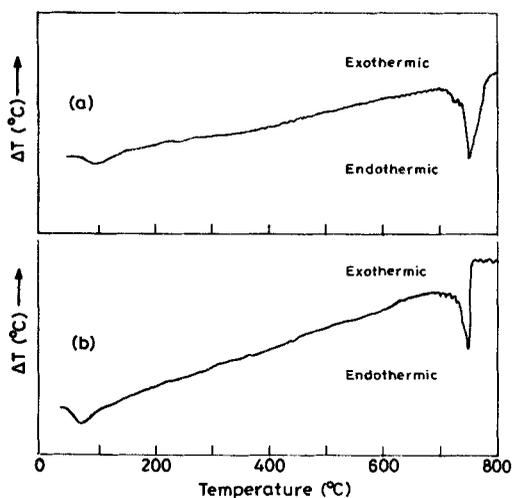


**Figure 2.** The DTA curves for (a) pure KCl and (b) KCl–40 mol% $Al_2O_3$ composite.

The SEM of KCl–30 mol% $Al_2O_3$ composite sintered at 650°C is shown in figure 3. The figure shows that $Al_2O_3$ particles are dispersed in the KCl matrix forming a composite.

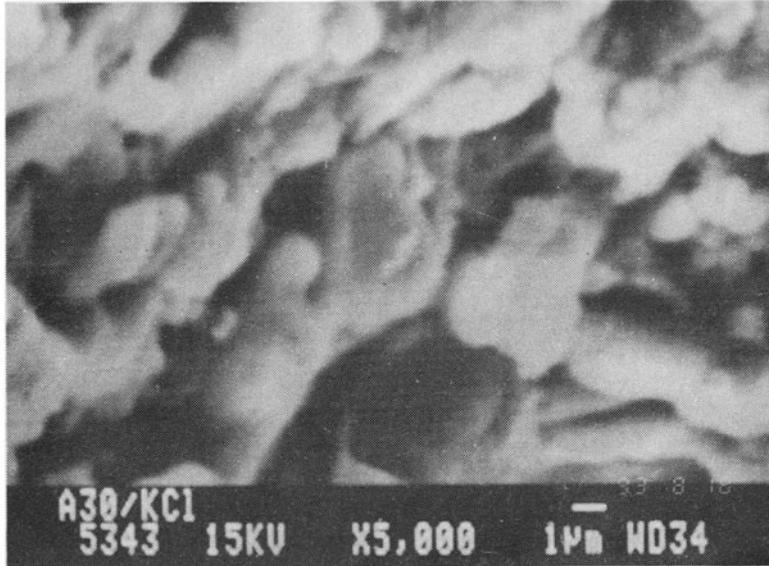Figure 4 shows variation of the conductivity as a function of concentration (mol%)



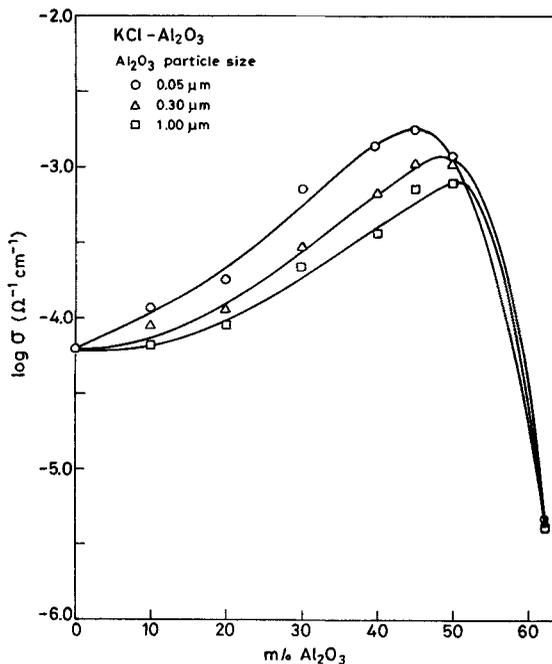**Figure 3.** SEM photograph of KCL–30 mol% $Al_2O_3$ composite sintered at 650°C.



**Figure 4.** Composition and particle size dependence of conductivity for KCl–$Al_2O_3$ composite system at 500°C.

of Al$_2$O$_3$ in KCl at 500°C for three different sizes of Al$_2$O$_3$ particles (0·05, 0·3 and 1·0 μm). The figure shows that as the concentration of Al$_2$O$_3$ increases, the conductivity increases slowly initially, then rather rapidly before it peaks at ∼ 45 mol% Al$_2$O$_3$. Moreover, as the particle size increases the enhancement in the conductivity decreases and the maximum conductivity occurs at higher concentration of Al$_2$O$_3$. These results show that the enhancement in the conductivity is by over an order of magnitude for KCl–45 mol% Al$_2$O$_3$ composite system, and that the enhancement in the conductivity is more pronounced at lower temperatures.

One may be tempted to ascribe the conductivity enhancement in KCl–Al$_2$O$_3$ composites to the excess K$^+$ vacancies generated by dissolution of Al$_2$O$_3$ molecules in KCl lattice as follows:

$$Al_2O_3 \rightarrow 2Al_K^{\cdot\cdot} + V_K' + 3O_{Cl}',$$
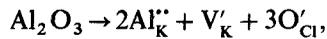
where the Kröger–Vink notation has been used. Thus one molecule of dissolved Al$_2$O$_3$ produces one excess cation vacancy. If this were the mechanism of conductivity enhancement in KCl–Al$_2$O$_3$ composite systems, a simple calculation using known mobility values of K$^+$ vacancy (Laurent and Benard 1957) would suggest that only a fraction of a mole per cent of Al$_2$O$_3$ is required to achieve the observed conductivity enhancement at 300°C. On the other hand, the experiments show that there is very little enhancement in the conductivity of KCl even with the addition of as large as 10 mol% of Al$_2$O$_3$ and the maximum enhancement in the conductivity occurs at ∼ 45 mol% of Al$_2$O$_3$. This clearly suggests that the classical doping mechanism cannot be used to explain the conductivity enhancement in KCl–Al$_2$O$_3$ composites. The dispersion of Al$_2$O$_3$ may also increase the dislocation density in the host matrix and the excess space charge at the dislocation may contribute to the excess conductivity. However, the dependence of conductivity on the processing and particle size indicates that the mechanism responsible for conductivity enhancement must involve the matrix–particle interface. The fact that KCl–Al$_2$O$_3$ composites exhibit a maximum in the conductivity at ∼ 45 mol% Al$_2$O$_3$ suggests that some sort of high-conducting channel forms through the conductor around this composition. It could be either due to formation of a high-conducting phase or a space charge layer along the interface.

Jow and Wagner (1979) were the first to present evidence for a space charge layer adjacent to the dispersoid in the composite solid electrolytes. They applied the concept that a pure ionic crystal in thermal equilibrium possessed a space charge region adjacent to the surface formed due to the difference in free energies of formation of individual defect species (Lehovec 1953; Kliewer and Koehler 1965; Kliewer 1966). If there is a chemically inert second phase instead of vacuum, which means there is no solubility or a global chemical reaction with the crystal, then the situation is as described above.

Maier (1984, 1985) gave a semiquantitative theory to account for the mechanism leading to the enrichment of defect concentration in the space charge region in composite solid electrolytes. According to this theory, the dispersoid acts as a nucleophilic surface, which attracts positively charged species. The increase in the ionic conductivity of the composite arises from the enhanced concentration of defects at the matrix–particle interface. Pure KCl is a Schottky disordered solid and primarily conducts via cation vacancies below 600°C (Dreyfus and Nowick 1962; Fuller *et al*

1968). The cation and anion vacancies are formed according to the reaction

$$O \rightarrow V'_K + V^{\cdot}_{Cl}.$$

Due to the condition of local electroneutrality, the concentration of defects (cation and anion vacancies) in the bulk is fixed by the Schottky constant. However, for pure KCl crystal at the surface, the free energy of formation of cation vacancies $V'_K$ is lower than that of the anion vacancies $V^{\cdot}_{Cl}$ (Kliewer and Koehler 1965). The introduction of dispersoid causes the positively charged species to be attracted towards the surface of the dispersoid, leaving a depletion zone with a greater concentration of cation vacancies. This depletion zone is the high-conducting space charge layer along the matrix–particle interface. The activation energies observed for conduction in various KCl–$Al_2O_3$ composites are comparable to the $K^+$ vacancy migration enthalpies reported for pure KCl (Fuller *et al* 1968). This is in accordance with the theory that the excess cation vacancies are induced in the matrix at the interface.

The random resistor network model (Roman *et al* 1986) which assumes the existence of a high-conducting space charge layer between a normally conducting matrix and a non-conducting dispersoid considers the problem of conductivity enhancement in composites from a macroscopic point of view and predicts the existence of two critical concentrations, viz. $p'_c$ and $p''_c$. At $p'_c$ the high-conducting layers begin to form connected pathways and at $p''_c$ the connected pathways get disrupted as they begin to form closed loops due to increased concentration of insulating bonds. The results in figure 4 do show that the conductivity rises initially, passes through a maximum and subsequently drops suddenly, and thus appear to be in conformity with the RRN model.

The generalized RRN model (Roman and Youssouff 1987) also qualitatively explains the dependence of conductivity on the particle size of $Al_2O_3$. The finer particles have higher surface area for a given concentration (mol%) of $Al_2O_3$, and thus the optimum interface required for maximum conductivity is attained at a lower concentration for finer $Al_2O_3$ particles. The results in figure 4 show that the conductivity peak shifts towards higher concentration of $Al_2O_3$ as particle size increases (i.e. surface area decreases) and are thus consistent with the random resistor network model.

The log $\sigma$ vs $10^3/T$ plots for various KCl–$Al_2O_3$ composites are shown in figure 5. The transport parameters, viz. the pre-exponential factor ($\sigma_0$) and the activation energy ($E_a$), are given in table 1 for various KCl–$Al_2O_3$ composites. The results for pure KCl are in agreement with the literature (Fuller *et al* 1968). The average activation energy for KCl–$Al_2O_3$ composites (10–50 mol% $Al_2O_3$) is 0·99 eV which is very close to that of pure KCl. This suggests that the mechanism of conduction in KCl, i.e. via migration of $K^+$ ion vacancies, does not change due to dispersion of $Al_2O_3$. This result convincingly leads to the conclusion that the enhanced conductivity in KCl–$Al_2O_3$ composites is due to the increased concentration of cation ($K^+$ ion) vacancies in the interfacial region. Figure 6 compares the log $\sigma$ vs $10^3/T$ behaviour for KCl–45 mol% $Al_2O_3$ samples prepared by conventional and solution casting methods. It is evident that the samples prepared by solution casting method show about an order of magnitude higher conductivity than those prepared by conventional method. This result can be qualitatively explained by the space charge theory (Maier 1985). As pointed out earlier, in the solution casting method, $Al_2O_3$ is added to the
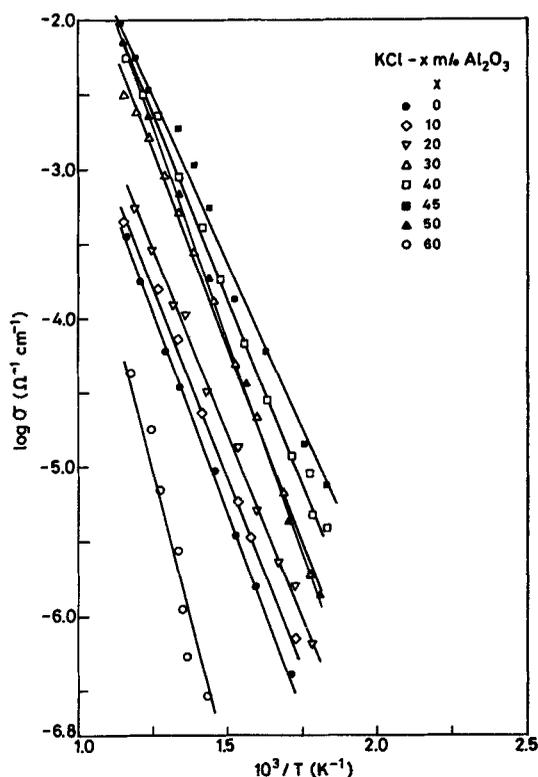
**Figure 5.** The variation of conductivity as a function of inverse temperature for various KCl–Al$_2$O$_3$ composites.

**Table 1.** Ionic transport parameters: the pre-exponential factor and the activation energy of KCl–Al$_2$O$_3$ composite.

| Composition (mol% Al$_2$O$_3$) | Temperature range (°C) | $E_a$ (eV) | $\sigma_0$ (ohm-cm)$^{-1}$ |
|---|---|---|---|
| 0 | 300–600 | 1·03 | 3·23 × 10$^2$ |
| 10 | 300–600 | 0·99 | 3·38 × 10$^2$ |
| 20 | 300–600 | 0·93 | 1·98 × 10$^2$ |
| 30 | 300–600 | 1·09 | 2·04 × 10$^3$ |
| 40 | 300–600 | 0·94 | 1·75 × 10$^3$ |
| 45 | 300–600 | 0·89 | 6·56 × 10$^2$ |
| 50 | 300–600 | 0·99 | 2·04 × 10$^3$ |
| 60 | 450–600 | 1·83 | 3·13 × 10$^6$ |

solution containing ionized alkali salts. The presence of water may increase the cation disorder reaction and lead to better stabilization of cations at the interface. This, possibly, results in a still higher concentration of cation vacancies in the space charge region, which gives rise to a larger enhancement in conductivity for samples prepared by the solution casting method. This result further supports the interface mechanism of conduction in the composite solid electrolytes.
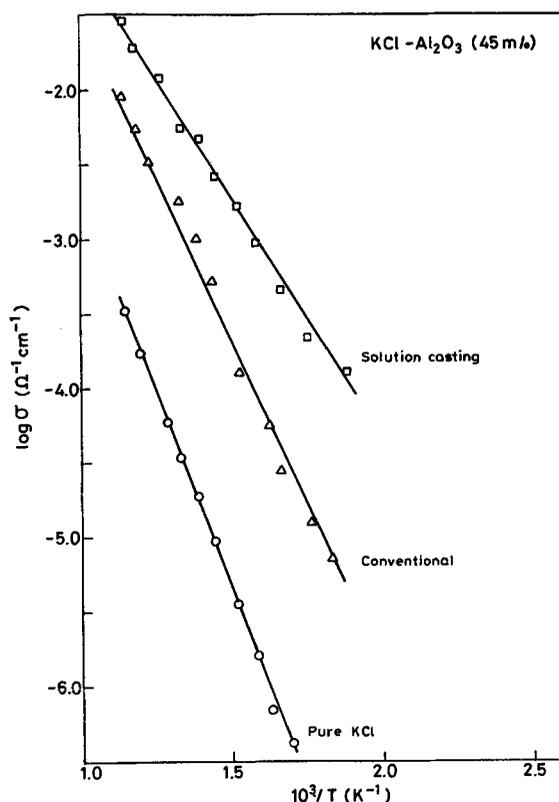
**Figure 6.** The variation of conductivity as a function of inverse temperature for KCl–45 mol% $Al_2O_3$ composites prepared by conventional and solution casting methods.

## 4. Conclusion

KCl containing dispersed phase $Al_2O_3$ particles show enhancement in ionic conductivity over its pure phase. That the interface between KCl matrix and $Al_2O_3$ particles contributes to this effect has been explained by dependence of conductivity on composition, particle size and processing conditions (preparation by conventional and solution casting methods). The enhanced conductivity is attributed to the increased concentration of cation vacancies at the matrix–particle interface.

## References

Bhatnagar S, Gupta S and Shahi K 1988 *Solid State Ionics* **31** 107
Bunde A, Dieterich W and Roman H E 1986 *Solid State Ionics* **18/19** 147
Chang M R-W, Shahi K and Wagner J B Jr 1984 *J. Electrochem. Soc.* **131** 1213
Dreyfus R W and Nowick A S 1962 *J. Appl. Phys.* **33** 473
Fujitsu S, Koumoto K and Yanagida H 1986 *Solid State Ionics* **18/19** 1146
Fuller R G, Reilly M H, Marquardt C L and Wells J C Jr 1968 *Phys. Rev. Lett.* **20** 662
Jow T and Wagner J B Jr 1979 *J. Electrochem. Soc.* **126** 1963
Kliewer K L and Koehler J S 1965 *Phys. Rev.* **A140** 1226
Kliewer K L 1966 *J. Phys. Chem. Solids* **27** 705

Laurent J F and Benard J 1957 *J. Phys. Chem. Solids* **3** 7
Lehovec K 1953 *J. Chem. Phys.* **21** 1123
Liang C C 1973 *J. Electrochem. Soc.* **120** 1289
Maier J 1984a *Ber. Bunsenges. Phys. Chem.* **88** 1057
Maier J 1984b *Phys. Status Solidi* **b 123** K89, **124** K187
Maier J 1985 *J. Phys. Chem. Solids* **46** 309
Maier J and Reichert B 1986 *Ber. Bunsenges Phys. Chem.* **90** 666
Nakamura O and Goodenough J B 1982 *Solid State Ionics* **7** 119
Pack S, Owens B B and Wagner J B Jr 1980 *J. Electrochem. Soc.* **127** 2177
Phipps J B, Johnson D L and Whitemore D H 1981 *Solid State Ionics* **5** 393
Phipps J B and Whitemore D H 1983 *Solid State Ionics* **9/10** 123
Roman H E, Bunde A and Dieterich W 1986 *Phys. Rev.* **B34** 3439
Roman H E and Youssouff M 1987 *Phys. Rev.* **B36** 7285
Shahi K and Wagner J B Jr 1981 *J. Electrochem. Soc.* **128** 6
Slade C T and Thompson I M 1988 *Solid State Ionics* **26** 287
Stoneham A M, Wade E and Kilner J A 1979 *Mater. Res. Bull.* **14** 661
Vaidehi N, Akila R, Shukla A K and Jacob K T 1986 *Mater. Res. Bull.* **21** 909
Wagner J B Jr 1980 *Mater. Res. Bull.* **15** 1691
Wang J C and Dudney N J 1986 *Solid State Ionics* **18/19** 112