



ELSEVIER

Solid State Ionics 101–103 (1997) 1201–1205



Electrical conductivity and thermal behavior of solid electrolytes based on alkali carbonates and sulfates

S. Brosda^{a,*}, H.J.M. Bouwmeester^b, U. Guth^a

^a*Institute of Physical Chemistry, University of Greifswald, Greifswald, Germany*

^b*University of Twente, Enschede, The Netherlands*

Abstract

Both thermal stability and electrical conductivity of alkali ion conducting Na_2CO_3 and Na_2SO_4 , were improved by adding alkaline earth carbonates and sulfates, respectively, as well as insulating materials like $\gamma\text{-Al}_2\text{O}_3$. The admixing of divalent compounds causes two effects. First a more or less extended solution can exist depending on the radius of the alkaline earth ion and is accompanied by an increase in electrical conductivity. Secondly, a phase mixture with an excess of dopant was observed that shows an enhancement in conductivity and mechanical stability. This phenomenon known as composite effect was observed in the following systems: $\text{Na}_2\text{CO}_3\text{-BaCO}_3$, $\text{Na}_2\text{CO}_3\text{-SrCO}_3$, $\text{Na}_2\text{SO}_4\text{-BaSO}_4$, $\text{Na}_2\text{SO}_4\text{-}\gamma\text{-Al}_2\text{O}_3$.

Keywords: Alkali carbonates; Alkali sulfates; Composite; Conductivity; Thermal stability

Materials: Na_2CO_3 ; BaCO_3 ; SrCO_3 ; CaCO_3 ; Na_2SO_4 ; SrSO_4 ; CaSO_4 ; BaSO_4 ; $\gamma\text{-Al}_2\text{O}_3$

1. Introduction

Solid sodium carbonate and sulfate are fast ionic conductors with negligible electronic conductivity at higher temperatures. They can be used as solid electrolytes in potentiometric cells for rapid determination of CO_2 and SO_x [1]. The pure salts exhibit a phase transition into a high temperature phase accompanied by a change of thermal expansion coefficient so that the production of long-term thermally stable sintered layers or discs is not possible.

Therefore, much work was devoted to stabilize the high temperature phase to ambient temperature by

well-known methods of doping. Additionally, the electrical conductivity is enhanced. Considerable effort is being made to develop in such a way Li^+ -based electrolytes in respect of high energy density batteries [2].

This paper intends to compare the results obtained from two new systems with those described in previous papers in order to show the different kinds of doping and their resulting electrical effects.

2. Experimental

Mixtures of carbonates and sulfates $(1-x)\text{M}_2\text{CO}_3 + x\text{MeCO}_3$, $(1-x)\text{M}_2\text{SO}_4 + x\text{MeSO}_4$ and $\text{M}_2\text{SO}_4 + \gamma\text{-Al}_2\text{O}_3$ with $\text{M} = \text{K}$, Na ; $\text{Me} = \text{Ca}$, Sr ,

*Corresponding author. Tel.: +49-3834 864 426; fax: +49-3834 864 303; e-mail: brosdag@gryps1.rz.uni-greifswald.de

Ba were prepared in a ball mill, pressed into pellets and sintered for 15 h at 50 K below their melting temperature. The electrical conductivity measurements were carried out using the four electrode dc method as well as by impedance spectroscopy. The results obtained were found to be equal for both methods. The experimental details were published elsewhere [3,4]. DSC (differential scanning calorimetry) measurements were performed on pressed compact samples in the temperature range 20–500°C at a heating rate of 5 K/min using α -alumina as a reference. The procedure of heating and cooling was carried out threefold.

For SEM/EDX investigations the equipment of Zeiss, Oberkochen, Germany was used.

3. Results and discussion

In the Arrhenius plots of conductivity, mostly three major regions can be distinguished with respect to their different slopes (Fig. 1). The high temperature region is determined due to formation of Frenkel defects (intrinsic disorder) according to:



In the medium temperature region the extrinsic disorder caused by doping with aliovalent ions or by impurities can be described by:

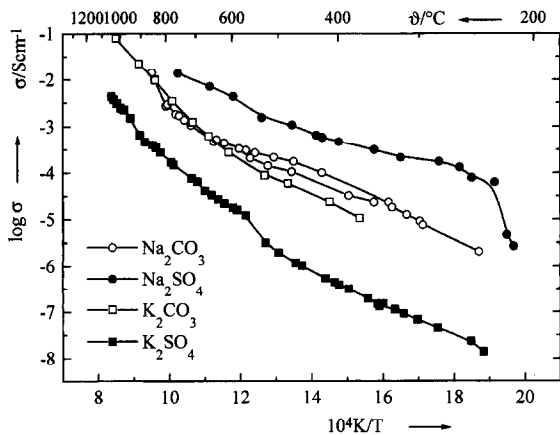
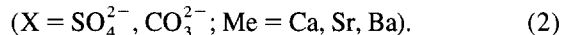
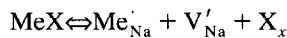


Fig. 1. Temperature dependence of conductivity of undoped alkaline carbonates and sulfates.



The low temperature region is governed by a much lower solubility of aliovalent ions in the low temperature phase, in some cases additional by formation of clusters.

3.1. Homogeneous doping

The solubility of divalent ions in sodium carbonate and sulfates depends on the ionic radii of the dopants as expected and occurs to be quite different. In the case of comparable radii, about 7 mol% of the dopant dissolves homogeneously. This behavior can be shown on the system K_2SO_4 – BaSO_4 [4]. This is in good agreement with results on Li_2SO_4 – CaSO_4 reported by Singh and Bhoga [5]. On the other hand, in Na_2CO_3 only less than 0.005 mol% are dissolved, as can be seen in the extrinsic region represented in Fig. 2. This small amount is sufficient for preparing long-term gas-tight discs that can be used as a solid electrolyte for the determination of CO_2 concentrations. Cell voltages could be measured with values according to the Nernst equation in the temperature region 380–650°C for 7 vol.ppm to 10 vol.% without cross sensitivity against water vapor [6]. It seems to be an influence of defects on the kinetics of the electrode reaction as was shown in our previous paper [7].

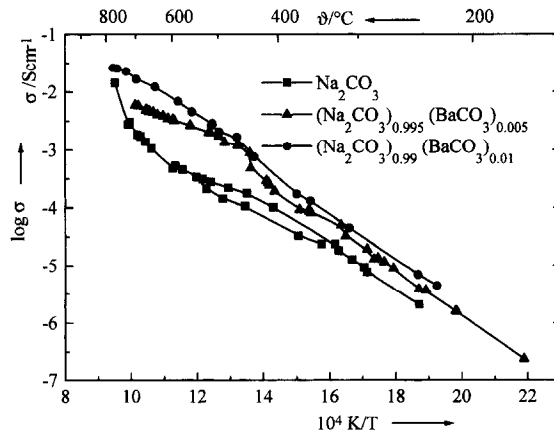


Fig. 2. Temperature dependence of conductivity of BaCO_3 -doped Na_2CO_3 .

3.2. Homogeneous and heterogeneous (mixed) doping

A phase mixture consisting of both, the homogeneous phase and the excess of dopant, is formed, by adding a dopant amount over the limit of solubility. The conductivity increases with regard to the extrinsic disorder as well as by defects formed at the phase boundary [8]



A maximum in conductivity was found to occur at about 20 mol% BaSO_4 as illustrated previously [4]. Although the enhancement in conductivity in these composites is not very large, it should be noted that the grain size of the dispersoid depends mainly on the preparation conditions and influences the electrical properties.

The comparison of the activation energy for $\text{Na}_2\text{CO}_3\text{--SrCO}_3$ and $\text{Na}_2\text{CO}_3\text{--BaCO}_3$ listed in Table 1 and shown in Fig. 3 represents both kinds of doping. In these mixtures, the mechanism in σ enhancement appears to be similar to that in alumina dispersed solid electrolytes first described by Liang [2]. Furthermore, the conductivity behavior is influenced by formation of a new compound as could be observed in the $\text{Na}_2\text{CO}_3\text{--SrCO}_3$ system with the composition $\text{Na}_2\text{Sr}_2(\text{CO}_3)_5$ [3].

This phenomenon in mixed doped phases detected

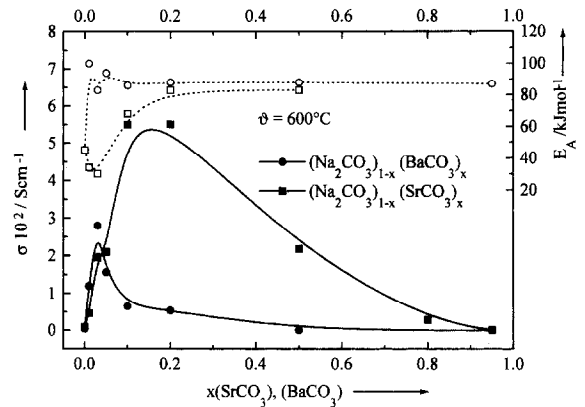


Fig. 3. Comparison of conductivities and activation energies between BaCO_3 - and SrCO_3 -doped Na_2CO_3 .

by electrical conductivity measurements could be shown semiquantitatively by SEM/EDX studies as well. In the system $\text{Na}_2\text{SO}_4\text{--BaSO}_4$ it can be distinguished between crystals from a homogeneous solid solution of BaSO_4 in Na_2SO_4 and a second BaSO_4 phase.

The mechanism of ion transport in this material is not well understood. The ‘paddle wheel’ mechanism introduced by Lunden [9] and a percolation model proposed by Secco et al. [10] have been discussed for cubic $\alpha\text{-Li}_2\text{SO}_4$. According to our previous measurements of activation energies, e.g., for $\text{K}_2\text{SO}_4\text{--BaSO}_4$ and the obtained effect of mixed doping, we found the percolation type transport mechanism [11] to be the more suitable model.

3.3. Heterogeneous doping

$\gamma\text{-Al}_2\text{O}_3$ as the most effective dispersoid was used to prepare Na_2SO_4 -based composites. The conductivity σ was enhanced by 1 to 2 orders of magnitude and its maximum was found to be at about 40 vol.% as reported in literature [2]. Furthermore after breaking, the microstructure of composites shows well-formed sodium sulfate crystals embedded in small alumina particles (Fig. 4). By adding alumina to mixtures of $\text{Na}_2\text{SO}_4\text{--BaSO}_4$ an enhancement in σ occurs as compared with those which contain no alumina [4]. Such composites look like porcelain and behave very well mechanically.

Kinetics of phase transformation $\text{Na}_2\text{SO}_4(\text{III}) \rightarrow$

Table 1

Comparison of σ_0 and activation energy E_A of doped Na_2CO_3 (in *italic* extrinsic region)

x (mole)	φ (°C)	σ_0 (S cm^{-1})	E_A (kJ mol^{-1})
$(\text{Na}_2\text{CO}_3)_{1-x}(\text{BaCO}_3)_x$ [this paper]			
0	<400	57.1 ± 4.7	76 ± 8
	<i>400...600</i>	<i>0.2 ± 2.3</i>	<i>45 ± 5</i>
	>600	$(3.6 \pm 0.1) \cdot 10^2$	101 ± 20
0.01	280...700	$(12 \pm 3.7) \cdot 10^3$	100 ± 8
0.03	300...700	$2.6 \cdot 10^2$	83
0.2	250...600	$(1.0 \pm 0.01) \cdot 10^3$	88 ± 2
0.5	380...650	12.5 ± 2.1	88 ± 5
$(\text{Na}_2\text{CO}_3)_{1-x}(\text{SrCO}_3)_x$ [3]			
0.01	620...785	6.4 ± 0.2	34 ± 2
0.03			29.7 ± 0.02
0.2	630...680	$(5 \pm 3) \cdot 10^2$	68 ± 10
0.5	470...700	$(18 \pm 3) \cdot 10^3$	83 ± 2



Fig. 4. SEM picture of the surfaces after breaking of a γ - Al_2O_3 -doped Na_2SO_4 sample.

$\text{Na}_2\text{SO}_4(\text{I})$ and vice-versa [12] were studied under dynamic conditions by DSC. For this reason, a pressed unsintered sample of Na_2SO_4 - γ - Al_2O_3 (60:40 vol.%) was heated at the linear rate of 5 K/min up to 500°C and cooled at the same rate. A shift in the transition temperature occurred differently during heating and cooling towards a lower temperature as compared to pure Na_2SO_4 . Surprisingly, by threefold repetition of this procedure the transition heat was diminished. In the first run, an almost appropriate amount of heat was measured whereas in the second run, much less heat was determined. The sintered samples showed the same behavior during the first run. Obviously, the more composite was formed by sintering the less intense the phase transition could be observed. The phase transition seems to be restrained kinetically. The

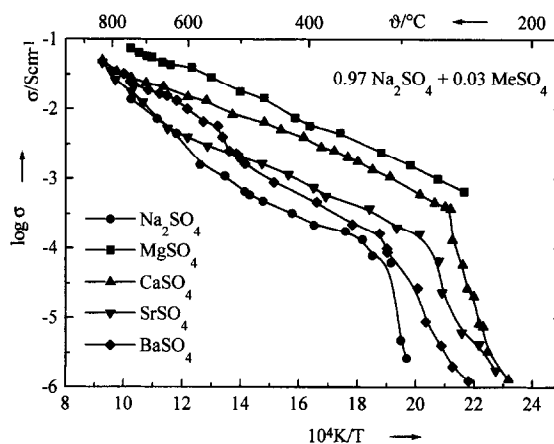


Fig. 5. Temperature dependence of conductivity of alkaline earth doped Na_2SO_4 .

results of DSC measurements are collected in Table 2.

The influence of dopants on the phase transition in equilibrium or steady state is studied in Fig. 5 for $(\text{Na}_2\text{SO}_4)_{0.97}(\text{MeSO}_4)_{0.03}$. The transition temperature (241°C) of the $\text{Na}_2\text{SO}_4(\text{III}) \rightarrow \text{Na}_2\text{SO}_4(\text{I})$ pure phase transition was shifted to the lower value with decreasing ionic radius of $\text{Me} = \text{Ba}, \text{Sr}, \text{Ca}, \text{Mg}$. The samples exhibited an excellent thermal shock resistivity.

4. Conclusion

In the systems Na_2CO_3 - MeCO_3 , Na_2SO_4 - BaSO_4 and Na_2SO_4 - γ - Al_2O_3 three main types of doping

Table 2
Results of DSC measurements obtained on different Na_2SO_4 - γ - Al_2O_3 composition

Composition	Phase transition temperature at heating-up in °C	Heat of transition in mJ mg^{-1}	Heat flow in mJ s^{-1}	Phase transition temperatures at cooling-down in °C	Heat flow in mJ s^{-1}
Na_2SO_4 pure	235.2	60.4	12.2	205.4	6.65
Na_2SO_4 - γ - Al_2O_3 (60:40)	1st run 233.4	32.9	6.6	206.5	4.78
	2nd run 227.7	18.5	5.2	206.5	4.01
	3rd run 227.5	18.5	5.4	207.4	4.13
Na_2SO_4 - γ - Al_2O_3 (sintered for 20 h)	227.5	6.2	1.0	207.8	—
	224.7	8.3	1.0	202.8	0.90

effects could be observed accompanied by an enhancement in conductivity:

(i) Homogeneous doping depending on solubility.

(ii) Homogeneous and heterogeneous (mixed) doping. This effect can be accompanied by the formation of a compound.

(iii) Heterogeneous doping with γ -Al₂O₃. This effect occurs in systems of (ii)-type as well.

Besides the enhancement in electrical conductivity, mixed and heterogeneous doping leads to both a better sinterability and, therefore, mechanical strength and an improved thermal shock resistance. The temperature of phase transition shifts towards lower values from higher to lower temperatures and the kinetic rate of transition becomes very slow as observed with the Na₂SO₄(III)→Na₂SO₄(I) system.

Acknowledgements

The authors wish to thank F. Barwisch, P. Schmidt, A. Simmich, B. Löscher, H. Wulff, H.-H. Möbius, P.J. Gellings and E. Nadler.

References

- [1] M. Gauthier, A. Chamberland, J. Electrochem. Soc. 124 (1977) 1579.
- [2] C.C. Liang, J. Electrochem Soc. 120 (1979) 1289.
- [3] U. Guth, F. Barwisch, H. Wulff, P. Schmidt, H.-H. Möbius, Cryst. Res. Technol. 22 (1987) 141.
- [4] U. Guth, S. Brosda, B. Löscher, A. Simmich, P. Schmidt, H.-H. Möbius, Mater. Sci. Forum 76 (1991) 137.
- [5] K. Singh, S.S. Bhoga, Solid State Ionics 39 (1990) 205.
- [6] H.-D. Wiemhöfer, S. Brosda, H. Keller, U. Guth, W. Göpel, Proc. Int. Symposium on Environmental Sensing '92, 22–26 June 1992, Berlin.
- [7] U. Guth, P. Schmidt, R. Jahn, S. Brosda, H.-H. Möbius, Solid State Ionics 36 (1989) 127.
- [8] J.B. Wagner Jr., Composite solid electrolyte conductors, in: T. Takahashi (Eds.), High Conductivity Solid Ionic Conductors, Singapore, 1989, p. 146.
- [9] A. Lunden, Solid State Ionics 28–30 (1988) 163.
- [10] E.A. Secco, Solid State Ionics 28–30 (1988) 168.
- [11] U. Guth, F. Barwisch, K. Elsner, J. Rosenkranz, P. Schmidt, H.-H. Möbius, Ionentransportprozesse in Festkörpern, Universität Jena, 1986, p. 176.
- [12] R.M. Murray, E.A. Secco, Can. J. Chem. 56 (1978) 2616.