

Preparation and characterization of composites in KCl-ZrO₂ system

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ABSTRACT

Composite solid electrolytes with enhanced conductivity have been prepared by chemical, mechanical and thermal treatment in KCl-ZrO₂ system. The composites so prepared have been characterized by measuring the electrical conductivity in wide range of compositions (upto 60 m/o ZrO₂). The conductivity has been observed to increase with increase of molar concentration of ZrO₂ up to 30 m/o ZrO₂, beyond which it decreases.

Key words: Two phase mixture, composites, KCl-ZrO₂, electrical conductivity.

INTRODUCTION

In recent years studies on the electrical properties of composites consisting of two phase mixture, particularly ionically conducting matrix, have attracted considerable attention because of their technological importance in solid state batteries and fuel cells. Although homogeneous doping has been known to increase the electrical conductivity for long time it suffers from disadvantages of solubility limit and also a possibility of chemical reaction between parent material and dopant. These difficulties have been overcome by heterogeneous doping i.e. by preparing a two phase mixture as composite. In such case dopant may be added to any extent in order to tailor the material with desirable properties. Addition of one phase to another often produces a composite with more desirable properties. Although enhancement in electrical conductivity of two phase mixture has been known for long time its technological importance was realized first time in 1973 only after the famous discovery of Liang¹. He observed an unusual increase in conductivity of LiI by the dispersion of fine particles of Al₂O₃ though according to

conventional approach conductivity of ionic matrix should decrease by the addition of insulator. Subsequently, considerable effort²⁻¹⁰ has been made to improve the electrical conductivity of ionically conducting matrix, e.g., LiI, LiBr, LiCl, KBr, KCl, AgBr, AgCl etc by the dispersion of fine particles of various categories of dispersoids such as Al₂O₃, SiO₂, ZrO₂, ZrO₂-CaO, LiBr, NaF, etc. Although KCl-ZrO₂ system appears to be attractive combination of two phase mixture so far no attempt has been made to study composites in this system. In the present work the composites in KCl-ZrO₂ system were prepared and characterized throughout a wide range of composition (1 to 60 m/o ZrO₂).

EXPERIMENTAL

Fine powders of KCl were prepared by slow evaporation of aqueous KCl solution. For this purpose AR grade KCl (Qualigens, India) was dissolved in triple distilled water, heated at 370 K and held at this temperature for several hours till complete evaporation. The KCl powders thus obtained were heated at 470 K for 4 hours for removal of moisture.

Fine powders of ZrO_2 (with an average size of 10 μ) were obtained by the calcinations (at 1000 K for 6 hours) of zirconium oxalate, which was precipitated from the zirconium oxychloride solution by oxalic acid in ammoniacal medium.

Appropriate amount of KCl and ZrO_2 were thoroughly mixed in agate mortar and pestle. The homogeneous powder mixture was compressed into pellets of 12 mm diameter and 4-5 mm thickness at the pressure of 150 Kg/cm^2 in a die and punch. The pellets were sintered at 1000 K for 30 hours in order to achieve near theoretical density.

A two-probe sample holder assembly used in the present investigation was made of piston type alumina tubes. The design, construction and operation of the assembly was similar to those described earlier¹¹. The platinum coated sample pellet, placed between two platinum discs, was pressed by two both end open alumina tubes kept in outer tube, with the aid of nichrome springs. To each of the platinum disc a platinum wire was welded. The platinum lead wires were taken out from the slotted portion of the outer alumina tube. This sample holder assembly was placed in one end closed alumina tube by the support of alumina rod. The entire experimental assembly was kept in horizontal Kanthal wound tube furnace and heated to the desired temperature. The temperature of the furnace was controlled to an accuracy of ± 0.5 K by means of a PID based digital temperature controller. The conductivity of the sample was measured by a conductivity bridge (Model No. CLOI/01A, Toshniwal, India) at a frequency of 3 kHz in the temperature

range of 663-930 K. In order to check the reproducibility of the results, readings were taken during heating as well as cooling cycles. Sufficient time (about 1 hour) was allowed at each temperature for attaining thermal equilibrium.

RESULTS AND DISCUSSION

Fig. 1 shows the variation of electrical conductivity of composites in KCl- ZrO_2 system with composition (m/o ZrO_2) at different temperatures. At each temperature the conductivity of composites has been found to increase with increasing molar concentration of ZrO_2 up to a critical composition of 30 m/o ZrO_2 , beyond which conductivity decreases. It is interesting to note that the variation of conductivity with composition is almost symmetrical. This behaviour is similar to that observed by Uvarov et al¹² in $\text{LiSO}_4\text{-Al}_2\text{O}_3$ system. Such type of variation could not be explained by the existing space charge layer theory^{13,14} and percolation model¹⁵.

The conduction process in this system has been analysed in term of activation energy. The activation energy has been calculated from the plot of logarithm of conductivity ($\ln \sigma$) against inverse of the temperature ($1/T$). The linear variation of $\ln \sigma$ versus ($1/T$) plot obtained at each composition indicates that the system KCl- ZrO_2 obeys Arrhenius relationship. The activation energies, as obtained from the slope of plot, are listed in Table 1. This Table clearly indicates that there is a very little increase in activation energy with increasing molar concentration of ZrO_2 in this system. This shows that the conduction mechanism in the composites in KCl- ZrO_2 system is same as that in pure KCl. Obviously charge carrier in the composites are K^+ ion vacancies.

Table 1: Activation energies of composites in KCl- ZrO_2 system

m/o ZrO_2	Activation energy(in eV)
0	0.84
1	0.84
5	0.85
10	0.90
20	0.97
30	0.99
40	1.00
50	1.01
60	1.02

The conductivity data of KCl- ZrO_2 system have also been analysed in term of normalized conductivity. The normalized conductivity is an absolute measure of enhancement in conductivity of composites with respect to pure matrix component (KCl) and may be defined as the ratio of conductivity of composite to that of pure component matrix. Table 2 incorporates the values of normalized conductivity of different composites in KCl- ZrO_2 system at different temperatures. This Table shows that at each composition the normalized conductivity increases

with increase of temperature up to a critical temperature and then started to decrease on further increase of temperature. The critical temperature corresponding to maximum enhancement (as shown in Fig. 2) increases with increasing molar concentration up to 20 m/o ZrO_2 and then remains constant on further increase of ZrO_2 concentration. Further Table 2 also reflects that maximum enhancement in conductivity is obtained at the

composition corresponding to 30 m/o ZrO_2 at any temperature in the range of 663-930 K. Thus from the Table 2 it may be concluded that the composite containing 30 m/o ZrO_2 in KCl- ZrO_2 system exhibits maximum enhancement in conductivity at a specific temperature of 894 K with respect to pure KCl. The enhancement in conductivity is more than 7 times with respect to that of pure matrix i.e. KCl.

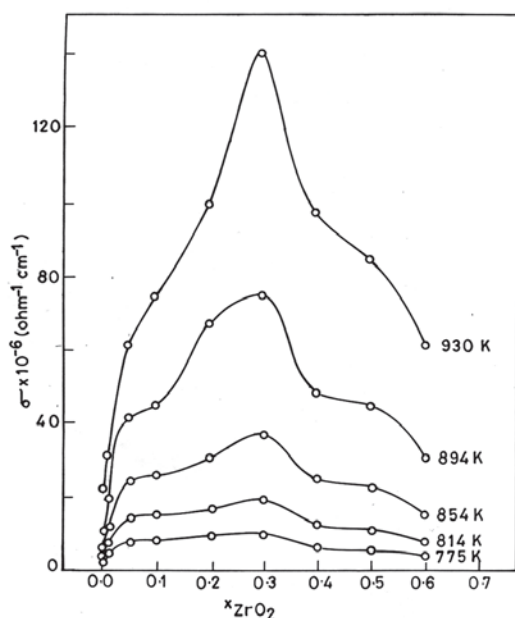


Fig. 1: Plot of electrical conductivity vs. composition in KCl- ZrO_2 system

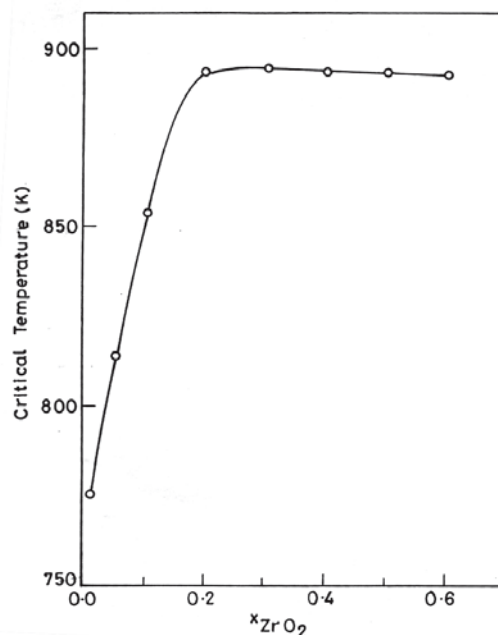


Fig. 2: Plot of critical temperature corresponding to maximum enhancement in electrical conductivity vs. composition in KCl- ZrO_2 system

Table 2: Normalised conductivity of composites in KCl- ZrO_2 system

m/o ZrO_2	Temperature (K)							
	663	702	740	775	814	854	894	930
1	1.7	1.9	2.0	2.3*	2.1	2.1	1.9	1.4
5	2.9	3.5	4.0	4.3	4.4*	4.3	4.0	2.7
10	2.8	3.5	4.0	4.3	4.4	4.5*	4.4	3.4
20	2.9	3.6	4.1	5.0	5.2	5.3	6.5*	4.5
30	2.9	4.0	4.3	5.2	5.4	6.5	7.3*	6.4
40	2.1	2.6	2.8	3.3	3.4	4.3	4.7*	4.4
50	1.8	2.0	2.3	2.7	3.0	3.9	4.6*	4.4
60	1.4	1.5	1.6	1.9	2.0	2.6	3.0*	2.7

*Value corresponding to maximum enhancement in conductivity at a particular composition

Conclusions

Composites in KCl-ZrO₂ system, as prepared by chemical, mechanical and thermal treatment, exhibit much higher electrical conductivity than the pure components. Enhancement in conductivity has been observed to increase with increase of temperature up to a maximum value and then start to decrease on further increase of temperature. Maximum enhancement in conductivity (over 7 times) has been obtained in the composite containing 30 m/o ZrO₂ at the temperature of 894 K.

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