Effect of Li Content on the DSC and Electrical Conductivity of $(Li_{1-x}K_x)_2SO_4$ Mixed Crystals

M. M. Ahmad* and M. A. Hefni[a]

Chemistry Department, Graduate School of Science, Hiroshima University, Kagamiyama,
Higashi-Hiroshima 739-8526, Japan
[a] Physics Department, Faculty of Science, Assiut University, Assiut 71516, Egypt

Reprint requests to M. M. A.; E-mail: mmahmad@sci.hiroshima-u.ac.jp

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Differential scanning calorimetry on $(Li_{1-x}K_x)_2SO_4$ mixed crystals, where $x = 0.01$, 0.1, 0.3 and 0.5, revealed that, as the potassium content increases, the first high temperature phase of the intermediate $LiKSO_4$ phase at $T = 432$ °C grows and shifts to higher temperature, and a double-phase mixture consisting of $LiKSO_4$ and Li_2SO_4 exists for $x < 0.5$. Ionic conductivity measurements on $(Li_{1-x}K_x)_2SO_4$ mixed crystals for $x \leq 0.5$ did show that the electrical conductivity increases as the Li_2SO_4 concentration increases, with an average activation energy of 0.9 eV. The enhanced electrical conductivity is primarily a result of the increase in the Li^+ ion (charge carriers) concentration and/or the formation of a diffuse space charge layer at the interface between the two phases.

Key words: $(Li_{1-x}K_x)_2SO_4$ Crystals; DSC; Ionic Conductivity; Diffuse Space Charge Layer.

1. Introduction

Mixed binary sulfates $MM'SO_4$ (M, M′ = Li, Na, K, Ag, NH_4, Zn, …) possess interesting electrical transport properties. Extensive studies have been carried out on Li_2SO_4-based solid electrolytes [1–4]. Li_2SO_4 undergoes a first-order phase transition from a low temperature monoclinic to a high temperature cubic (f.c.c.) phase at ~ 570 °C [5], whereas K_2SO_4 undergoes a $\beta \rightarrow \alpha$ transition from an orthorhombic (space group Pmcn) to a hexagonal (space group $P6_{3/mmc}$) phase at 587 °C [7].

Lithium potassium sulfate undergoes at least two structural phase transitions above room temperature at 435 and 670 °C [8]. Its symmetry is hexagonal at room temperature and above 670 °C. The structure of the intermediate phase ($435 < T < 670$ °C) was proposed to be orthorhombic [9], while other authors suggested a modulated structure, commensurate between 435 and 470 °C and incommensurate between 470 and 670 °C [10]. Recently, single-crystal X-ray diffraction of $LiKSO_4$ was studied by Pinheiro et al. [11], and the intermediate phase was discussed on the basis of ordered and disordered models, using harmonic and anharmonic atomic displacements and considering a twinned crystal composed of three orthorhombic domains.

The effect of neutron irradiation on the thermodynamics properties of $(Li_xK_{1-x})_2SO_4$ was studied by El-Khatib et al. [12]. They found that the phase transition at 432 °C disappears as the lithium content decreases, and the specific heat decreases sharply on neutron irradiation and increases once more. In addition, Hamed et al. studied the thermal properties of lithium potassium rubidium sulfate, $(Li_{0.5-x/2}K_{0.5-x/2}Rb_x)_2SO_4$, and lithium potassium caesium sulfate, $(Li_{0.5-x/2}K_{0.5-x/2}Cs_x)_2SO_4$ systems after partial replacement of K_2SO_4 and Li_2SO_4 by Rb_2SO_4 and Cs_2SO_4 [13, 14]. They observed that insertion of Rb_2SO_4 into $LiKSO_4$ crystal altered its thermal behavior less than insertion of Cs_2SO_4.

In [15, 16] we have studied the effect of γ-ray irradiation on the EPR spectra, IR spectra and electrical conductivity of polycrystalline $LiKSO_4$. We found that the electrical conductivity of $LiKSO_4$ is mainly ionic due to the migration of interstitial Li^+ ions with an activation energy of 1.1 eV. In addition it was found that decreases after γ-irradiation and the number of paramagnetic centers increases as the γ-ray dose is increased. In the present paper we report on the DSC and electrical conductivity of $(Li_{1-x}K_x)_2SO_4$.

2. Experimental

$Li_2SO_4 \cdot H_2O$ and K_2SO_4, were obtained from BDH laboratories. The $(Li_{1-x}K_x)_2SO_4$ mixed crystals for

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* On leave from: Physics Department, Faculty of Education, Assiut University, The New Valley, El-Kharga, Egypt.

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$x = 0.01$, 0.1, 0.3, and 0.5 were prepared by the precipitation technique from $Li_2SO_4 \cdot H_2O$ and K_2SO_4. $Li_2SO_4 \cdot H_2O$ and K_2SO_4 were dissolved in distilled water for each x value, and then absolute ethanol was added to the hot saturated solution of the pure components. In this mixture, crystallization occurs immediately from the solution. To insure homogeneity, the solution was vigorously stirred during the precipitation. The precipitate was then immediately filtered and washed several times with alcohol. All crystals were dried at about 120 °C for a few hours and finally ground to get a fine powder.

The thermal characterization of the mixed samples was done on a Dupon 2000 differential scanning calorimeter. The samples of about 6 mg were put in an aluminum crucible in a flowing nitrogen atmosphere (50 ml/min). The transition temperature T_t (up to 600 °C) was obtained with a heating rate of 10 °C/min.

For the electrical conductivity measurements, fine powders of the polycrystalline samples were compressed under 8 tons/cm^2 to form discs of 1–2 mm thickness and 13 mm diameter. The samples were then placed between two copper electrodes. The temperature was measured with a K-type thermocouple and the conductivity with a Keithley electrometer type 610c.

3. Results and Discussion

3.1. Differential Scanning Calorimetry

The DSC curves of the $(Li_{1-x}K_x)_2SO_4$ mixed crystals, shown in Fig. 1, reveal the presence of two phases, corresponding to $LiKSO_4$ and Li_2SO_4, for $x = 0.01$, 0.1, and 0.3. For $x = 0.5$, only one endothermic peak at 436 °C, corresponding to $LiKSO_4$, was observed. Also, as the potassium content increased, the phase transition of the intermediate $LiKSO_4$ compound grew and shifted to higher temperature. The monoclinic-cubic (f.c.c) phase transition of Li_2SO_4 with 1% K_2SO_4 was observed as an endothermic doublet peaking at 565 and 573 °C. This is in sufficient agreement with the two peaks observed at 535 and 567 °C for the transition of Li_2SO_4 with 2.5% K_2SO_4 [3]. These observations indicate that there is a slight solubility of K_2SO_4 in f.c.c Li_2SO_4. There is a discrepancy between Schroeder et al. [2, 3] and Balaya and Sunandana [5] concerning the monoclinic-cubic transition in pure Li_2SO_4: Balaya and Sunandana reported two peaks and take this as evidence for two groups of structurally distinguishable sulfate ions. However, Schroeder et al. reported only one sharp peak at 574 °C [2, 3], and this result has been confirmed by later studies of transition enthalpies. The riddle was solved when Balaya and Sunandana checked the purity of the salt used in their first study and found that there was some carbonate present [6]. A comparison with the phase diagram of $Li_2SO_4 - Li_2CO_3$ [17] shows why Balaya and Sunandana found two peaks near 575 °C.

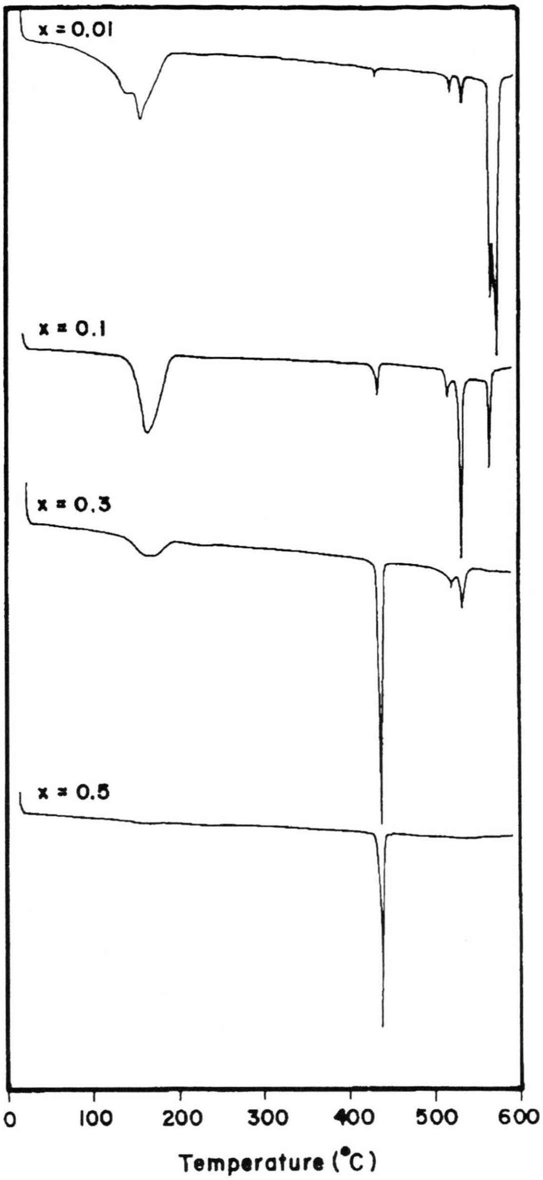

Fig. 1. DSC traces of $(Li_{1-x}K_x)_2SO_4$ for $x = 0.01$, 0.1, 0.3 and 0.5.

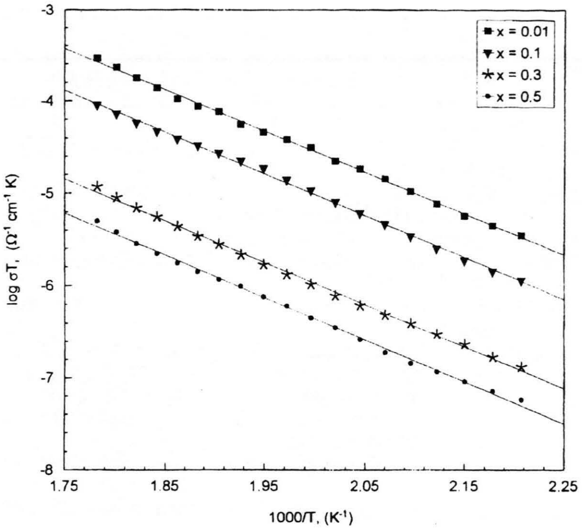

Fig. 2. Temperature dependence of the ionic conductivity of $(Li_{1-x}K_x)_2SO_4$ for $x = 0.01$, 0.1, 0.3 and 0.5.

Table 1. The Electrical Conductivity Data for $(Li_{1-x}K_x)_2SO_4$ mixed crystals.

x Values	E_a (eV)	σ_0 (Ω^{-1} cm^{-1})	σ at 240 °C (Ω^{-1} cm^{-1})
0.01	0.887	2.45×10^4	8.88×10^{-8}
0.1	0.898	1.10×10^4	3.61×10^{-8}
0.3	0.901	1.27×10^3	3.25×10^{-9}
0.5	0.908	6.20×10^2	1.48×10^{-9}

The peaks at 156, 166, and 170 °C are mainly attributed to the dehydration process for $x = 0.01$, 0.1, and 0.3, respectively (the dehydration process disappears for $x = 0.5$), and the dehydration peak for $x = 0.01$ splits into about three components, implying three sub-stages of this process.

3.2. Electrical Conductivity

Figure 2 shows $\log \sigma T$ versus $1000/T$ for $(Li_{1-x}K_x)_2SO_4$ mixed crystals. Evidently the conductivity of these samples obeys the Arrhenius relationship

$$\sigma T = \sigma_0 \exp(-E_a/kT), \tag{1}$$

where σ_0 represents the composite constant $(ne^2 \lambda^2 \nu/k)$ with n the number of ions per unit volume, e the ionic charge, λ the distance between two jump positions, ν the jump frequency and k the Boltzmann constant. E_a is the apparent activation energy for ion migration. From Fig. 2 and (1), the electrical conductivity σ at 240 °C, σ_0 and E_a are determined and listed in Table 1. Evidently the electrical conductivity increases as the Li_2SO_4 concentration increases. This behavior is similar to that obtained for the Na_2SO_4–Li_2SO_4 mixed system with Na_2SO_4 concentrations above 50%, where the electrical conductivity increases with increasing Li_2SO_4 concentration in the whole concentration range [18]. It is also interesting that the activation energy of conduction was about the same over the whole concentration range with an average value of about 0.9 eV. Thus the decrease of the ionic conductivity with the increase of the concentration of K_2SO_4 may be attributed to the decrease of the concentration (n) of mobile ions (Li^+ ions) due to the replacement by the guest ions (K^+ ions).

In order to discuss the electrical conductivity behavior of $(Li_{1-x}K_x)_2SO_4$ mixed crystals, two composition regions are to be considered: (i) the region in which the two salts form a solid solution and (ii) the two phase mixture. It is well known that the dispersion of fine insulating particles of Al_2O_3 in a solid electrolyte matrix enhances the ionic conductivity [19]. However, the studies on Li_2SO_4–LiCl [20], β-Li_2SO_4–Na_2SO_4 [21], Li_2WO_4–Li_2SO_4 [22], Li_2SO_4–Li_2CO_3 [17], Li_2SO_4–$CaSO_4$, Li_2SO_4–$MgSO_4$ [23], etc., did show that the enhanced electrical transport in multiphase mixtures is a rather general phenomenon and not merely limited to fine Al_2O_3 particles.

The models developed in the area of composite solid electrolyte systems are limited to (a) polycrystalline materials (MX/MX) [24], (b) conducting – conducting (MX/MX′) [25] and (c) conducting – nonconducting (MX/A) systems [26]. The present system has two ionically conducting constituents (for $x < 0.5$), namely: (i) Li_2SO_4 and (ii) $LiKSO_4$, having one or two different mobile species. Thus, the total conductivity in the present system is considered to be due to the contributions from (i) Li_2SO_4, (ii) $LiKSO_4$ and (iii) the interface region between these phases. The enhancement in the conductivity σ for $x < 0.5$ is primarily a result of the increase in the Li^+ ion (charge carriers) concentration and/or the formation of diffuse space-charge layers at the interface region between the two different phases present in the system.

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