

Ionic Conductivity and Solid-Phase Transitions in Li_2SO_4 - Li_2WO_4 System Relating to Ion Transport Mechanism

A. STEWART CAMPBELL,* KEVIN G. MACDONALD,*
AND E. A. SECCO†

*Chemistry Department, St. Francis Xavier University, Antigonish,
Nova Scotia, Canada B2G 1C0*

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The results of ac electrical conductivity and DSC calorimetry measurements on the Li_2SO_4 - Li_2WO_4 system show two solid-phase transitions at 572 and 595°C. The maximum conductivity and the minimum total molar enthalpy of transition occur at 90 mole% Li_2SO_4 . The total molar enthalpy of transition shows a maximum at 67-68 mole% Li_2SO_4 . There is no evidence of melting up to 650°C over the complete composition range. Assuming WO_4^{2-} to be incorporated as guest ion in the SO_4^{2-} sublattice in Li_2SO_4 -rich compositions the enhanced conductivity effect for the $\text{Li}_2\text{SO}_4/\text{WO}_4$ composition is interpreted as convincing evidence that the anion-rotation-assisted movement of cations or "paddle-wheel" mechanism does not contribute significantly to fast Li^+ ion conductivity in Li_2SO_4 -based compositions. These results are consistent with the interpretation of fast ion transport in Na_2SO_4 -based compositions via a percolation-type mechanism where lattice "free volume" plays a predominant role. © 1989 Academic Press, Inc.

Introduction

Li_2SO_4 and its mixed compositions, LiNaSO_4 compound (1) and LiAgSO_4 solid solution (2), undergo a first-order phase transition to a high-temperature cubic phase, monoclinic \rightarrow cubic. The cubic phase exhibits very high cationic conductivity and is commonly referred to as a superionic conductor or solid electrolyte (3). The predominant charge carrier in each case is the highly mobile Li^+ ion. The high-conductivity phase is described as "inor-

ganic rotator phase" and the enhanced Li^+ ion mobility is attributed to the strongly coupled rotational motion of the translationally static SO_4^{2-} ions. The strong coupling of the sulfate ion motion is assumed to arise from insufficient space for free rotation (4). This anion-rotation-assisted movement of cations has been called the "cogwheel" or "paddle-wheel" mechanism of ion transport.

Recent conductivity studies have shown that Na_2SO_4 -based compositions undergoing phase transitions are also accompanied by very high Na^+ ion conductivity (5-7). The hexagonal high-temperature form of Na_2SO_4 I is characterized by strong orientational disorder of the SO_4 tetrahedra (8) and

* American Chemical Society—Petroleum Research Fund Scholars.

† To whom correspondence should be addressed.

it was suggested that the oscillation of the tetrahedra facilitated the mobility of Na^+ ions paralleling the "paddle-wheel" mechanism.

A critical test for the effectiveness of the anion-rotational mechanism in Na_2SO_4 (9) and Li_2SO_4 (10) was devised: each of the anions WO_4^{2-} and SiO_4^{4-} was incorporated in the SO_4^{2-} sublattice. The presence of the larger radius isovalent WO_4^{2-} with 1.5 times the moment of inertia of SO_4^{2-} and the aliovalent SiO_4^{4-} accommodated either by excess Na^+ or Li^+ ions on interstitial sites or by vacancies to maintain electrical neutrality would lead to lower conductivity if the anion-rotational mechanism were operative. The guest ion in each case enhanced the Na^+ or Li^+ ion conductivity by factors up to 10. These enhanced conductivity results for Li_2SO_4 -based and Na_2SO_4 -based compositions were interpreted as convincing experimental evidence that the anion-rotation "paddle-wheel" mechanism does not contribute significantly to the high mobility of Li^+ and Na^+ ions in sulfate compositions.

Recent literature reports (4, 11) continue to emphasize the effective role of SO_4^{2-} ion rotation in the enhancement of Li^+ ion mobility in the high-temperature phase of Li_2SO_4 -based compositions. Lunden challenged the validity of the WO_4^{2-} results by raising the question of the solubility limits of the Li_2SO_4 - Li_2WO_4 system with reference to the purported two-phase eutectic at 596°C and 68 mole% Li_2SO_4 (12-14). It is claimed that the higher conductivity of the $\text{Li}_2\text{SO}_4/\text{WO}_4$ composition resides in the existence of a eutectic and its liquid phase presence. This question and claim demands experimental clarification. Recent ac electrical conductivity and calorimetry measurements over the complete composition range of the Li_2SO_4 - Li_2WO_4 presented herein focus directly on the specific claim that the "liquid" phase presence contributes to the higher conductivity.

Experimental

The Li_2SO_4 - Li_2WO_4 compositions were prepared from Alfa Products $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ ultrapure and Li_2WO_4 98% by fusing the requisite mixture of the two compounds, well ground manually, in Pt crucible.

The ac electrical conductivity measurements were done on compressed polycrystalline samples in a stainless-steel conductivity cell following the procedure previously described (15). The conductivity was measured as a function of temperature, heating rate 60°hr^{-1} , by two methods: (i) manual recording by the null method using a GR 1608-A impedance bridge and (ii) continuous automatic recording using a GenRad 1688 LC Digibridge interfaced to an Apple IIe microcomputer and an Epson PX-85 printer. The measured conductivity and transition temperature data are in excellent agreement for both methods.

The calorimetry measurements were carried out using a differential scanning DSC cell with a DuPont 1090B thermal analyzer equipped with Disk Memory and Data Analyzer. The transition temperature T_t and enthalpy ΔH_t were obtained on samples up to 650°C in a flowing N_2 (ultrapure) atmosphere using ignited Al_2O_3 as reference material.

Results and Discussion

The ionic conductivity σ in a solid phase is a composite quantity $\sigma = nqu$ where n is the number of charge carriers, q , per unit volume, and u is the mobility of these carriers. The dependence of the ionic conductivity on temperature usually follows the Arrhenius-type expression.

$$\sigma T = \sigma_0 \exp(-Q_c/RT) \\ = nq^2\lambda^2\nu\gamma/k \exp(-Q_c/RT). \quad (1)$$

In this equation ν is the jump frequency, λ the intersite distance, γ the intersite geometric constant, and Q_c the apparent acti-

vation energy for mobility, and k and R are fundamental constants.

On the basis of Eq. (1) typical heat and cool mode plots of $\log \sigma T$ versus $T(\text{K})^{-1}$ at 1 kHz are given in Fig. 1 for 80:20 and 10:90 mole ratios $\text{Li}_2\text{SO}_4 : \text{Li}_2\text{WO}_4$. Parallel plots for pure Li_2SO_4 and 90:10 mole ratio $\text{Li}_2\text{SO}_4 : \text{Li}_2\text{WO}_4$ were presented in an earlier report (10). The jump in conductivity occurs at $\sim 570^\circ\text{C}$. The $\log \sigma T$ values at 578°C versus mole fraction Li_2WO_4 obtained from $\log \sigma T$ versus T^{-1} plots presented in Fig. 2 show a maximum value at 90:10 mole% $\text{Li}_2\text{SO}_4 : \text{Li}_2\text{WO}_4$. This conductivity versus composition behavior parallels the maximum value at 80:20 and 90:10 mole% in the $\text{Na}_2\text{SO}_4 : \text{Na}_2\text{MoO}_4$ sys-

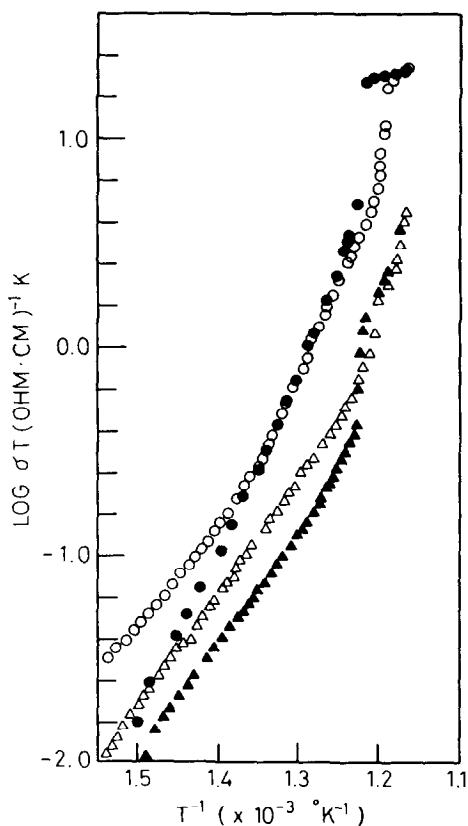


FIG. 1. Plots of $\log \sigma T$ versus $T(\text{K})^{-1}$ of $\text{Li}_2\text{SO}_4\text{-Li}_2\text{WO}_4$ in mole ratios 80:20 (○, ●) and 10:90 (△, ▲) heat and cool modes, respectively.

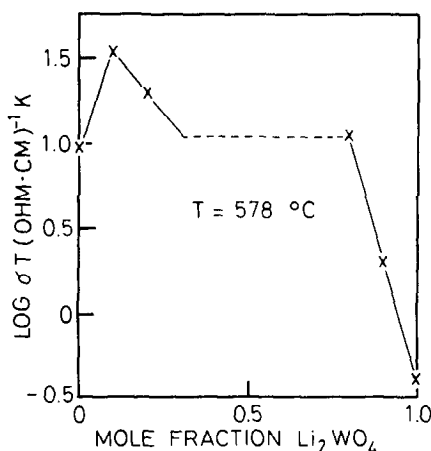


FIG. 2. Plot of $\log \sigma T$ versus mole fraction Li_2WO_4 at 578°C .

tem (7). These compositions suggest the optimum presence of the larger radius guest anion in the host sulfate effecting lattice expansion and more “free” volume to allow greater facility for Li^+ or Na^+ mobility leading to higher conductivity. No evidence of disk deformation or dimensional changes was observed in the cooled disk after the conductivity experiments. It is significant that the σT value of pure Li_2SO_4 equals the value of the Li_2WO_4 -rich composition, i.e., 20:80 mole% $\text{Li}_2\text{SO}_4 : \text{Li}_2\text{WO}_4$.

Typical DSC heating traces are given in Fig. 3 for 80:20 and 10:90 mole ratios $\text{Li}_2\text{SO}_4 : \text{Li}_2\text{WO}_4$. Two endotherms with peak temperatures 572 and 595°C occur in the Li_2SO_4 -rich region; the peak temperatures shift to 565 and 587°C in the Li_2WO_4 -rich region. The onset temperatures of the phase transition as determined by DSC and conductivity measurements are within 5 K. The molar ΔH_t values for the 572 and 595°C endotherms along with their sum values are plotted versus mole fraction Li_2WO_4 in Fig. 4. The ΔH_t for the 572°C transition plot *a* decreases monotonically from pure Li_2SO_4 to pure Li_2WO_4 . On the other hand, the ΔH_t for the 595°C transition plot *b* increases from zero at 100% Li_2SO_4 to a maximum at

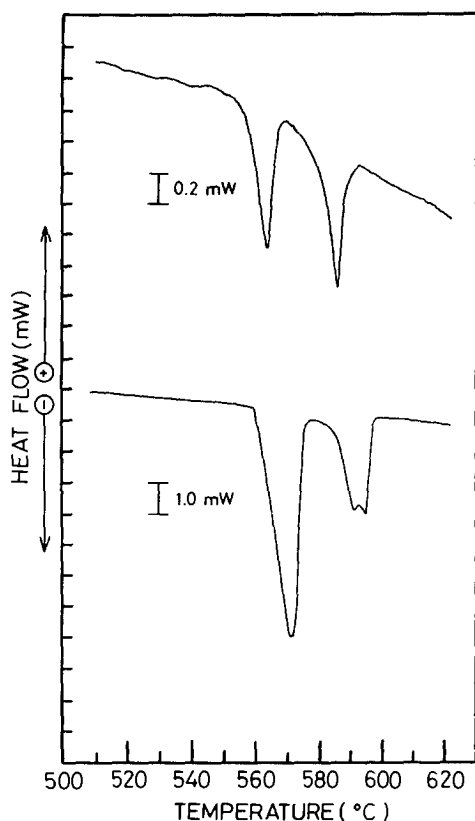


Fig. 3. Differential scanning calorimetry traces of $\text{Li}_2\text{SO}_4\text{-Li}_2\text{WO}_4$ in mole ratios 80:20 (bottom, 1.0 mW) and 10:90 (top, 0.2 mW).

67–68 mole% Li_2SO_4 and then decreases monotonically to zero at 100% Li_2WO_4 . It is significant that the sum of the two ΔH_t values plot *c* shows a minimum at 90 mole% and a maximum at 67–68 mole% Li_2SO_4 . There was no discernible evidence of melting up to 650°C over the complete composition range. These observations of the transition temperature at 595°C with a maximum endothermic ΔH_t at 67–68 mole% Li_2SO_4 are concordant with the literature reports (12–14). In view of attempts to associate high ion conductivity with high ΔH_t relative to the ΔH_t of melting in Li_2SO_4 -based compositions (4, 11) it should be noted that the maximum conductivity

occurs at 90 mole% Li_2SO_4 where its ΔH_t value is lower than the pure Li_2SO_4 ΔH_t value. Furthermore the maximum in the sum ΔH_t occurs at 67–68 mole% Li_2SO_4 and decreases with Li_2WO_4 content while the conductivity remains effectively constant from 67–68 to 20 mole% Li_2SO_4 . These conductivity and DSC results do not support the suspected interpretation based on a eutectic or “liquid” presence in our $\text{Li}_2\text{SO}_4\text{-Li}_2\text{WO}_4$ conductivity measurements as submitted by Lunden.

The Li^+ ion conductivity in the high-temperature conductivity phase of Li_2SO_4 -based compositions is in line with the Na^+ ion conductivity of Na_2SO_4 -based compositions at 575°C, viz., NaRbSO_4 and $\text{Na}_2(\text{SO}_4)_{0.8}(\text{MoO}_4)_{0.2}$ (7). Furthermore, the fact that Q_c values for Li_2WO_4 (16), Li_2SO_4 -based, and Na_2SO_4 -based compositions are effectively the same, i.e., 47 ± 5 kJ/mole or 0.45 ± 0.05 eV, in their high-temperature phase suggests the mechanism for enhanced cation conductivity in these different compositions and different crystal structures to be essentially identical.

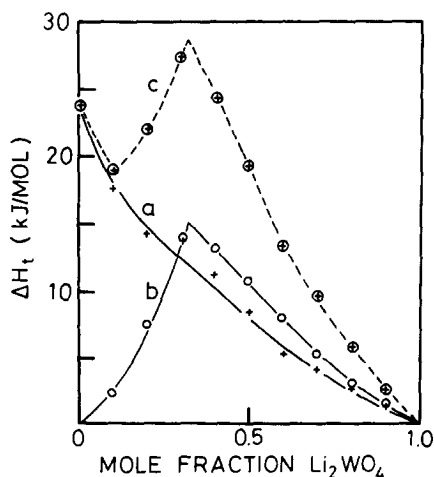


Fig. 4. Plots of ΔH_t values versus mole fraction Li_2WO_4 of DSC endotherms: (a) +, 572°C; (b) O, 595°C; (c) ⊕, 572°C + 595°C.

Various factors can play major roles in facilitating intersite mobility of cations in the enhancement of ionic conductivity, viz., lattice structure and disorder, number of mobile ions, "free" volume and a high ratio of available sites per mobile ion, lower vibration amplitudes of nonparticipating guest ions, ion-ion interactions, etc. To a first approximation, however, the results in this paper add further support to the existing literature (10, 17) reports that fast ion transport in Li_2SO_4 -based compositions occurs by a percolation-type mechanism where lattice "free volume" plays a predominant role. All the experimental results cited in earlier communications (10, 17) along with these results show convincingly that the anion-rotation-assisted movement of cations or "paddle-wheel" mechanism does not contribute significantly to the fast Li^+ ion conductivity in Li_2SO_4 -based compositions.

Acknowledgments

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