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Estimation of charge-carrier concentration and ac conductivity scaling properties near the *V-I* phase transition of polycrystalline Na_2SO_4

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The conductivity spectra of polycrystalline Na_2SO_4 have been investigated in the frequency range 42 Hz–1 MHz at different temperatures below and above the *V-I* phase transition temperature. The conductivity data have been analyzed using Almond-West formalism. The dc conductivity, the hopping frequency of the charge carriers, and their respective activation energies have been obtained from the analysis of the ac conductivity data, and the concentration of charge carriers was calculated at different temperatures. The power-law exponent n of the conductivity spectra has average values of 0.43 and 0.61 in phases V and I, respectively, which indicates different conduction properties in the two phases. Moreover, scaling of the conductivity spectra at the low- and high-temperature phases was performed in accord with Ghosh's scaling approach. It is found that the scaling properties depend on the structure of the investigated material.

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I. INTRODUCTION

Dynamic processes in ion conducting materials are studied by a variety of spectroscopic techniques. Electrical relaxation measurements are commonly used, mostly in the frequency domain, and the experimental data obtained is often presented and analyzed in terms of the complex conductivity.[1] However, other authors[2] contend that the electric modulus formalism is the best option. In the conductivity representation, the real part of the conductivity of ionic conductors exhibits a power law behavior that could be described by the Almond-West expression[3]

$$\sigma'(\omega) = \sigma_{\mathrm{dc}}[1 + (\omega/\omega_H)^n], \tag{1}$$

where σ_{dc} is the dc conductivity, ω is the angular frequency, n is the power-law exponent describing the electrical relaxation behavior of the material, mostly with $0.5 \leqslant n \leqslant 0.9$,[4] and ω_H is the hopping frequency (in Hz) of the charge carriers, which represents the crossover frequency from dc to the dispersive conductivity region at $\omega > \omega_H$. The frequency-independent dc conductivity σ_{dc} represents the random process in which the ions diffuse throughout the network by performing repeated hops between charge-compensating sites. Usually, the hopping frequency ω_H and the dc conductivity σ_{dc} are both thermally activated with almost the same activation energy, indicating that they are originated from the ionic migration.

The power-law dispersion indicates a nonrandom process wherein the ion motion is correlated. Since the exponent n usually ranges between 0.5 and 0.9, this correlation motion is subdiffusive and indicates a preference on the part of ions that has hopped away to return to where it started. Several models have been proposed in order to determine the mechanism responsible for the electrical relaxation behavior in crystalline and glassy materials.[5–11] Ngai has suggested that this correlated motion arises from some form of interionic interactions (ion coupling), leading to systematic change of the observed power-law exponent with ion concentration.[8,9] In contrast, Sidebottom[12] showed that the exponent n is independent of both temperature and ion concentration, and instead it is found to be influenced by the dimensionality of the free ions' conduction space. In his recent survey of the power-law exponent obtained from ac conductivity of ion conductors, the value of $n=0.67$ was commonly observed for isotropic oxide glasses, while values of $n=0.55\pm0.05$ and $n=0.3\pm0.1$ were observed for two-dimensional (Na β-alumina) and one-dimensional (hollandite) crystalline conductors, respectively, i.e., the exponent n decreases with decreasing dimensionality.

The dc conductivity σ_{dc} in Eq. (1) due to the diffusion of hopping ions throughout the lattice can be given by the Nernst-Einstein relation

$$\sigma_{\mathrm{dc}} = en_c\mu = \frac{n_c e^2 \gamma \lambda^2}{kT}\omega_H, \tag{2}$$

where n_c is the mobile charge carriers concentration, μ is their mobility, e is the electronic charge, γ is a geometrical factor for ion hopping ($\gamma=1/6$ for isotropic materials), λ is the hopping distance, and k is Boltzmann's constant. Using Eq. (2), Eq. (1) can be written in the form

$$\sigma'(\omega) = (n_c e^2 \gamma \lambda^2/kT)\omega_H[1 + (\omega/\omega_H)^n]. \tag{3}$$

Accordingly, by extracting the dc conductivity and the hopping frequency values from the ac conductivity data, it is possible, using Eq. (2), to estimate the values of the charge-carrier concentration and their variation with temperature.

For many ion-conducting materials, it has been found that the ac conductivity at different temperatures can be scaled into a single curve. The existence of such a master curve is referred to as the "time-temperature superposition principle" (TTSP), and $\sigma'(\omega)$ then follows a scaling law of the form

$$\frac{\sigma'(\omega)}{\sigma_{\mathrm{dc}}} = F\left(\frac{\omega}{\omega_p}\right), \tag{4}$$

where ω_p is a characteristic frequency. In the past few years, renewed interest (where different scaling models have been proposed) has developed regarding the scaling of the conductivity spectra of ion-conducting materials.[13–16] Among these models, Ghosh's scaling model that is given by the relation[16]

$$\frac{\sigma'(\omega)}{\sigma_{\mathrm{dc}}} = F\left(\frac{\omega}{\omega_H}\right), \tag{5}$$

where the hopping frequency ω_H is used as the scaling parameter for the frequency axis, is expected to be more appropriate for scaling the conductivity spectra of ionic conductors, since it takes into account the dependence of the conductivity spectra on structure and the possible changes of the hopping distance experienced by mobile ions.[16] Therefore, a test of the scaling properties for a crystalline material with a structural phase transition, where both the charge-carrier concentration and the hopping distance may change, is desired. However, the test sample should have a moderate conductivity value in the high-temperature phase, so that the dispersion region could be covered in the frequency window of the LCR meter, normally up to few MHz. Hence, polycrystalline Na_2SO_4 sample, which has a first-order phase transition at 513 K and an increase in the conductivity value by a factor of 6 after the transition, was chosen for this study.

II. EXPERIMENT

Phase transition temperature of Na_2SO_4 is determined by DTA measurements over the 400–560 K temperature range with a heating rate of 4 K/min. The *V-I* transition is characterized by an endothermic peak with onset temperature at 513 K. Complex impedance measurements were performed using a compressed pellet of ~13 mm diameter and 1–2 mm thickness. Carbon paint was evenly applied on both sides of the pellet for better electrical contact, the sample was then held between two spring-loaded electrodes. The impedance $|Z^*|$ and phase angle θ were measured with a computer interfaced HIOKI 3532 LCR meter (42 Hz–1 MHz) in the temperature range from 450 to 575 K with a heating rate of 0.5 K/min. The temperature was controlled with a precision of 1 K.

III. RESULTS AND DISCUSSION

Crystals of anhydrous Na_2SO_4 are usually in phase *V* at ambient temperature, which has an orthorhombic structure with space group *Fddd*.[17] On heating, Na_2SO_4 transforms to phase *I* above 513 K. The high temperature phase *I* has a hexagonal structure with space group $P6_3/mmc$.[18] In the literature, conflicting results exist regarding the defect structure of Na_2SO_4.[19,20] However, cationic Frenkel defects are most likely to prevail in Na_2SO_4,[21,22] with Na^+ ion vacancies being the more mobile species.[20,23] Although the electrical properties of pure and doped Na_2SO_4 have been studied extensively in the past, almost all of these measurements were focused on the temperature dependence of the dc conductivity in order to explore the conduction mechanism and/or to enhance the electrical conductivity of the investigated material.[19] In some cases, ac conductivity data were obtained either from monofrequency measurements or from impedance spectra recorded in a very limited frequency range.[20–25] Therefore, there is not much information on the dynamics of charge carrier transport in Na_2SO_4.

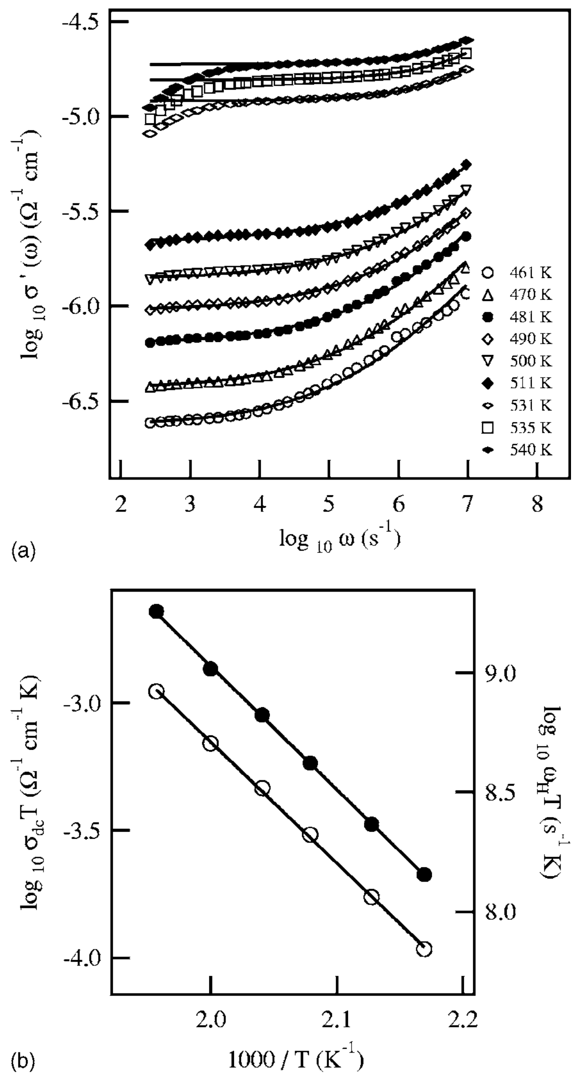

FIG. 1. (a) Conductivity spectra for Na_2SO_4 at several temperatures. The solid curves are the best fits of Eq. (1). (b) Temperature dependence of the dc conductivity (open circles) and the hopping frequency (solid circles) for Na_2SO_4. The solid lines are the least-squares straight-line fits.

The frequency dependence of the real part of the complex conductivity of Na_2SO_4 is shown in Fig. 1(a) at several temperatures below and above the phase transition temperature. The conductivity spectra in Fig. 1(a) exhibit common features usually found in ionic conductors. At low frequencies, random diffusion of the ionic charge carriers via activated hopping gives rise to the frequency-independent dc conductivity. At higher frequencies, $\sigma'(\omega)$ shows dispersion and increases in a power-law fashion described by Eq. (1). The effect of electrode polarization is observed at high temperatures. The conductivity spectra in Fig. 1(a) have been analyzed by Almond-West formalism, Eq. (1), in order to determine the values of the power-law exponent n, the dc conductivity, σ_{dc}, and the hopping frequency, ω_H, of the mobile ions. Such fits at different temperatures are shown in Fig. 1(a) as solid lines and the fitting parameters are summa-

TABLE I. The dc conductivity σ_{dc}, the hopping frequency ω_H, the exponent n and the concentration of charge carriers n_c obtained from the analysis of the conductivity spectra as described in the text.

T (K)	$\log_{10}\sigma_{\mathrm{dc}}$ (S cm^{-1}) (±0.01)	$\log_{10}\omega_H$ (Hz) (±0.02)	n (±0.01)	$\log_{10} n_c$ (cm^{-3}) (±0.02)
461	−6.63	5.49	0.43	20.70
470	−6.43	5.69	0.44	20.71
481	−6.20	5.94	0.44	20.70
490	−6.02	6.13	0.43	20.69
500	−5.86	6.32	0.42	20.69
511	−5.66	6.55	0.42	20.66
531	−4.92	7.53	0.59	20.68
535	−4.81	7.65	0.61	20.68
540	−4.73	7.72	0.63	20.70

rized in Table I. The reciprocal temperature dependence of the dc conductivity σ_{dc} and the hopping frequency ω_H is shown in Fig. 1(b), which shows that both σ_{dc} and ω_H obey Arrhenius relations. The value of the activation energy, $E_H = 1.01$ eV, of the hopping frequency obtained from the least-squares straight-line fit of the data in Fig. 1(b) is close to the activation energy of the dc conductivity, $E_\sigma = 0.94$ eV. This implies that the concentration of the mobile charge carriers is independent of temperature and the conductivity is determined primarily by the mobility of the charge carriers.[26]

Moreover, the exponent n is found to increase from an average value of 0.43 in phase V to a value of about 0.61 in the high-temperature phase I. The low value of 0.43 of the exponent n is typical for low-dimensional conductors, whereas $n \sim 0.61$ represents an isotropic conduction process.[12] These values of n could be understood from the Choi and Lockwood study of the electrical conductivity of single crystal Na_2SO_4.[27] They found that the conductivity for the [101] direction of phase V is three orders of magnitude lower than the conductivity for [001] and [100] directions. This large conductivity anisotropy can be understood from the structure of phase V, where open tunnels in the [101] and $[10\bar{1}]$ directions exist. They also observed that the conductivity in the [001] direction of phase V is about two times larger than in the [100] direction. This is because the open tunnel in the [101] direction makes an angle of 30.8° with the [001] axis in the low-temperature phase. Therefore, it is possible to consider Na_2SO_4 sample in phase V as a low-dimensional conductor. On the other hand, the conductivity in the high-temperature phase I is isotropic, i.e., shows three-dimensional conduction properties.

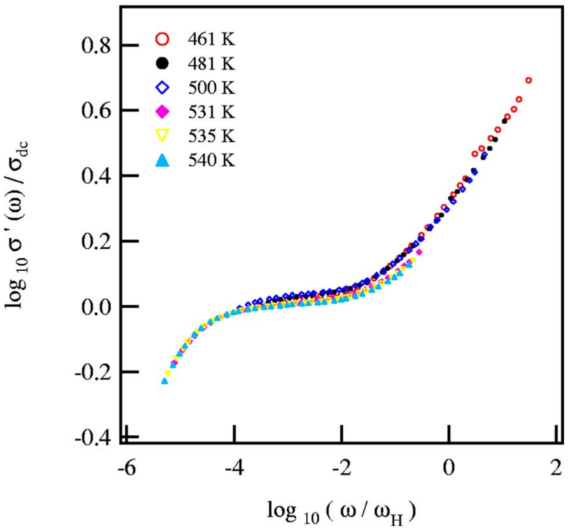

FIG. 2. (Color online) Scaling curves of the conductivity spectra for Na_2SO_4 at different temperatures scaled according to Eq. (5).

Almond-West formalism has been widely used to estimate charge-carrier concentration[26,28–30] and has been verified experimentally recently.[30] With the values of the dc conductivity, σ_{dc}, and the hopping frequency ω_H are determined, it is now possible, using Eq. (2), to calculate the concentration of charge carriers n_c that contribute to the conduction process. In Eq. (2), the values of the hopping distance $\lambda = 3.61 \times 10^{-8}$ cm,[27] and the geometrical factor γ between 1/2 and 1/4 in the low-temperature phase V and $\lambda = 3.55 \times 10^{-8}$ cm,[31] and $\gamma = 1/6$ in the high-temperature phase I were used. The calculated values of n_c are shown in Table I. It is clear that the values of n_c are almost constant of the order of $\sim 5 \times 10^{20}$ cm^{-3} and are independent of temperature in both the low- and high-temperature phases. This result indicates that the conduction mechanism in the low- and high-temperature phases of Na_2SO_4 is intrinsic due to the hopping of Na^+ ion vacancies, and the mobility rather than the concentration of mobile ions controls the ion dynamic process in Na_2SO_4.

Scaling of the conductivity spectra is performed according to Ghosh's scaling law [cf. Eq. (5)]. The scaling results of the conductivity spectra for Na_2SO_4 at different temperatures are shown in Fig. 2. In this figure, two sets of scaling curves representing the conductivity spectra in the low- and high-temperature phases, separated by a horizontal shift, are

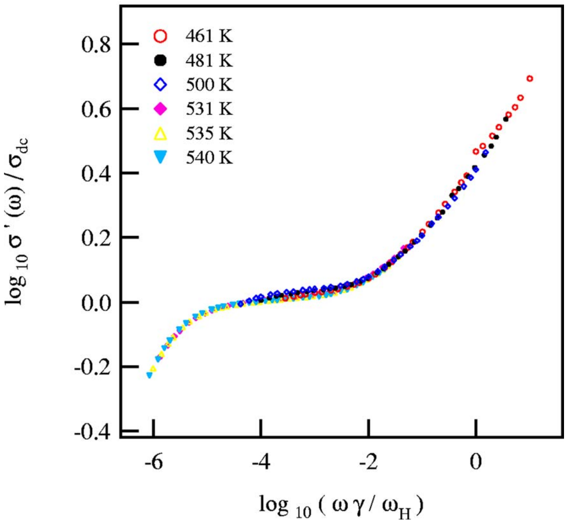

FIG. 3. (Color online) Scaled conductivity spectra for Na_2SO_4 at different temperatures where the frequency axis is scaled by ω_H/γ.

observed. One can understand these results on the basis of Eq. (2). In this equation, the parameters that change after the phase transition are the hopping distance λ and the geometrical factor γ. However, the change in λ is negligible as seen above; therefore it will not affect the scaling behavior significantly. On the other hand, the change in γ (from about $1/3$ to $1/6$ for phases V and I, respectively) is expected to be the reason for the observed scaling behavior. If this is the case, it is expected that scaling the conductivity spectra at different temperatures using ω_H/γ as the scaling parameter for the frequency axis will lead to a single master curve. The result of this hypothesis is shown in Fig. 3, where a single master curve of the conductivity spectra at different temperatures is obtained.

IV. CONCLUSIONS

Ion dynamics and relaxation in polycrystalline Na_2SO_4 have been studied over a wide frequency range in the low- and high-temperature phases. The hopping frequency of the charge carriers, the dc conductivity, and their respective activation energies have been obtained from the analysis of the conductivity spectra using Almond-West formalism. The estimated activation energies for the dc conductivity and the hopping frequency are almost equals, which indicates that the conductivity arises from the hopping motion of the Na^+ ion vacancies. The power-law exponent n of the conductivity spectra is found to increase from a value of 0.43 in the low-temperature phase V to $n=0.61$ in the high-temperature phase I. These results suggest a transition from low-dimensional conduction properties in phase V to isotropic (three-dimensional) conduction process in phase I. Moreover, the estimated values of the charge-carrier concentration are constant and independent of temperature in both phases. Scaling of the conductivity spectra with Ghosh's model lead to two separate master curves, representing the two phases of the sample, due to change in the conduction dimensionality over the phase transition.

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