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High-Temperature Phase Transition Studies in a Novel Fast Ion Conductor, $Na_2Cd(SO_4)_2$, Probed by Raman Spectroscopy

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Temperature-dependent Raman spectroscopic studies were carried out on $Na_2Cd(SO_4)_2$ from room temperature to 600 °C. We observe two transitions at around 280 and 565 °C. These transitions are driven by the change in the SO_4 ion. On the basis of these studies, one can explain the changes in the conductivity data observed around 280 and 565 °C. At 280 °C, spontaneous tilting of the SO_4 ion leads to restriction of Na^+ mobility. Above 565 °C, the SO_4 ion starts to rotate freely, leading to increased mobility of Na^+ ion in the channel.

Introduction

Solid electrolytes (fast ion conductors) have been a subject of considerable attention due to their potential use in various electrochemical devices such as batteries, fuel cells, sensors, and reactors.[1,2] This class of materials exhibits high ionic conductivity (approximately $10^{-3}-10^{-1}$ S/cm) at relatively modest temperatures (500−700 °C) and has been one of the major themes in material design. Recently, bimetallic sulfates, which are intercalation compounds of alkali ions generated by frameworks of tetrahedral and octahedral moities, have been shown to achieve high ionic conductivity. One of the examples is $Na_2Cd(SO_4)_2$ (NCSO), which has been investigated as a possible ionic conducting material.[3] NCSO is a bimetallic sulfate where Cd atom is at 2-fold rotational symmetry having a Wyckoff position 4e in the space group *C*2/*c*.[3] The structure (see Figure 1) is built of alternating sulfate tetrahedra linked to Cd octahedra forming a chain along the ξ direction, which in turn is cross-linked with a chain running 90° to this plane, effectively generating a two-dimensional framework. Every Cd atom has two short, two medium, and two long bonds with symmetry-related oxygen atoms. Likewise, every S atom has one short, two normal, and one long tetrahedral bond, while the Na atom located in the two-dimensional framework generates a weak eight-coordinated link that extends along the *z*-axis, forming a channel-like structural motif. Indeed, the Na atoms are located in the space generated by the combination of covalently bound octahedra and tetrahedra. This suggests the possibility of facile Na^+ ion migration through the framework, and the rather high ionic conductivity of 10^{-2} S/cm at 600 °C appears as a consequence. Furthermore, the dielectric and conductivity data showed two possible transitions around 280 and 555 °C.[3]

To understand the relationship between conductivity and NCSO structure, a detailed investigation on ionic conductivity and phase transformations is very much essential. We have carried out a Raman spectroscopic study of NCSO as a function of temperature to probe these changes across the phase transition. It is well-known that Raman scattering is sensitive to variations of local structure/environment and thus can give information on aspects such as short-range versus long-range structural order. The sensitivity of this technique to local environments makes it an ideal probe to answer questions related to short or medium range mobility. In this work, temperature-dependent Raman spectroscopy was used to probe the dynamics of the SO_4 tetrahedra around the phase transformation by studying the internal modes of SO_4 tetrahedra and their line shapes, which are shown to be sensitive to molecular reorientation.[4−7]

Experimental Details

Single crystals of NCSO were grown by slow evaporation from aqueous solution containing equimolar quantities of the $3CdSO_4 \cdot 8H_2O$ and Na_2SO_4, based on the method described in ref 3. The temperature evolution of the Raman spectra of NCSO was recorded in the 180° backscattering geometry, using a 532 nm excitation from a diode pumped frequency doubled Nd-YAG solid state laser (model GDLM-5015 L, Photop Suwtech Inc., China) and a custom-built Raman spectrometer equipped with a SPEX TRIAX 550 monochromator and a liquid nitrogen cooled CCD (Spectrum One with CCD 3000 controller, ISA Jobin Yovn - SPEX). The details of the spectrometer are given elsewhere.[8] Laser power at the sample was ~15 mW, and a typical spectral acquisition time was 1−2 min. The spectral resolution was 2 cm^{-1}. The temperature was controlled with an accuracy of ±0.1 K by using a temperature-controller (Linkam TMS 94) equipped with a heating stage unit (Linkam THMS 600). The spectral profile was fitted using Lorentzian functions with the appropriate background.

Results and Discussion

The normal-mode analysis of a free tetrahedral SO_4 ion in a T_d symmetry predicts four modes, $\nu_1(A_1)$, ν_2 (E), ν_3 (F_2), and ν_4 (F_2).[9] All of these modes are Raman active, whereas ν_3 and ν_4 modes are IR active.[9] In the crystalline environment, the tetrahedral symmetry of SO_4 may be lowered, and as a result band positions will shift and also split. The nondegenerate symmetric stretching mode (ν_1) appears as a very intense band in the Raman spectrum.[6] The triply degenerate asymmetric stretching mode (ν_3) of the SO_4 ion appears with large splitting

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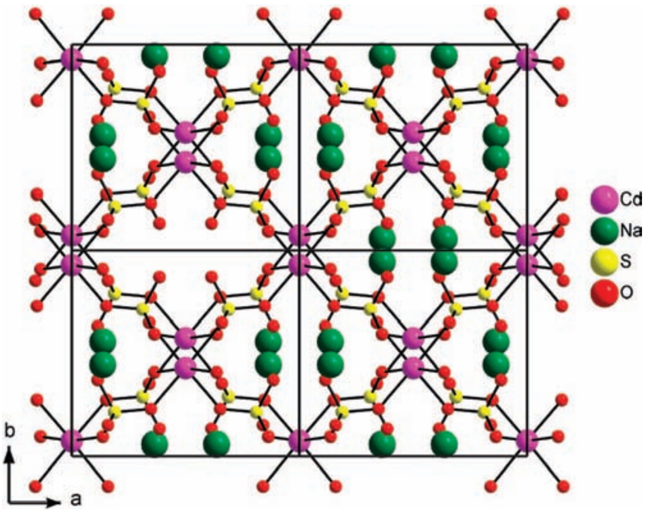

Figure 1. Packing diagram of $Na_2Cd(SO_4)_2$, view down the *z*-axis.

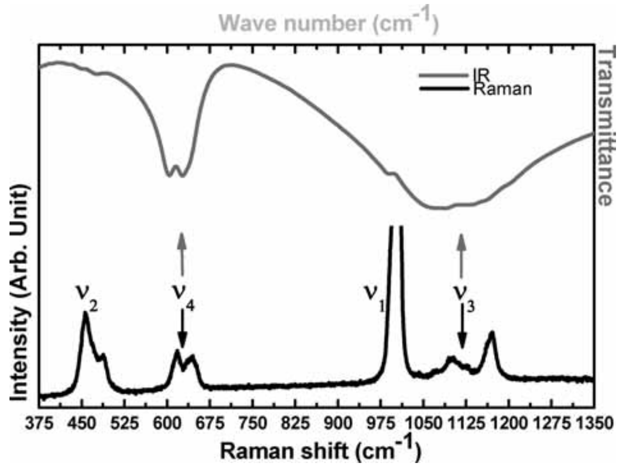

Figure 2. Room-temperature infrared and Raman spectra of $Na_2Cd(SO_4)_2$ showing the SO_4 internal vibrational modes.

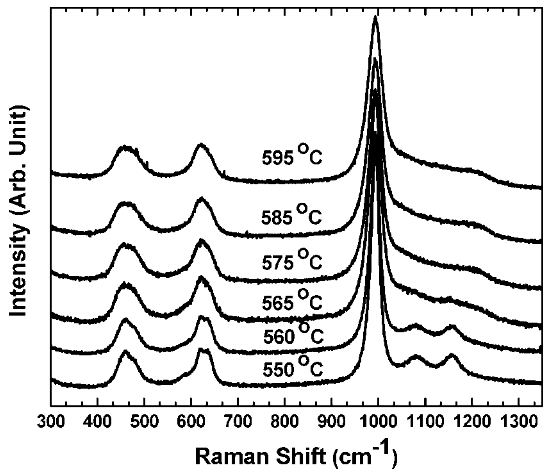

Figure 3. Temperature evolution of the Raman spectra of $Na_2Cd(SO_4)_2$ in the temperature interval 550−595 °C.

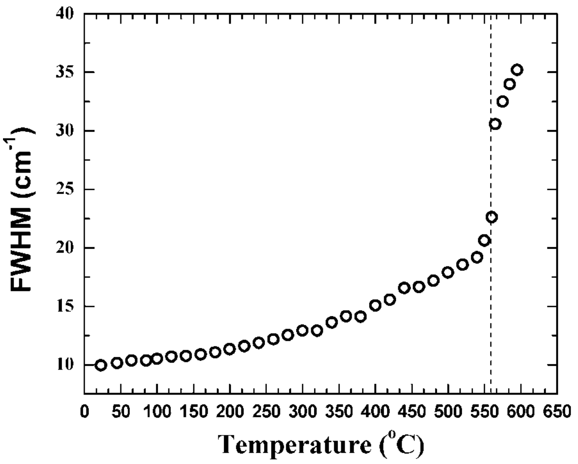

Figure 4. Temperature dependence of the fwhm of the ν_1 mode of the SO_4 ion in the temperature interval 24−595 °C.

in both FTIR and Raman spectra.[6] Figure 2 shows a comparison of room-temperature Raman and FTIR spectra in the SO_4 internal vibration region. On the basis of the assignments discussed earlier, we have labeled the internal vibration modes ν_1, ν_2, ν_3, and ν_4 of the tetrahedral SO_4 group in Figure 2. Wu and Frech, who recorded the vibrational spectra of several sulfate crystals, suggest that in the case of SO_4 groups, ν_1, ν_2, ν_3, and ν_4 range between 985−1017, 455−473, 1097−1217, and 611−670 cm^{-1}, respectively.[10] Hence, the strong Raman band at ~993 cm^{-1} is indeed the ν_1 mode. Similarly, the Raman bands associated with ν_2 region appear at 458 cm^{-1} (ν_{2a}) and 487 cm^{-1} (ν_{2b}). The Raman and infrared bands around 1092 and 1161 cm^{-1} are assigned to the ν_{3a} and ν_{3b}, respectively. Also, the bands occurring at 623 cm^{-1} (ν_{4a}) and 651 cm^{-1} (ν_{4b}) are assigned to the ν_4 vibration. As expected, the infrared spectra show stronger absorption in the ν_3 and ν_4 regions.

The temperature evolution of the Raman spectra of NCSO measured in the SO_4 internal vibration region in the temperature interval from 24 to 550 °C does not show any large-scale changes in the spectral profile. Hence, in Figure 3 we have only shown the temperature dependence of the Raman spectra in the temperature interval 550−595 °C. Significant changes in the spectra are observed beyond ~565 °C. The splitting of the ν_3 band disappears, and a broadband centered at around 1180 cm^{-1} appears. At the same time, the ν_1 mode also showed an appreciable broadening during this transformation. The temperature dependence of the full width at half-maximum (fwhm) of the ν_1 stretching mode measured in the temperature interval from 24 to 600 °C is shown in Figure 4. The width of this band is around 10 cm^{-1} at room temperature, but it gradually broadens to 23 cm^{-1} at 560 °C. However, the line width of this band increased abruptly from 23 to 31 cm^{-1} in the temperature interval 560−565 °C. The reason for this abrupt change is discussed below. Figure 5 shows the temperature dependence of the ν_2 and ν_4 mode frequencies. There is a change in slope ($d\omega/dT$) around 260 °C for both ν_2 and ν_{4b} modes. The changes in mode frequency associated with the ν_2 and ν_4 mode could be associated with tilting of the SO_4 tetrahedra, which could prevent the smooth migration of the Na^+ ion. This will result in a small decrease in conductivity as observed earlier as shown in the conductivity data where there is a small kink at 280 °C.[3] Small discontinuities were observed at 565 °C for both ν_2 and ν_4 modes. This we attribute due to the reorientation of the SO_4 tetrahedra.

The abrupt jump in the line width of ν_1 mode, major changes in the spectral profile in the ν_3 mode, and discontinuities in the frequencies for both ν_2 and ν_4 modes observed in the temperature interval between 560 and 565 °C could arise due to an increase in the rotational degree of freedom of the SO_4 ion at high temperatures. The reduction of the mode frequencies of most of the modes (ν_1, ν_2, and ν_4 modes) signifies that mobility of Na^+ in the channel makes the oxygens in the SO_4 units move away from the sulfur,

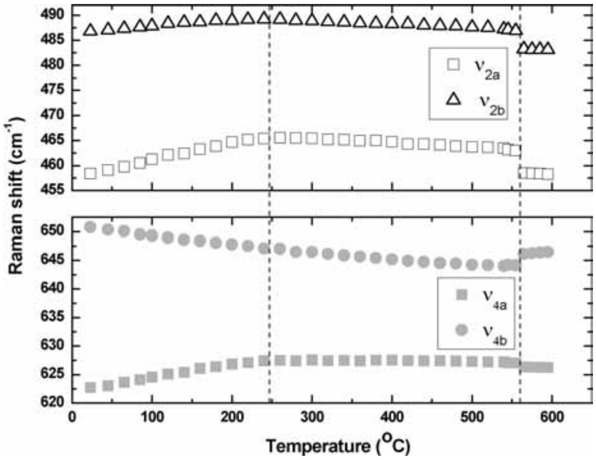

Figure 5. Temperature dependences of the ν_2 and ν_4 modes of the SO_4 ion in the temperature interval 24−595 °C.

decreasing the bond strength of the S−O bonds in the SO_4 units. The role of sulfate internal modes in Li_2SO_4[11] and $LiKSO_4$[12] has long been investigated in a similar context. Also, similar high-temperature behavior was reported in Na_3PO_4,[5] which has been attributed to rotational motion (anion reorientation) of the translationally fixed PO_4. Moreover, coherent quasielastic neutron scattering study[13] and careful X-ray analysis[14] probing oxyanion reorientation revealed a 3-fold symmetry distribution of the SO_4 tetrahedron orientations around the crystallographic *c*-axis. The introduction of some disorder in the sulfate orientations or the cation positions can cause the observed increase in the phonon damping versus temperature, which in principle will depend on the particular eigenvector of any vibration.[11] It is possible that a particular Eigen mode assists the jumps between the different configurations and this relatively stronger coupling to the disordering process, causing an abrupt change in the phonon lifetime and hence the width of ν_1 mode. We believe that rapid rotational motion of the disordered SO_4 tetrahedra defines the channel better, hence enhancing the Na^+ migration and resulting in high conductivity across this transition. This is corroborated in the conductivity data measured earlier.[3]

Conclusion

From the temperature evolution of the Raman spectra of NCSO, we confirm the change in conductivity observed in the earlier conductivity measurement[3] is associated with the local structural distortions of the SO_4 tetrahedra due to increased rotational degree of freedom as a function of temperature. The sudden jump in the conductivity across the transition at the high-temperature phase is attributed to the rapid rotational motion of the SO_4 tetrahedra. The rotational motion of the SO_4 ions enhances the Na^+ migration, resulting in high conductivity during the transition. The reorientational motion of the SO_4 ions revealed by temperature-dependent Raman spectroscopy studies and their coupling with sodium ion motion inferred from electrical conductivity measurements strongly suggest that there is a correlation between the structural and dynamic changes across this phase transformation.

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