CONTRASTING BEHAVIOR OF THE $\text{SO}_4^{2-}$ SYMMETRIC RAMAN MODE IN HIGH AND LOW CONDUCTING SULFATES

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Raman spectra of fast ion conducting sulfates give evidence for sulfate ion reorientations, whereas no reorientational motion is observed in the low conducting sulfates case. The results suggest that fast ion conducting sulfates, in contrast to low conducting sulfates, are described by rotator phases. New results for high conducting bcc LiNaSO$_4$ and low conducting hexagonal Na$_2$SO$_4$ are compared with previous results for fast ion conducting fcc Li$_2$SO$_4$ and bcc LiAgSO$_4$. The obtained reorientational time decreases with increasing temperature to a value of $\omega_1$ ps close to the melting points (848 - 1133 K) of solid electrolytes. The results are typical for plastic materials and in accordance with predictions from molecular simulation studies. Furthermore, if sulfate ion reorientations are coupled to the fast ion diffusion, then the surprisingly large activation energies of cation diffusion may be explained by the also high activation energies of sulfate ion reorientation found in the present study.

INTRODUCTION

A group of solid sulfates with both monovalent and divalent cations shows a high temperature phase of excellent conductivity ($\approx 10^{-1}$ cm$^{-1}$) (1). In these materials neutron scattering demonstrates that the fast ion conducting phase is characterized by a high degree of orientational oxygen disorder (2). This, together with a high heat of transition compared to the heat of fusion (3), suggests a premelting process with rapid rotational reordering of the sulfate groups (3). Raman scattering results on some sulfate systems below the phase transition suggest a beginning sulfate rotational motion as the phase transition is approached (4,5). Molecular dynamics simulation studies indicate a sulfate ion rotational time of $\omega_1$ ps in the fast ion conducting phase (6). Recently in this laboratory Raman scattering in fcc Li$_2$SO$_4$ and bcc LiAgSO$_4$ shows a component due to sulfate ion reorientation, which could be separated from the spectra by comparing the anisotropic and isotropic spectral bandwiths for the symmetric sulfate internal mode, $\nu_1$, (7). Thus a plastic behavior of some crystals in the high conducting phase is confirmed.

In the present study the fast ion conducting sulfate, bcc LiNaSO$_4$,
as well as a low conducting sulfate, hexagonal Na$_2$SO$_4$, have been chosen for a Raman investigation of the dynamics of the sulfate ion in the two cases. The conductivity of bcc LiNaSO$_4$ is approximately three orders in magnitude larger than that of Na$_2$SO$_4$ at a comparable temperature (8,9,10). Data on the structure, temperature range, heat of transition, conductivity and activation energy for bcc LiNaSO$_4$ and low conducting Na$_2$SO$_4$ are shown in Table I together with data on high conducting Li$_2$SO$_4$ and LiAgSO$_4$. From the table it can be seen that the hexagonal phase of low conducting Na$_2$SO$_4$ covers the temperature ranges of the three high conducting sulfates, which makes comparable studies at corresponding temperatures possible. The aim of the work is to investigate whether a rotator phase is a general characteristic of the fast ion conducting phase or if it is merely a result of the high temperature of these phases. Also, it has been suggested that rotations of the sulfate ions are enhancing cation diffusion and that this mechanism is partly responsible for the high conductivity in the fast ion conducting sulfates (13). Therefore, the temperature dependence of the symmetric mode $\nu_1$ will be analyzed in detail to investigate any possible relation between sulfate ion reorientations and fast ion diffusion.

Previous results for fcc Li$_2$SO$_4$ and bcc LiAgSO$_4$ (7) will be summarized together with new data on bcc LiNaSO$_4$ and hexagonal Na$_2$SO$_4$.

Table I Heat of solid-solid phase transition, electrical conductivity and activation energy of cation diffusion in three fast ion conducting sulfates and in Na$_2$SO$_4$.

|                | $\Delta H$ (kJ kg$^{-1}$) | $\sigma$ at 823K (S cm$^{-1}$) | $E$ (eV) | Ref    |
|----------------|---------------------------|-------------------------------|---------|--------|
| Li$_2$SO$_4$ fcc: 848-1133K | 214                       | 0.86                          | 0.34    | 3,11,1 |
| LiNaSO$_4$ bcc: 791-883K   | 17.9                      | 0.93                          | 0.63 (Li$^+$) | 12,8,1 |
|                     |                           |                               | 0.64 (Na$^+$) | 1     |
| LiAgSO$_4$ bcc: 728-848K   | 155                       | 1.17                          | 0.52 (Li$^+$) | 3,11,1 |
|                     |                           |                               | 0.52 (Ag$^+$) | 1     |
| Na$_2$SO$_4$ hexagonal: 513-1157K | 80   | $1\times10^{-3}$ | 1.68    | 3,10  |

EXPERIMENTAL

Polarized and depolarized Raman spectra were analyzed by a Spex double monochromator model 1403 with holographic gratings (1800 lines mm$^{-1}$). The spectrometer slits were set to give a measured resolution of 2 cm$^{-1}$. An Ar$^+$ laser operating at 488.0 nm was used as a light source. Lock-in technique was employed to minimize the effect of thermal radiation. A high-temperature cell, essentially the same
as that described elsewhere (14), controlled the temperature within 1K in the range, 500-1100 K, of investigation. The samples, grown by the Bridgman method, were unoriented and kept in a cylindrical quartz cell (diameter 3 mm). The salts, suprapur Li$_2$SO$_4$ and Na$_2$SO$_4$, were dried 24 h in a vacuum oven before sample preparation. The crystals were approximately 3 mm long and perfectly transparent.

RESULTS AND DISCUSSION

In the Raman spectra of bcc LiNaSO$_4$ no external modes are present in accordance with the observations by Frech et al (4). In the latter report the external modes were studied in the phase below the high conducting phase and they disappeared at the transition temperature. The four internal sulfate modes, $\nu_1$, $\nu_2$, $\nu_3$ and $\nu_4$, of bcc LiNaSO$_4$ are shown in Fig. 1 as well as a spectrum for hexagonal Na$_2$SO$_4$. As can be seen in the figure, the widths of the components of the high conducting LiNaSO$_4$ are broader than those of the corresponding components of low conducting Na$_2$SO$_4$. This is in agreement with the observation that the fast ion conducting phase is a phase of significant disorder, and it is a general finding for solid electrolytes (15).

The frequency shifts obtained for the internal sulfate modes in LiNaSO$_4$ are given in Table II where previous results for Li$_2$SO$_4$ and LiAgSO$_4$ (7) are included for a comparison. The results are mean values over the observed temperature ranges since the frequency decrease with temperature is small and about the same as the accuracy of the peak positions, $\pm$1 cm$^{-1}$ over the temperature range of stability of each crystal. Table II demonstrates the decreasing frequency shift with increasing size of the cation; this has been observed in other systems as well (16).

|     | Li$_2$SO$_4$ | LiNaSO$_4$ | LiAgSO$_4$ | Na$_2$SO$_4$ |
|-----|--------------|-------------|-------------|--------------|
|     | fcc (a)      | bcc         | bcc (a)     | hexagonal    |
| $\nu_1$ (cm$^{-1}$) | 993          | 989         | 970         | 980          |
| $\nu_2$ (cm$^{-1}$) | 455          | 455         | 453         | 454          |
| $\nu_3$ (cm$^{-1}$) | 1107         | 1110        | 1097        | 1100         |
| $\nu_4$ (cm$^{-1}$) | 629          | 627         | 614         | 621          |

a) Ref. 7

The halfwidth and its temperature dependence on the $\nu_2$ and $\nu_4$ isotropic (polarized) components are about the same as those of the anisotropic (depolarized) components for all studied crystals, see Fig. 1 for the LiNaSO$_4$ case. The halfwidth of the $\nu_3$ mode could not be obtained in the case of the solid electrolytes due to an overlapping with the high intensity $\nu_1$ mode, see Fig. 1. For the $\nu_1$ mode,
however, the anisotropic width, $\Gamma_{\text{aniso}}$, increases more rapidly with temperature than the width of the isotropic component, $\Gamma_{\text{iso}}$, in the case of the fast ion conducting systems. The observation is an immediate indication of reorientational motion of the sulfate ion with a reorientational time $\tau$ determined by

$$\tau^{-1} = 2\pi c \Gamma_R = 2\pi c (\Gamma_{\text{aniso}} - \Gamma_{\text{iso}})$$

where $c$ is the speed of light and $\Gamma_R$ is the broadening due to a rotational motion. In the simple approximation that vibrational and rotational motions are uncorrelated and that dipole-dipole coupling and collision induced effects may be neglected, Eq. (1) is applicable for a symmetric Raman mode of low depolarization ratio like the $V_1$ mode of the present systems. To determine $\Gamma_{\text{aniso}}$ of $V_1$, any contribution of $V_3$ must be minimized. A Lorentzian was fitted to the $V_3$ by using its shape of the high frequency side. $V_3$ is then subtracted from the spectrum and the resulting $V_1$ is also fitted to a Lorentzian. The isotropic $V_1$ mode was also found to be Lorentzian in shape. Results for $\Gamma_{\text{aniso}}$ and $\Gamma_{\text{iso}}$ are shown in Fig. 2.

Table III Reorientational broadening and time due to sulfate ion reorientations in bcc LiNaSO$_4$

| $T$ (K) | $\Gamma_R$ (cm$^{-1}$) | $\tau$ ($10^{-12}$s) |
|---------|-----------------|-----------------|
| 806     | 0.6             | 8.8             |
| 817     | 0.7             | 7.6             |
| 829     | 1.7             | 3.1             |
| 841     | 2.7             | 2.0             |
| 853     | 2.7             | 2.0             |
| 865     | 3.0             | 1.8             |
| 876     | 3.2             | 1.7             |
| 876     | 4.1             | 1.2             |

For LiNaSO$_4$ an increased difference in half-widths is observed, see Fig. 2a and Table III, where $\Gamma_R$ and the corresponding reorientational time are tabulated. The values are to be compared with the value, 2 ps, reported in a molecular dynamics simulation study of fcc Li$_2$SO$_4$ (6). For Li$_2$SO$_4$ and LiAgSO$_4$ the previous Raman study (7) also indicated a component due to sulfate ion reorientations, and the reported values of $\Gamma_R$ are shown in Table IV for the three sulfate crystals at a temperature in the middle of the range of the fast ion conducting phase. In the last column of Table IV $\tau$ is compared with the free rotor time, $\tau_{\text{FR}}$, defined as

$$\tau_{\text{FR}} (41^\circ) = \left(\frac{41^\circ}{360^\circ}\right) \times 2\pi (I/kT)^{\frac{1}{2}}$$

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where $\tau_{FR} (41^\circ)$ is the time for a free rotor to travel $41^\circ$ which is the relevant time for a comparison with $\tau$ of Eq. (1) (17). Present values of $\tau/\tau_{FR}$ are close to the reported value, $\approx 4$, for free diffusion liquids including some plastic crystals (17). Plastic phases are normally associated with a large heat of transition. This is true for the high conducting sulfates, see Table I, which show values almost more than three times larger than the heat of fusion (3). The elastic constants, reported from a Brillouin scattering study of fcc Li$_2$SO$_4$, also give results typical for a plastic material (14,18).

Table IV  Reorientational broadening and time compared to the free rotor time in three fast ion conducting crystals

| T (K) | $\Gamma_R$ (cm$^{-1}$) | $\tau$ ($10^{-12}$s) | $\tau/\tau_{FR}(41^\circ)$ |
|-------|------------------------|----------------------|---------------------------|
| Li$_2$SO$_4$ (a) 993 | 4.8 | 1.1 | 3.8 |
| LiNaSO$_4$ 841 | 2.7 | 2.0 | 6.0 |
| LiAgSO$_4$(a) 792 | 4.5 | 1.2 | 3.5 |

(a) Ref. 7

For low conducting hexagonal Na$_2$SO$_4$, however, no excess broadening was found in the corresponding temperature range, see Fig. 2b. Thus, plastic behavior and rotation characteristics seem to be the general attribute of fast ion conducting sulfates and are not due to the high temperature at which these phases of high conductivity exist.

If the transition into the high conducting phase is associated not only with rotational motion of the sulfate ion, as has now been observed, but also with a suggested coupling between the reorientational motion and fast ion diffusion (13), then a similar temperature dependence of the two processes may be expected. To make a comparison we therefore assume an Arrhenius behavior of the reorientational contribution

$$\Gamma_R = A e^{-E/kT}$$

where $E$ is the activation energy necessary for reorientations and $A$ is a constant. In Fig. 3 results for log$\Gamma_R$ are plotted vs. $1/T$ and previous results of Li$_2$SO$_4$ and LiAgSO$_4$ are also included (7). The activation energies obtained for Li$_2$SO$_4$, LiNaSO$_4$ and LiAgSO$_4$ are 0.40, 0.86 and 0.72 eV, respectively, which are comparable to the activation energies of cation diffusion (see Table I). In fast ion conducting sulfates the activation energies of cation diffusion are significantly higher than in other solid electrolytes (e.g. in $\alpha$-AgI the activation energy is only $\approx 0.1$ eV (19)). If there is an interaction between sulfate ion reorientation and cation diffusion, then the high values for cation diffusion may be explained by the also
high activation energies for sulfate ion reorientations obtained in the present study.

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REFERENCES

1. A. Lundén, A. Bengtzelius, R. Kaber, L. Nilsson, K. Schroeder and R. Tärneberg, Solid State Ionics 9/10 (1983) 89.
2. L. Nilsson, Ph.D. thesis, Chalmers University of Technology, Göteborg, Sweden (1981).
3. K. Schroeder and C.A. Sjöblom, High Temp. High Pressures 12 (1980) 327.
4. D. Teeters and R. Frech, Phys. Rev. B, 26 (1982) 5897.
5. R. Frech and E. Cazzanelli, Solid State Ionics 9/10 (1983) 95.
6. R.W. Impey and M.L. Klein, J. Phys. C. 17 (1984) 3941.
7. L. Börjesson and L.M. Torell, Phys. Rev. B (in press)
8. A.-M. Josefson and A. Kvist, Z. Naturforsch. 24a (1969) 466.
9. A. Kvist, A. Bengtzelius and A. Schiraldi, in A.N. Sherwood, A.K. Chadwick, W.M. Muirand and F.L. Swinton (eds), Diffusion Processes 2, 523 (Gordon and Breach, London 1971).
10. M.A. Careem and B.E. Mellander, Solid State Ionics 15, (1985) 327.
11. A. Kvist and A. Lundén, Z. Naturforsch 20a (1965) 235; 22a (1967) 208.
12. A.F. Polishchuk and A.K. Bogdanova, Russ. J. Phys. Chem. 51 (1977) 1195.
13. L. Nilsson, J.O. Thomas and B.C. Tofield, J. Phys. C13 (1980) 6441.
14. R. Aronsson, Ph. D. thesis, Chalmers University of Technology, Göteborg, Sweden (1983).
15. M.J. Delaney and S. Ushioda in Superionic Conductors, ed. M.B. Salamon (Springer, Berlin 1979)

16. M.H. Broker and M.A. Bredig, J. Chem. Phys. 58 (1973) 5319.

17. F.J. Bartoli and T.A. Litovitz, J. Chem. Phys. 56 (1972) 404; 56 (1972) 413.

18. R. Aronsson, H.E.G Knape and L.M. Torell, J. Chem. Phys. 77 (1982) 677.

19. A. Kvist and R. Tärneberg, Z. Naturforsch. 25a (1970) 257.
Fig. 1. Internal Raman sulfate modes in the
a) isotropic spectrum of Na$_2$SO$_4$ at 923 K
b) isotropic and c) anisotropic spectra of LiNaSO$_4$ at 806 K.

Fig. 2. Halfwidth vs temperature for the anisotropic and isotropic components of the symmetric internal sulfate mode $\nu_1$ in a) high conducting LiNaSO$_4$ and b) low conducting Na$_2$SO$_4$.

Fig. 3. Logarithmic plot of the reorientational contribution $\Gamma_R$ (in cm$^{-1}$) to the bandwidth of the symmetric internal sulfate mode in three fast ion conducting sulfates.