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Vibrational Study of Selenate-Doped Lithium Sulfate: Single Crystals and Fused Salts

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Polarized Raman spectra were measured in single crystals of lithium sulfate doped with different concentrations of lithium selenate. Weak features observed in the Ag scattering geometry on the low-frequency side of the sulfate ion ν_1 mode were identified as originating in the ν_1 and ν_3 intramolecular modes of the selenate ion. The site group splitting of the guest selenate ion in the host lithium sulfate crystal was the same as that observed in pure lithium selenate. The vibrational spectrum of a more concentrated fused salt sample was dominated by disorder effects. © 1988 Academic Press, Inc.

Introduction

The doping of small amounts of a polyatomic guest ion into a host crystal offers the possibility of using the guest ion to probe the potential energy environment of the host. This can be particularly interesting if the guest ion can be isomorphously substituted into a host sublattice which consists of polyatomic ions of the same molecular symmetry as the guest. If the vibrational modes of the guest and the host are well-separated in frequency, vibrational coupling effects between the two are negligible. This effectively separates site group effects from correlation field effects by switching off the latter.

Although Li_2SeO_4 and Li_2SO_4 belong to different space groups, the similarity of anions suggests that solid solutions of low concentrations might be formed with this pair of compounds. The selenate ion and the sulfate ion are both tetrahedral oxyanions of similar ionic radius, 2.43 and 2.3 Å, respectively (*1*). A similar study of solid solutions of $BaSO_4$ and $BaSeO_4$ has been reported by Tarte and Nizet (*2*).

Experimental

Single crystals of lithium sulfate, Li_2SO_4, doped with selenate ion, SeO_4^{2-} were grown from a saturated aqueous solution of Li_2SO_4, containing small amounts of Li_2SeO_4, by a technique previously described (*3*). The doped crystals grew in a needle-like morphology with a rhombic cross section, similar to the undoped crystals. Crystals were selected with 1 and 5% (mole%) nominal doping levels, that is, the solutions

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in equilibrium with the crystals contained those percentages of selenate ion to sulfate ion. Of course the actual concentration of dopant anion can differ greatly from the solution value. A rough estimate can be deduced from the relative intensities of the ν_1 bands of the selenate and sulfate ions. The ratio of the absolute intensities of this mode in the two pure materials is calculated from the Raman spectra of mixed powders of known composition. This results in a value of $I(SeO_4^{-2})/I(SO_4^{-2}) \simeq 2$. Assuming that there are no solid-state correlation effects which would significantly change this ratio in the fused salts, the concentrations of selenate ion in the host lithium sulfate crystal was found to be about 20–30 times smaller than the nominal solution values. The host lithium sulfate crystal is monoclinic, with a tetramolecular unit cell in the $P2_1/b$ (C_{2h}^5) space group (*4, 5*). The sulfate ions occupy Wyckoff 4e sites of C_1 point group symmetry, which are also the sites presumably occupied by the dopant selenate ions.

The single crystals were observed in a conventional $z(yy)x$ scattering experiment in which the coordinates have been previously defined (*3*). The Raman spectra were obtained with a Spex Ramalog 14018 spectrometer at ~3 cm^{-1} spectral bandpass. The exciting light was the 488.0-nm line of a 4-W argon ion laser at an output power of 400 mW.

Spectral Data

Figure 1 shows the low frequency side of the intense ν_1 sulfate ion symmetric stretching mode centered at 1014 cm^{-1}. In the pure crystal there is an extremely weak, very broad feature extending from 830 to 920 cm^{-1}, suggestive of a multiphonon, multibranch process perhaps involving the ν_2 or ν_4 multiplet. In the nominal 1% spectrum of Fig. 1, there is a weak although reasonably narrow band visible at roughly 882 cm^{-1}, with the hint of additional structure at a somewhat higher frequency. The spectrum of the nominal 5% sample clearly shows bands at 882, 918, and 935 cm^{-1}. These three modes were only observed in scattering geometries in which only modes of Ag symmetry were allowed.

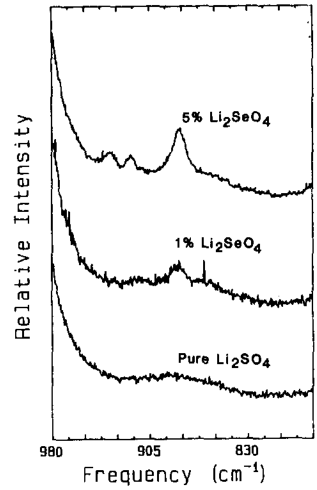

FIG. 1. Raman scattering spectra of pure Li_2SO_4 and Li_2SO_4 doped with 1% Li_2SeO_4 and 5% Li_2SeO_4 (nominal concentrations). The increase in intensity at 980 cm^{-1} is due to the low-frequency wing of the sulfate ion mode.

The assignment of these features is not simple. As the doping level of the selenate ions is increased, the intensity of the three bands increases in a region in which multiphonon, multibranch processes in the undoped host lithium sulfate crystal are known to occur. Although disorder-induced scattering at first seems to be a reasonable explanation, the relative sharpness of all three bands is slightly troublesome. There is an alternate explanation which is preferred by the authors.

The vibrational spectrum of single-crystal lithium selenate, Li_2SeO_4, was recently measured (*6*). In a polarized Raman spectrum in which only modes belonging to the totally symmetric Ag representation are allowed, two components of ν_3 were observed, at 917 and 899 cm^{-1}. In addition, an intense band due to ν_1 was observed at 863 cm^{-1}. The frequency differences between these three modes is the same, to within a wavenumber, as the frequency differences between the three bands observed in the selenate-doped samples. Therefore the band at 882 cm^{-1} in the doped samples is assigned as selenate ion ν_1 mode and the two bands at 918 and 935 cm^{-1} are assigned as ν_3 components.

Although the crystal structure of lithium selenate is trigonal, with a hexamolecular unit cell in space group $R3$ (C_{3i}^2), the spectroscopic data strongly argue that the vibrational potential energy environment in lithium selenate is surprisingly similar to that in lithium sulfate. The ν_3 mode of both sulfate and selenate ion belongs to the F_2 irreducible representation of the isolated ion Td point group. On a site of sufficiently low symmetry such as the C_1 site in both Li_2SO_4 and Li_2SeO_4, the threefold degeneracy should be lifted into three nondegenerate components. The fact that in both Li_2SeO_4 and selenate-doped Li_2SO_4, the Ag spectrum shows only two components separated by equal frequency differences is a compelling argument for the similarity of the vibrational potential energy environments in these two systems.

A mixed powder of the Li_2SO_4 and Li_2SeO_4 results in a spectrum which is a superposition of the pure powder spectra and is shown in Fig. 2. This spectrum results from a 3 : 1 molar ratio of lithium sulfate to lithium selenate and is prepared by grinding the two components together. However when the two salts are fused and allowed to cool, the spectrum which results is also shown in Fig. 2. Studies using X-ray diffraction techniques clearly eliminate the possibility of glass formation. Instead, two highly disordered phases of the starting materials are present, with traces of a third phase which is a solid solution of dilute composition. In the two highly disordered phases both the selenate ion and the sulfate ion internal mode structure are considerably altered. The sulfate ν_1 mode, although not undergoing any noticeable frequency shift, shows disorder-induced structure on the low-frequency side. The selenate ion ν_1 mode shifts from 861 cm^{-1} in the powder to 876 cm^{-1} in the fused salt and also shows apparent disorder-induced low-frequency structure. The ν_3 multiplet originating from the sulfate ions tends to broaden and collapse slightly toward a common frequency. In the corresponding selenate ion multiplet, both ν_3 components broaden, shift to higher frequencies, and collapse. A comparison of the frequencies of the selenate ion ν_1 and ν_3 modes in pure Li_2SeO_4, the fused salts, and the selenate-doped Li_2SO_4 crystals suggests that the Li_2SO_4 crystal field effects tend to "stiffen" the guest selenate ion internal vibrations. It would also appear that disorder effects dominate the spectrum of the fused salt.

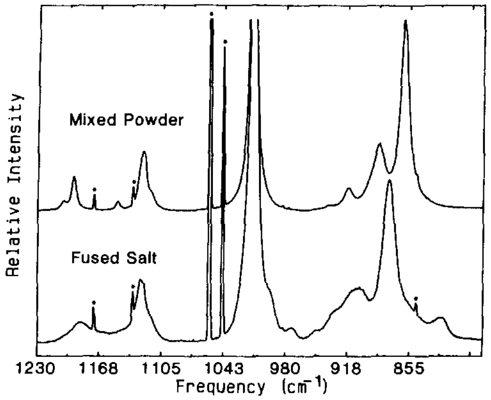

FIG. 2. Raman scattering spectra of a mixed powder and a fused mixture of Li_2SO_4 and Li_2SeO_4 at a 3 : 1 molar ratio. Plasma lines are indicated with an asterisk.

Acknowledgment

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