High temperature X-ray synchrotron study on LiNaSO₄: Anharmonic thermal vibrations and effective atomic potentials

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At increasing temperature anionic groups in many simple salts undergo rotational disorder which may lead to an enhanced mobility of the cationic species. This disorder results in a phase transition above which the material is a solid electrolyte. The low temperature structure of LiNaSO₄ (SG P31c, Z=6) is built up of SO₄ and LiO₄ tetrahedra. Three non-equivalent sulphate groups O(1)-S(1)-O₃(4), O(2)-S(2)-O₃(5) and O(3)-S(1)-O₃(6) are centered at the threefold axes with the S(1)-O(1), S(2)-O(2) and S(3)-O(3) bonds parallel to c. Each of the three O(4), O(5) and O(6) atoms are located in the trigonal basis plane perpendicular to c. Along c the SO₄ and LiO₄ tetrahedra form chains with strong covalent-type Li-O-S bonding. Perpendicular to c the linkage results in a channel-like structure. The Na⁺-ions are located inside the channels (Fig. 1).

Above the strongly first order phase transition at T_tr = 788K the average structure of LiNaSO₄ is cubic (SG Im3m, Z=2) with a high degree of disorder. The sulphate ions rotate and the cations diffuse through the lattice in a 'liquid-like' manner [1].

In order to understand the structural and dynamic changes that are observed when the phase transition is approached high temperature single crystal X-ray synchrotron experiments have been carried out at 516K, 626K and 736K. The crystal had a regular shape with edge lengths ≈250µm. Synchrotron intensities were measured up to sinθ/λ = 0.65 Å⁻¹ (λ = 0.4 Å). The lattice parameters were found to be in good agreement with the data obtained from a former study on the trigonal-to-cubic phase transition [1] (Fig. 2). Structural refinements were based on |Fo| using the program PROMETHEUS [2]. Reflections with |Fo| < 3σ(|Fo|) were rejected. No absorption correction was applied. The |Fo| values were weighted according to w = 1/σ²(|Fo|), where σ²(|Fo|) = σ²(|Fo|) + (Rint|Fo|)². σ²(|Fo|) is based on counting statistics; Rint is the internal agreement factor of the data. Anharmonic motion of O, Na and Li up to the third order of a Gram-Charlier expansion was refined. Thermal tensor components with c < 1σ(c), 2σ(c), 3σ(c) have been successively set to zero in the course of the refinement. Thereby, the number of refined parameters is drastically reduced. The reliability of the structural parameters was checked by comparison of the p.d.f. maps, R and GOF values and the change of e.s.d.’s. The agreement factors at 516K, 626K and 736K are R (wR) = 0.023(0.036), 0.025(0.049) and 0.034(0.056), respectively. The sulphate groups can be treated as 'rigid bodies' since the S-O bond lengths turn out to be almost independent of temperature when a thermal correction using the riding-model (d_śo, = 1.478 Å) is applied. The thermal mobility of the sulphate groups increases strongly with increasing temperature as indicated by the pronounced non-linear behaviour of the mean-square displacements <u²> along the principal axes of the thermal vibrational ellipsoids of the O(4), O(5) and O(6) atoms. The degree of rotational motion increases in the order O(4) < O(5) << O(6) (Fig. 3).
Further structural and dynamic details can be studied if anharmonic thermal vibrations are considered. The effect of anharmonic motion is illustrated on the O(2) and the O(6) atom which show strong deviations from the harmonic temperature-factor behaviour. The p.d.f. map of the O(2) atom at 736K in the (001) plane shows a very pronounced threefold symmetry (Fig. 4). In order to resist against bond shortening towards the Na-ion the direction of lowest thermal vibrations nearly coincide with the O(2)-Na bond. This is highlighted by the mean one-particle potential of O(2) in the section of maximum anharmonicity which evidently deviates from the harmonic approximation (Fig. 4). The potential has a steep flank towards the Na-ion and is stretched in the opposite direction. A similar behaviour is observed for the O(1)-Li bond. The O(6) atoms undergo strong thermal vibrations in form of a rotation around the S(3) atom. Oxygen pathways lie on a circular section centered at the S(3) atom which is inclined by only a few degree from (001) (Fig. 5). As it can be expected from the smaller $\langle u^2 \rangle$ values, the effect is much less pronounced for the O(4) and the O(5) atom.

References