07. MATERIALS SCIENCE

07.3-4 CONDUCTORS Li$_3$Sc$_2$(PO$_4$)$_3$ AND Li$_3$Fe$_2$(PO$_4$)$_3$ AT 293 AND 593 K. By B.A. Mak mimov, B.A. Genkin, L.A. Khedr and V. Simonov, Institute of Crystallography, USSR Acad. Sci., Moscow, USSR.

At 600 K the conductivity of Li$_3$Sc$_2$(PO$_4$)$_3$ and Li$_3$Fe$_2$(PO$_4$)$_3$ crystals, obtained by solid-phase synthesis, reaches (2-5) x 10$^{-4}$ cm$^2$/V·sec. The fast-ionic domains have the following measurements: a = 8.850(1), b = 12.271(2), c= 9.022, V= 953 Å$^3$, z = 4. In the fast-ionic state, at T= 2540 K, the fast-ionic domains are monoclinic, Fedorov group $P2_1/n$, and the symmetry is changed to orthorhombic (Fedorov group $P2_1/b$). The data were collected using a CAD-4F diffractometer equipped with a graphite monochromator (step scanning method W-technique, sin 2θ/λ = 1 Å$^{-1}$).

At room temperature Li$_3$Sc$_2$(PO$_4$)$_3$ crystals are monoclinic, Fedorov group $P2_1/n$, a= 8.850(1), b = 12.271(2), c = 9.022, V= 953 Å$^3$, z = 4. In the fast-ionic state, at T= 2540 K, the symmetry is changed to orthorhombic (Fedorov group $P2_1/b$). The data were collected using a CAD-4F diffractometer equipped with a graphite monochromator (step scanning method W-technique, sin 2θ/λ = 1 Å$^{-1}$).

The basis of the structure of lithium-scandium phosphate and lithium-iron phosphate is its sulfur tetramer, namely (TMTSF)$_2$X (for recent results, see J. Physique (1985), Colloque C3, pp. 767-1136). TMTSF is tetramethyltetraselenafulvalene, TMTTF is tetramethyltetraselenafulvalene, and X is an anion, e.g. BF$_4$, CO$_3$, ReO$_4$, PF$_6$ or TaF$_6$. These materials exhibit unusual physical properties, such as low-dimensional metallic transport properties, and superconductivity has been demonstrated in several cases including (TMTSF)$_2$TaF$_6$ at temperatures below 1 K and pressures above 10 kbar. The crystals are all isoostructural at room temperature and they consist of TMTSF cation-radicals stacked along the c axis. The stacks are connected (via Se-Se or S-S contacts) to sheets separated by anion layers parallel to the ab plane (see e.g. Thorup et al. Acta Cryst. (1981) B37, 1256).

The present work focuses on the structural details of the title compounds and, in particular, the differences between them. In both cases, however, the octahedral anions seem to be disordered in a very similar fashion. Each octahedron can take on two of the orientations, which are very close. The triclinic cell dimensions at 295 K are:

\[ a = 12.00(1) \quad b = 12.39(2) \quad c = 8.55(2) \quad \alpha = 90.02(1) \quad \beta = 91.28(1) \quad \gamma = 96.53(2) \]

07.3-5 PHASE TRANSITIONS IN SUPERIONIC CONDUCTOR CaHSO$_4$ STUDY BY NEUTRON DIFFRACTION AND INELASTIC SCATTERING. By A.V. Belushkin, 1. Ratkevics, N.M. Fritsda, I. Shalnov*, J. Wasicki, Joint Institute for Nuclear Research, 141980 Dubna, USSR, Institute of Crystallography, 117333 Moscow, USSR.

Simultaneous measurements of neutron diffraction (ND) and inelastic incoherent neutron scattering (IINS) on a powder sample of CaHSO$_4$ in the temperature range of 5-423 K have been performed at the IBR-2 pulsed reactor. Three phase transitions have been detected by ND when a sample was heated from the room temperature up to 423 K. As it is seen from the IINS spectra the dynamics of protons significantly changes at the first transition near 325 K and at the superionic transition at 414 K as well. The phase upper 325 K has a metastable character and can be easily supercooled. Proton jumps in the superionic phase at 423 K should have a frequency lower than 10$^{-11}$ sec, because we have not observe quasi-elastic broadening within our 6% resolution at the 4.9 meV elastic line. Using vibrational frequency obtained from IINS we estimate the diffusion coefficient for protons:

\[ D = 2.7 \times 10^{-5} \text{cm}^2/\text{sec.} \]

Necessary resolution to observe such a diffusion is of the order of 0.02 meV.