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Crystal structures of di-tin-hexa(seleno)hypodiphosphate, $\text{Sn}_2\text{P}_2\text{Se}_6$, in the ferroelectric and paraelectric phase

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Received March 4, 1997; accepted July 25, 1997

Abstract. The crystal and molecular structure of $\text{Sn}_2\text{P}_2\text{Se}_6$ in the low temperature ferroelectric phase is determined by single crystal X-ray diffraction techniques. These results are compared with the crystal structure of the same compound in the paraelectric phase, which was redetermined at room temperature.

In both phases, the structure crystallizes in the monoclinic system. The ferroelectric phase with $a = 6.8145(3) \text{ \AA}$, $b = 7.7170(3) \text{ \AA}$, $c = 11.694(1) \text{ \AA}$, $\beta = 124.549(4)^\circ$, space group Pc , $V = 506.52(6) \text{ \AA}^3$, $Z = 2$ was determined at $T = 173 \text{ K}$ and the paraelectric phase with $a = 6.808(2) \text{ \AA}$, $b = 7.682(3) \text{ \AA}$, $c = 11.667(7) \text{ \AA}$, $\beta = 124.75(6)^\circ$, space group $P2_1/c$, $V = 501.4(5) \text{ \AA}^3$, $Z = 2$ was determined at $T = 293 \text{ K}$. Both structures were solved by automated Patterson methods and refined by least squares methods. For the ferroelectric phase final refinement resulted in $R = 0.038$ for 3763 reflections (with $I > 2\sigma(I)$). Refinement of the paraelectric modification revealed disorder of the Sn^{2+} cations (the two Sn sites being separated by approximately 0.34 \AA) and resulted in $R = 0.062$ for 2211 reflections (with $I > 2\sigma(I)$).

Comparison of the two structures showed that the tin ions shift to positions of about 0.13 \AA from an individual disorder-site in the high temperature phase (paraelectric) to the corresponding tin position in the low temperature phase (ferroelectric). The shift from the average Sn-position in the paraelectric phase to the Sn-positions in the ferroelectric phase is about 0.30 \AA (on average 10° off the vector $\mathbf{a} + \mathbf{c}$), and is clearly related to the spontaneous polarization. Moreover, the average direction of these displacements is perpendicular to the modulation wave vector

direction in the incommensurate phase, showing the prime importance of such movements to the incommensurate phase formation.

Introduction

$\text{Sn}_2\text{P}_2\text{Se}_6$ is one of the members of the family of proper ferroelectrics $\text{Sn}_2\text{P}_2(\text{S}_{1-x}\text{Se}_x)_6$ (Vysochanskii, Slivka, 1992), which is of interest for both fundamental and applicational reasons.

Of fundamental interest is the presence of a Lifshitz point on the composition-temperature phase diagram (Vysochanskii et al., 1992). The occurrence of an incommensurate phase in $\text{Sn}_2\text{P}_2\text{Se}_6$ and its gradual diminishment with increasing sulphur concentration (and disappearance at the Lifshitz point $x_L = 0.28$, $T_L = 295 \text{ K}$) is expected to originate mainly from a change of interatomic forces with composition x . This has motivated phonon investigations by Raman, inelastic neutron and infrared spectroscopic studies on $\text{Sn}_2\text{P}_2(\text{S}_{1-x}\text{Se}_x)_6$ crystals (Vysochanskii, Slivka, Buturlakin, Gurzan, Chepur, 1978; Gommonai, Vysochanskii, Gurzan, Slivka, 1983; Volkov, Kozloc, Afanas'eva, Vysochanskii, Grabar, Slivka, 1983; Eijt, Maior, Vysochanskii, 1996; Eijt, Currat, Lorenzo, Katano, Saint-Grégoire, Hennion, Vysochanskii, 1997), in which clear soft mode behavior has been observed related to the phase transitions. However, electronic properties may also be of importance, since the compounds are semiconductors. For example, the modulation wave vector in the incommensurate phase in $\text{Sn}_2\text{P}_2\text{Se}_6$ can be stabilized in a small temperature interval by manipulating the population density of electrons in trapping levels (Maior, Rasing, Eijt, van Loosdrecht, van Kempen, Molnar, Vysochanskii, Motrij, Slivka, 1994). In this context, it is important for structural studies to compare the crystals $\text{Sn}_2\text{P}_2\text{Se}_6$ and $\text{Sn}_2\text{P}_2\text{S}_6$ to show detailed changes in the interatomic distances and an-

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ion value of Dy³⁺ within experimental accuracy. Platinum and germanium atoms carry no magnetic moments. Changes of the conduction band by Pt and Ge are supposed to influence the type of magnetic Dy order. Indirect exchange by conduction band electrons is responsible for the magnetic interaction in rare earth intermetallics. Magnetization measurements as well as supplementary neutron diffraction on monocrystals must be carried out in order to determine the anisotropy direction and the crystal field parameters quantitatively.

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