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Structural phase transitions and their influence on Cu^+ mobility in superionic ferroelastic Cu_6PS_5I single crystals

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The structural origin of Cu^+ ion conductivity in Cu_6PS_5I single crystals is described in terms of structural phase transitions studied by X-ray diffraction, polarized light microscopy and calorimetric measurements. Below the phase transition temperature at T_c = (144–169) K, Cu_6PS_5I belongs to the monoclinic, ferroelastic phase, with the space group *Cc*. Above T_c, the crystal changes its symmetry to a cubic superstructure, with the space group $\bar{F}43c$ (a' = 19.528); finally, at 274 K, the disordering of Cu^+ ions increases to the symmetry $\bar{F}43m$ (a = 9.794). The phase transition at 274 K coincides well with a strong anomaly in electrical conductivity observed on the Arrhenius plot. Diffusion paths for Cu^+ ions are evidenced by means of atomic displacement factors and a split model. The influence of copper stoichiometry on T_c is also discussed.

Key words: *fast-ion conductor; structural phase transition; X-ray diffraction; argyrodite*

1. Introduction

The investigations presented in this work are a part of the research on ferroelastic, superionic $Cu_6PS_5I_xBr_{1-x}$ crystals which exhibit mixed ionic-electronic conduction. They belong to the argyrodite family of compounds with an icosahedric structure [1, 2]. Among the crystals of this family, Cu_6PS_5Hal (Hal = Cl, Br, I) have been recently extensively studied, because of possible applications in high energy density batteries and sensors, and due to the possibility of phase transitions and order-disorder

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studies [3–7]. Despite numerous papers related to the optical, dielectric, and thermodynamic properties of these compounds, knowledge about the low-temperature crystal structures remains very limited. Furthermore, the temperatures of polymorphic phase transitions reported by different research groups do not correspond to each other. For example, according to Studenyak et al. [8] two phase transitions (PT) are observed at low temperatures, a first-order superionic PT at T_s = (165–175) K and second-order, ferroelastic one at T_c = 269 K. Girnyk et al., on the other hand, report T_s at 210 K and T_c at 180 K [3]. As far as this crystal is concerned, conductivity measurements have been performed only on powder samples. The total conductivity was measured by Khus et al. in the range of 293–300 K [1]. It was established that at room temperature, the conduction is purely ionic ($\sigma_I \approx 4\times10^{-4}$ at RT), with an electronic contribution (hole conductivity σ_h) less than 1%. At higher temperatures, σ_h increases and at 423 K it becomes equal to σ_I. Low-temperature conduction was measured by Beeken et al. [9]; a strong anomaly with a broad and continuous change in activation energy was observed on the Arrhenius plot at 270 K, and much weaker one around 194 K.

In the present work, we analyse the structural changes in Cu_6PS_5I single crystals using X-ray diffraction, domain structure observations, and calorimetric investigations. Our main purpose is to correlate the changes in the structural disordering of Cu^+ mobile ions with the electrical conductivity of this compound.

2. Experimental

Cu_6PS_5I crystals were obtained by the conventional vapour transport method [10] at the Uzhhorod State University. Calorimetric measurements were performed from 130 K to 233 K using a Perkin-Elmer DSC-7 instrument with the scanning rate of 20 K/min. The weight of the sample, consisting of small single crystals obtained under the same growth conditions, was 31.447 mg. Ferroelastic domain studies were carried out using a polarizing microscope equipped with a Linkam temperature controller, for which ΔT = 0.1 K, for thin plate samples oriented in the cubic phase perpendicular to the <100> direction.

Single-crystal X-ray data were collected on a Kuma KM-4 CCD diffractometer with a CCD camera (MoK_α radiation, graphite monochromator) equipped with a nitrogen gas-flow cooling system (Oxford Criosystem Controller), with ΔT = 0.3 K. To minimize the absorption effect, a sphere 0.25 mm in diameter was prepared in a compressed air mill and absorption correction for the sphere was applied. The lattice parameters were determined by the Bond procedure [11] on a Bond diffractometer (CuK_α radiation, graphite monochromator). Data were collected for a spherical sample at 150 K, 235 K, and 293 K. Structure refinement was carried out by direct methods with the SHELXL-97 program package. The positions of Cu^+ ions were taken from the differential Fourier maps.

3. Results and discussion

3.1. DSC and domain structure, and the temperatures and the sequence of structural phase transitions

Differential scanning calorimetry shows that on heating and cooling there are three thermal anomalies connected to the phase transitions, with temperatures on the cooling run as follows: 274 K, 160 K, and 144 K (Fig. 1). A large hysteresis in the low-temperature range and a weaker one in the high temperature range indicate first-order phase transitions.

An investigation of a real ferroelastic domain structure and its temperature behaviour was performed and compared with DSC measurements. On the basis of these studies, the temperature of the ferroelastic phase transition was established and the possibility of an intermediate phase existing between the high- and low-temperature phases was checked.

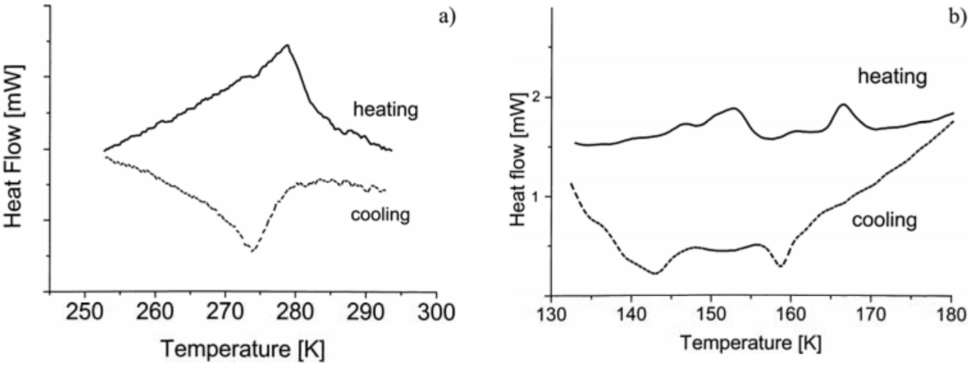

Fig. 1. DSC curves of Cu_6PS_5I: a) high low temperature range, b) low temperature range

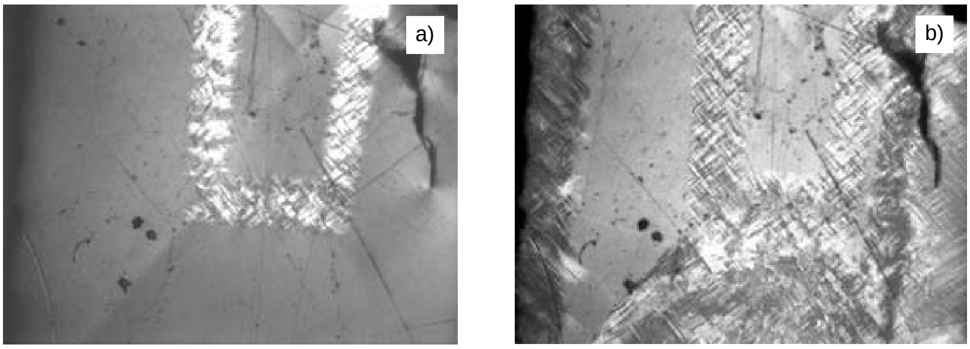

Fig. 2. Domain structure in Cu_6PS_5I in the <100> direction: a) 165 K, b) 144 K

Cu_6PS_5I crystals remain optically isotropic down to 165 K, which corresponds to the second peak on the DSC diagram. Surprisingly, only a part of the sample (rectangular in shape) undergoes the transition (Fig. 2a). Domain structure appears below 144 K in the whole sample (Fig. 2b). This transition corresponds to the third peak on the DSC diagram. It was shown by Studenyak [12] that different technological procedures used in a vapour transport method result in the synthesis of crystals with various copper contents. This leads to different temperatures of the superionic phase transition. In our case, the samples were prepared under the same growth conditions, therefore it seems that seeds with different copper content were obtained.

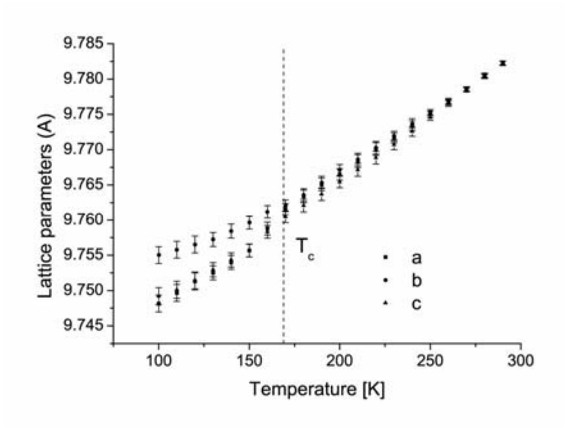

Fig. 3. Temperature dependence of lattice parameters *a*, *b*, and *c* [Å]

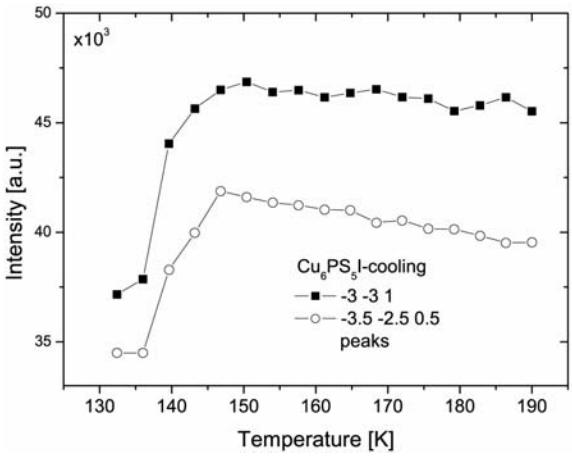

Fig. 4. Temperature dependence of the intensities of selected reflections indexed in the cubic *F*-43*m* phase

The temperature of the ferroelastic phase transition coincides with the temperature of the superionic phase transition based on the absorption edge energy reported by Studenyak (T_s = 169 K). This means that in Cu_6PS_5I crystals $T_c = T_s$, and two phase transitions occur, a structural one at 274 K, which does not change the crystallographic system, and the other, ferroelastic transition below 169 K with the transition temperature dependent on Cu content in the sample. To confirm these results, two samples were measured by X-ray diffraction. Precise lattice parameters versus temperature were refined using the Bond method for the first sample, in which the splitting of lattice parameters below 169 K is well pronounced (Fig. 3). In the case of the second sample, changes in the Bragg peak intensities and half widths of the 12 2 2 peak versus temperature were measured (Figs. 4 and 5). Sharp changes in these values occur at 144 K, supporting our interpretation and being in perfect agreement with the results obtained by DSC and domain structure studies. The results are summarized in Fig. 6.

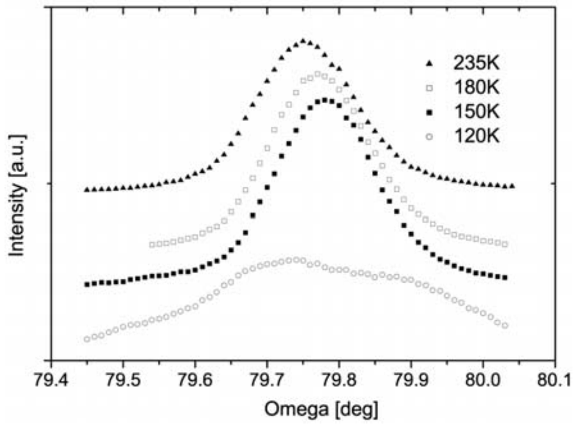

Fig. 5. Temperature dependence of the 12 2 2 Bragg peak profile

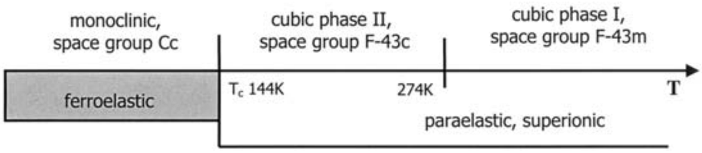

Fig. 6. Phase transitions in Cu_6PS_5I

Above 274 K, Cu_6PS_5I has a cubic structure with the F-43m symmetry (cubic phase I), common for all Cu_6PS_5Hal. The extinction conditions reflection data set observed below 274 K is in agreement with the F-43c space group with doubled lattice parameters, a = 19.528 Å (cubic phase II). Below 169 K, the crystal undergoes a ferroelastic and superionic first-order phase transition from a cubic to monoclinic system with the space group *Cc* [13]. The temperature of this phase transition depends on the copper content in the sample. Phase transitions in Cu_6PS_5I are connected with the ordering of the Cu sublattice, leading to the identical arrangement and full occupation of Cu sites in all cells of the monoclinic phase. The basic icosahedral anion sublattice is preserved after the change of symmetry.

Due to the low temperature of the ferroelastic phase transition and existence of cubic phase II between *F*-43*m* and *Cc* symmetries, a detailed study of Cu ordering can be performed in Cu_6PS_5I crystals in the entire range of the superionic phase.

3.2. Cu $^+$ ionic migration

In cubic phase I, 24 Cu^+ ions partly occupy two systems of equivalent tetrahedral sites within a framework of interpenetrating, centred, distorted anion icosahedra. These ions are distributed among 72 positions in unique cells, which provides a favourable means for ionic migration. Cu^+ ions on 48-fold (m) positions are coordinated by distorted S_3I tetrahedra, and ions occupying 24-fold (2mm) sites are coordinated by a planar, triangular S_3 configuration (Fig 7a). The change in symmetry to *F*-43*c* at phase II provides six independent 96-fold Cu positions with point symmetry C_1 in the rigid skeleton of an anion framework and two different tetrahedral coordinations for Cu^+ ions: $I1S_3$ and $I2S_3$. Two tendencies in the ordering process of the Cu sublattice are observed with changing temperature. The $I2S_3$ tetrahedral site is strongly preferred by Cu^+ ions. On decreasing temperature, Cu^+ ions shift from a planar S_3 configuration towards the tetrahedral $I2S_3$ site (Fig. 7b, c). At 165 K, this position is almost fully occupied (Fig. 7d, e). From the other side, ions coordinated by $I1S_3$ tetrahedra prefer the planar triangular S_3 configuration. The occupancy of this site increases with decreasing temperature, but even at 165 K the Cu^+ ions are not

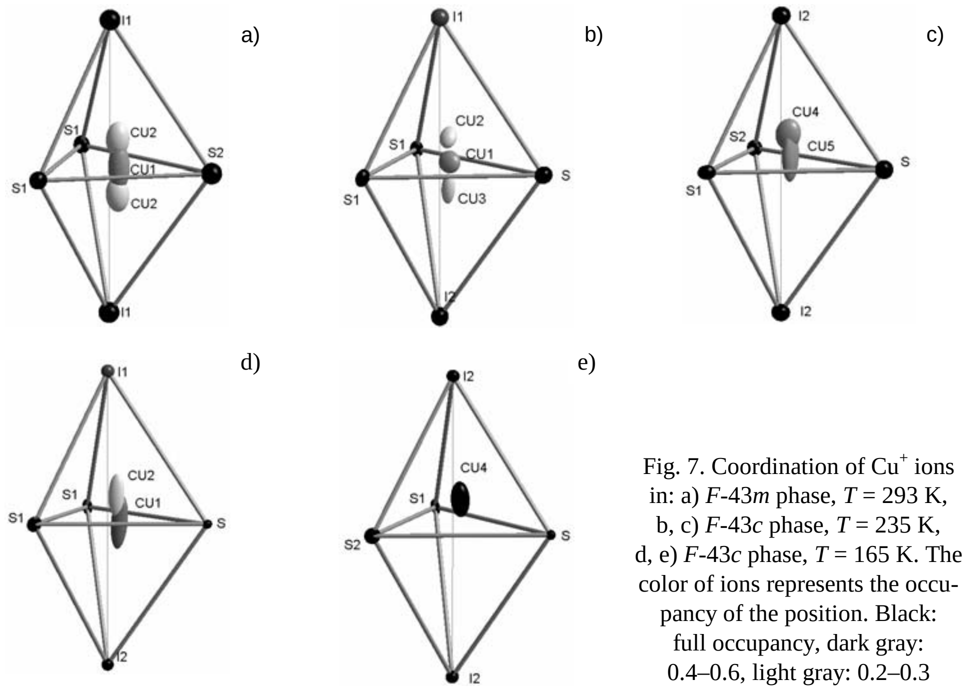

Fig. 7. Coordination of Cu^+ ions in: a) *F*-43*m* phase, $T = 293$ K, b, c) *F*-43*c* phase, $T = 235$ K, d, e) *F*-43*c* phase, $T = 165$ K. The color of ions represents the occupancy of the position. Black: full occupancy, dark gray: 0.4–0.6, light gray: 0.2–0.3

well localized. Temperature displacement factors are elongated along the axis of the tetrahedra. This strong tendency to occupy triangular planar configurations corresponds to the monoclinic *Cc* phase model of Cu arrangement proposed by Haznar et al. for Cu_6PS_5Br compounds [13]. All these structural changes have a great influence on ionic migration. The energy barrier associated with the motion along mobile pathways, from the minima at tetrahedral sites to barrier triangular sites, increases during the ordering of Cu^+ ions in tetrahedral sites. Also, the distances between Cu atoms become longer, thus undoubtedly suppressing the mobility of Cu^+ ions.

4. Conclusions

Structural changes resulting from polymorphic phase transitions have been studied in Cu_6PS_5I single crystals by means of X-ray diffraction, DSC and optical measurements. Below the temperature of the phase transition at T_c = (144–169) K, the crystal belongs to the ferroelastic phase with the space group *Cc*. T_c depends on the copper content in the sample. Above T_c, the crystal changes its symmetry to the cubic superstructure *F*-43*c*, and at 274 K to the *F*-43*m* system in a structural phase transition. In the *F*-43*c* phase, Cu^+ ions have a tendency to locate in tetragonal and planar triangular sites with decreasing temperature, which suppresses ionic mobility.

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