
X,T-Phase Diagram of the $\text{Cu}_6\text{PS}_5\text{J}_x\text{Br}_{1-x}$ Mixed Crystals. Optical, Dilatation and Ultrasonic Velocity Studies

¹I.Girnyk, ²D.Kaynts, ¹O.Krupych, ¹I.Martunyk-Lototska and ¹R.Vlokh

¹Institute of Physical Optics, 23 Dragomanov Str., 70005 L'viv, Ukraine

²Uzhgorod National University, 46 Pidhirna Str, 88000 Uzhgorod, Ukraine

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Abstract

On the basis of studies of the domain structure and the temperature dependences of thermal expansion and the ultrasonic velocity, the x,T -phase diagram of $\text{Cu}_6\text{PS}_5\text{I}_x\text{Br}_{1-x}$ mixed crystals is obtained. It is shown that all the compounds possess the first-order superionic (SI) phase transitions (PTs). Their temperatures are determined with the aid of thermal expansion measurements. The mixed crystals with the concentration $x=0\div 1$ possess the second-order structural PTs into a ferroelectric-ferroelastic (FF) phase. In the composition range $x=0\div 0.75$, the temperature of the structural PT slowly decreases and the line of T_C crosses the line of T_S approximately at $x=0.75$ (at heating) and at $x=0.9$ (at cooling). Due to a wide temperature hysteresis of T_S in the range of $\Delta x=0.75\div 0.9$, the sequence of PTs should depend on the particular temperature scan process – cooling or heating. In this range of the composition the polycritical point exists, in which the crossed curves of PTs separate the following phases: paraelectric-paraelastic-SI (the symmetry $\bar{4}3m$), paraelectric-paraelastic-nonSI ($\bar{4}3m$), ferroelectric-ferroelastic-SI (m) and ferroelectric-ferroelastic-nonSI (m). The coordinates of the polycritical point are determined as $(x;T)=(0.76;217\text{K})$.

Key words: ferroelastics, superionics, domain structure, thermal expansion, ultrasonic velocity

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Introduction

$\text{Cu}_6\text{PS}_5\text{Br}$ and $\text{Cu}_6\text{PS}_5\text{J}$ crystals belong to the argyrodite family and are known as fast-ion conductors [1,2]. These crystals possess the cubic symmetry $\bar{4}3m$ at the room temperature [2]. They are grown with the chemical vapor transport method [3]. The crystals with the general chemical formula $\text{Cu}_6\text{PS}_5\text{Hal}$ (Hal being J, Cl and Br) are interesting first of all from the point of view of their phase transitions (PTs) into superionic (SI) and the other structural phases. Below we analyze in brief the data on this subject known from the literature.

The SI properties of the $\text{Cu}_6\text{PS}_5\text{Br}$ and $\text{Cu}_6\text{PS}_5\text{J}$ crystals have been found by Kuhs W.F. et al [2]. The total conductivity has been measured versus temperature and it has been

shown that the electronic part of conductivity at the room temperature is less than 1% of its total value. The copper ions are responsible for the ionic conductivity, due to partial occupation of Cu positions in the lattice [4]. The SI PT temperature T_S has been determined with both the specific heat [3] and calorimetric measurements [5]. It has been shown that the SI PT in $\text{Cu}_6\text{PS}_5\text{Br}$ crystals is of the first order, with a wide range of PT hysteresis ($T_S=169\text{K}$ at cooling and $T_S\approx 198\text{K}$ at heating) [5]. The behaviour of the SI PT in $\text{Cu}_6\text{PS}_5\text{J}$ crystals is similar ($T_S\approx 235\text{K}$ at cooling) [3]. From the viewpoint of conductivity properties, it is worthwhile to note that the ionic conductivity in both crystals is of the same order, while the electronic one is higher in $\text{Cu}_6\text{PS}_5\text{J}$ crystals [3]. Both crystals pos-

sess the SI PT of the first order. From the other side, it has been mentioned in [1] that $\text{Cu}_6\text{PS}_5\text{Br}$ crystals also manifests a structural transformation into the monoclinic phase, with the point symmetry group m at approximately -5°C . The fact of the ferroelectric-ferroelastic PT (FFPT) (more exactly, the structural PT into the ferroelectric-ferroelastic (FF) phase) existing in $\text{Cu}_6\text{PS}_5\text{Br}$ crystals at $T_C=268\text{K}$ has been confirmed by different authors who have studied the temperature dependences of the lattice parameters [5], dielectric and optical properties [6], as well as the domain structure [7]. The FFPT in $\text{Cu}_6\text{PS}_5\text{Br}$ crystals is of the second order. Concerning the $\text{Cu}_6\text{PS}_5\text{J}$ crystals, unambiguous data about the existence of FFPT are still lacking. Some reports [8,9] indicate that the crystals exhibit a weak anomalous behaviour of the dielectric permittivity and the ultrasonic velocity around 269K. But there is no direct data that could definitely confirm the availability of the FFPT in these crystals. On the other side, it has been noted in [2] that the FFPT in $\text{Cu}_6\text{PS}_5\text{J}$ crystals appears at $T_C=113\text{K}$. Thus, the existence of the FFPT in $\text{Cu}_6\text{PS}_5\text{J}$ crystals, as well as the exact determination of its temperature, represent a problem which has not yet been solved.

In order to do that, we have undertaken the combined studies of x,T -phase diagram of $\text{Cu}_6\text{PS}_5\text{J}_x\text{Br}_{1-x}$ mixed crystals, using the ultrasonic velocity, thermal expansion and the domain structure observation methods.

Experimental

The $\text{Cu}_6\text{PS}_5\text{J}_x\text{Br}_{1-x}$ mixed crystals with the concentrations $x=0; 0.25; 0.5; 0.75$ and 1.0 were grown by the chemical vapour transport method at Uzhgorod National University. The average dimensions of the crystals were $2\times 2\times 2\text{mm}^3$. The results of X-ray-fluorescent analysis show that mixed crystals possess the excess of the iodine ions and deficiency of bromide ions. Since the x,T -diagram that will be obtained by us can be only approximate.

The domain structure in the FF phase was

studied with the optical polarization microscope equipped with temperature-controlling accessories. The images of the domain structure were registered with the photo camera. The acoustic velocity measurements of the longitudinal ultrasonic waves have been performed on the $\text{Cu}_6\text{PS}_5\text{J}_x\text{Br}_{1-x}$ mixed single crystals with the pulse-echo overlap method [10]. The accuracy of the absolute velocity determination was about 0.5%. The acoustic waves in samples were excited with the LiNbO_3 transducers, using the resonance frequency of $f=10\text{ MHz}$, the bandwidth $\Delta f=0.1\text{ MHz}$ and the acoustic power $P_a=1-2\text{ W}$. The thermal expansion has been measured with the capacity dilatometer.

Results and discussion

(a) Domain structure observation

The appearance of the domain structure in $\text{Cu}_6\text{PS}_5\text{J}_x\text{Br}_{1-x}$ may serve as a criterion of temperature of the FFPT. In the mixed crystals with $x=0; 0.25; 0.5; 0.75$ and 1.0 , the domain structure appeared at $T_C=268\text{K}, 265\text{K}, 230\text{K}, 234\text{K}$ and 180K , respectively (Figure 1). We did not observe the phase boundary movement at T_C in these compounds. The domain structure is visible due to the optical indicatrix rotation in the neighbouring domains. The quantity of different orientation states and the domain wall orientation correspond to the PT with the point symmetry group change $\bar{4}3mFm$ (a more detail description of the domain structure has been reported in [7]). The pure $\text{Cu}_6\text{PS}_5\text{J}$ crystals remain optically isotropic down to 180K , i.e. they are cubic. The samples of $\text{Cu}_6\text{PS}_5\text{J}$ crystals were also studied with the imaging polarimetry technique in the temperature range of $220\text{K}\div 293\text{K}$. The results confirm the optical isotropy of $\text{Cu}_6\text{PS}_5\text{J}$ crystals throughout the whole sample bulk. Further experiments performed on the polarization microscope have shown that both optical anisotropy and domain structure in $\text{Cu}_6\text{PS}_5\text{J}$ crystals appear at $T_C=180\text{K}$, thus indicating the existence of the FFPT at this temperature.

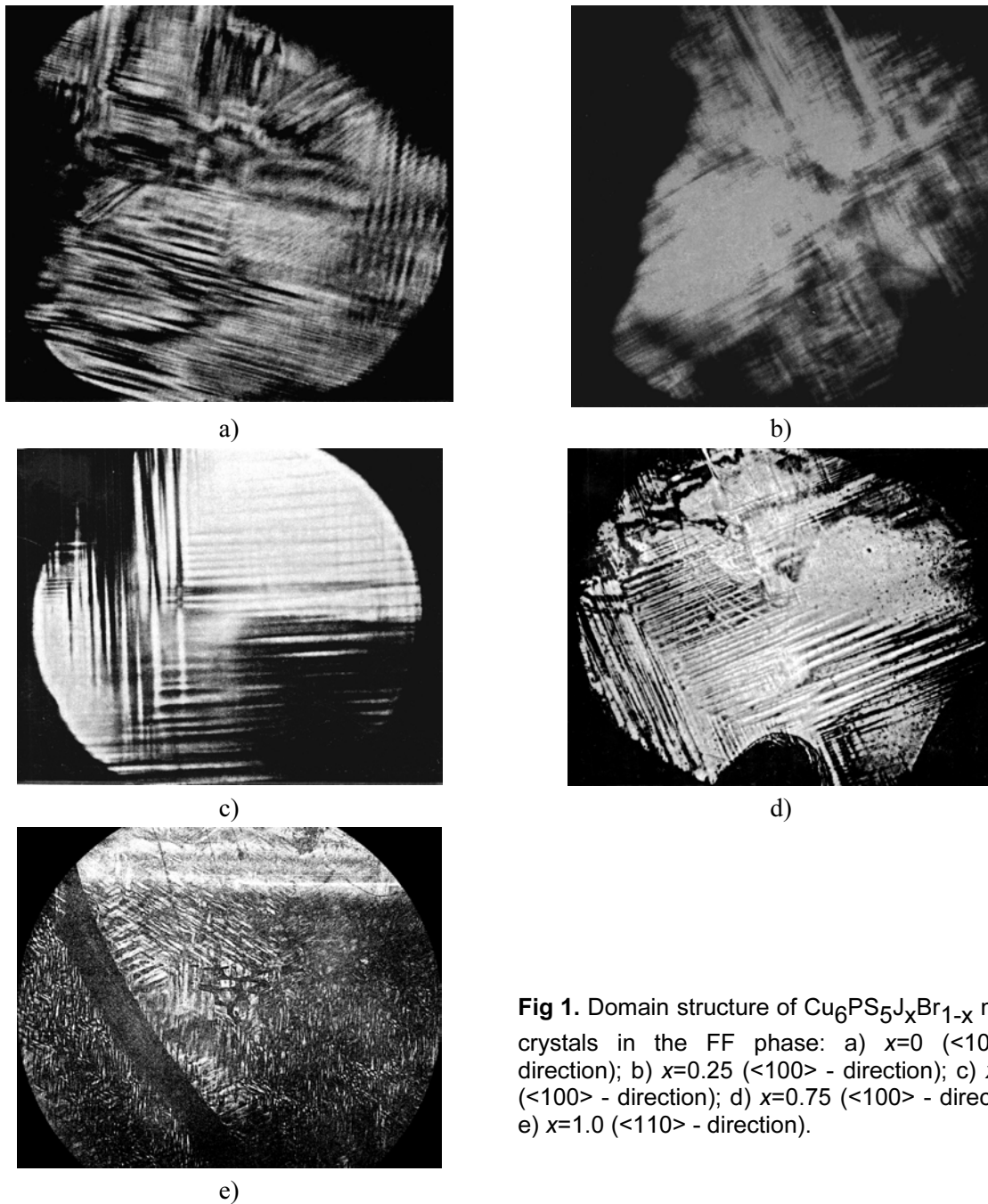


Fig 1. Domain structure of $\text{Cu}_6\text{PS}_5\text{J}_x\text{Br}_{1-x}$ mixed crystals in the FF phase: a) $x=0$ ($\langle 100 \rangle$ - direction); b) $x=0.25$ ($\langle 100 \rangle$ - direction); c) $x=0.5$ ($\langle 100 \rangle$ - direction); d) $x=0.75$ ($\langle 100 \rangle$ - direction); e) $x=1.0$ ($\langle 110 \rangle$ - direction).

(b) Thermal expansion

The results for the thermal expansion in $\text{Cu}_6\text{PS}_5\text{J}_x\text{Br}_{1-x}$ mixed crystals are presented in Figure 2.

As seen from Figure 2, the temperature dependences for the pure $\text{Cu}_6\text{PS}_5\text{Br}$ crystals become anomalous at the FFPT ($T_C=268\text{K}$). The temperature of this PT is the same at cooling and heating. Moreover, we did not observe any jump-like changes of the thermal expansion at

this temperature. It means that the FFPT in $\text{Cu}_6\text{PS}_5\text{Br}$ crystals is of the second order. In the mixed crystals the anomalous behaviour of thermal expansion at the FFPT is shadowed by a strong anomaly at SI PT. The temperature dependences of the thermal expansion coefficient around T_C are shown in Figure 2 (see the inserts). The SI PT at T_S is accompanied by either expansion of the sample (at heating) or its compressing (at cooling). Such a behaviour of thermal expansion at T_S indicates the first-order SI

PT and the absorption (at heating) or emission (at cooling) of the latent heat. The absorption and emission of the latent heat at T_S just lead to the expansion and compressing of the sample. Furthermore, the temperature hysteresis of T_S is quite wide (approximately $\Delta T_h \approx 45\text{K}$). Hence,

the anomalous behaviour of thermal expansion at T_S may be a criterion for determining the SI PT temperature. It is necessary to note that there is no change of symmetry in $\text{Cu}_6\text{PS}_5\text{Br}$ crystals at the SI PT and the other physical properties do not exhibit any anomalous behaviours.

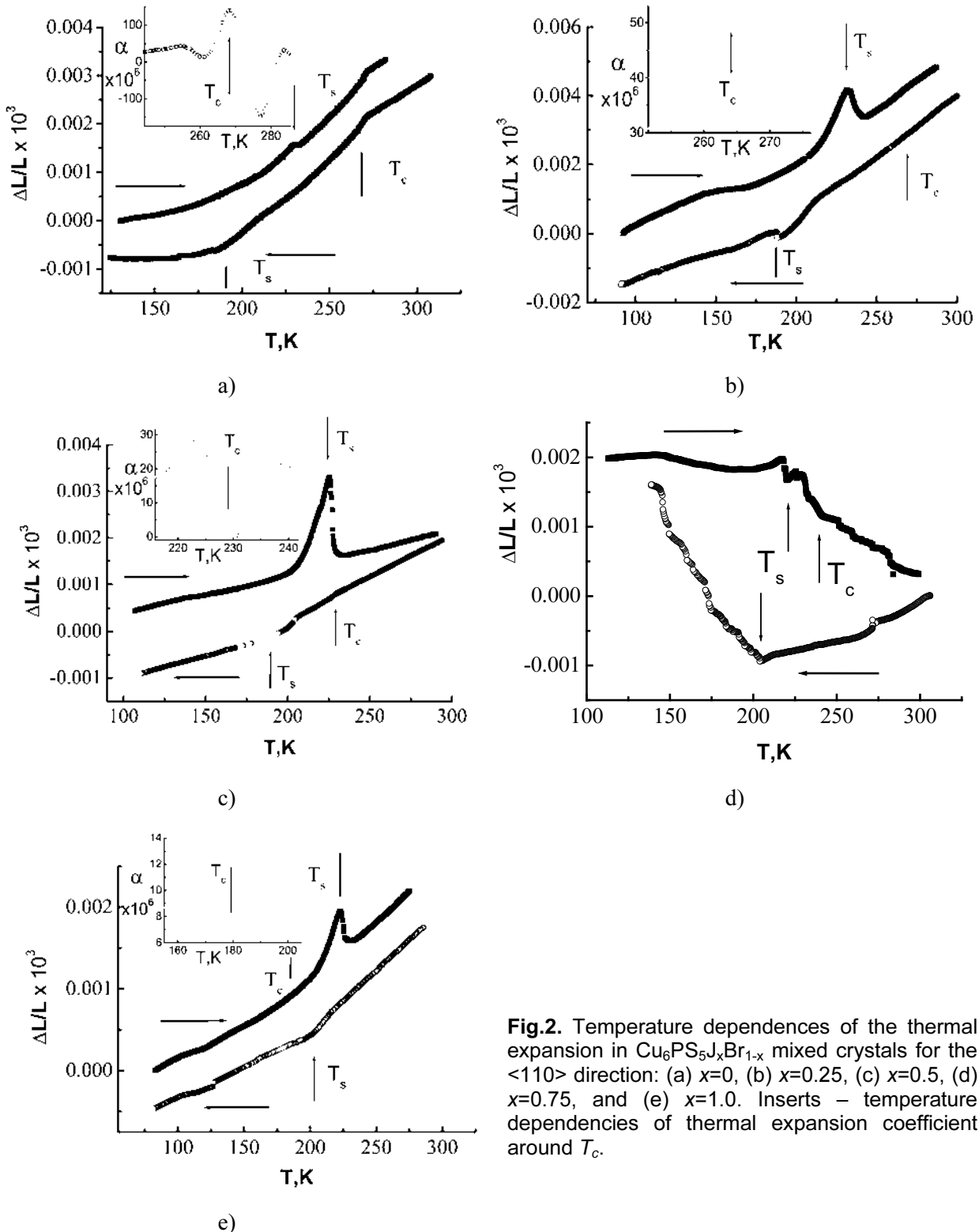
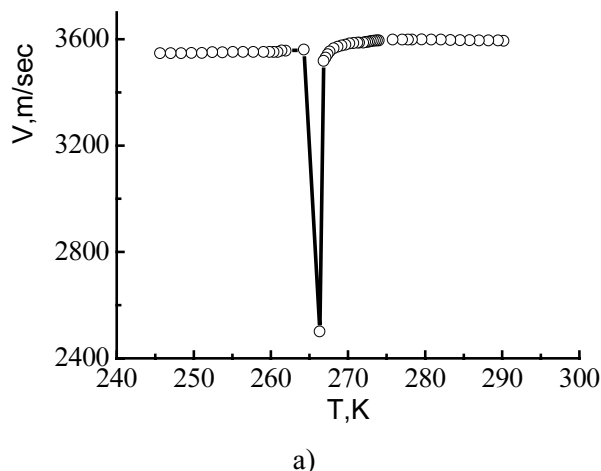


Fig.2. Temperature dependences of the thermal expansion in $\text{Cu}_6\text{PS}_5\text{J}_x\text{Br}_{1-x}$ mixed crystals for the $\langle 110 \rangle$ direction: (a) $x=0$, (b) $x=0.25$, (c) $x=0.5$, (d) $x=0.75$, and (e) $x=1.0$. Inserts – temperature dependences of thermal expansion coefficient around T_c .

The SI PT temperatures can be easily determined from the similar anomalous temperature dependences of thermal expansion for the mixed crystals with $x=0.25, 0.5, 0.75$, and 1.0 (see Figure 2). The temperature hysteresis of T_S and the sharp change in thermal expansion due to the absorption and emission of the latent heat characterize all of these PTs. The SI PT hysteresis width decreases with increasing x (e.g., it is equal to $\Delta T_h \approx 12\text{K}$ for the pure $\text{Cu}_6\text{PS}_5\text{J}$ crystals). It is interesting to notice that the temperatures of SI PTs and FFPTs are very close to each other in case of $x=0.75$ at the heating run. Moreover, the temperature dependence of thermal expansion for the mixed crystals with $x=0.75$ differs from those for the other crystals. It is clearly seen that the mentioned temperature dependence does not represent a monotonic function, i.e. the mixed crystals with $x=0.75$ correspond to the range of concentrations with instability and large fluctuations present. Furthermore, if we remember that $T_C > T_S$ in the mixed crystals with $x=0 \div 0.5$ and $T_C < T_S$ at $x=1.0$, it is possible to conclude that a polycritical point (or a polycritical range) should exist on the x, T -phase diagram of $\text{Cu}_6\text{PS}_5\text{J}_x\text{Br}_{1-x}$ mixed crystals.

(c) Ultrasonic velocity study

The results of the ultrasonic velocity measurements in the $\text{Cu}_6\text{PS}_5\text{J}_x\text{Br}_{1-x}$ mixed crystals with $x=0$ and 0.25 are represented in Figure 3.



The FFPT in the crystals with $x=0$ and 0.25 is characterized by decreasing ultrasonic velocity at T_C . Unfortunately, we were unable to study the ultrasonic wave velocity in the other compounds for the reason of small dimensions of the samples.

(d) x, T -phase diagram

The x, T -phase diagram of the $\text{Cu}_6\text{PS}_5\text{J}_x\text{Br}_{1-x}$ mixed crystals is shown in Figure 4. In the composition range of $x=0 \div 1$, the temperature of FFPT slowly decreases and the line of T_C crosses that of T_S approximately at $x=0.75$ (at heating).

It is interesting to note that, owing to a wide temperature hysteresis of T_S in the range of $\Delta x=0.75 \div 0.9$, the sequence of the PTs should depend on the temperature scan process (i.e., cooling or heating). In this range of composition the polycritical point exists, at which the crossed curves of PTs separate the following phases: paraelectric-paraelastic-SI (the symmetry $\bar{4}3m$), paraelectric-paraelastic-nonSI ($\bar{4}3m$), FF-SI (m), and FF-nonSI (m). Let us keep in mind that, according to our data, the crystals at $x=1.0$ remain cubic down to $T_C=180\text{K}$. Then one can conclude that the curve of T_C above $x=0.75$ sharply tends towards low temperatures. This curve of second-order FFPTs separates the phases with the symmetries $\bar{4}3m$ and m . On the other hand, the SI PT is depicted in Figure 4 by

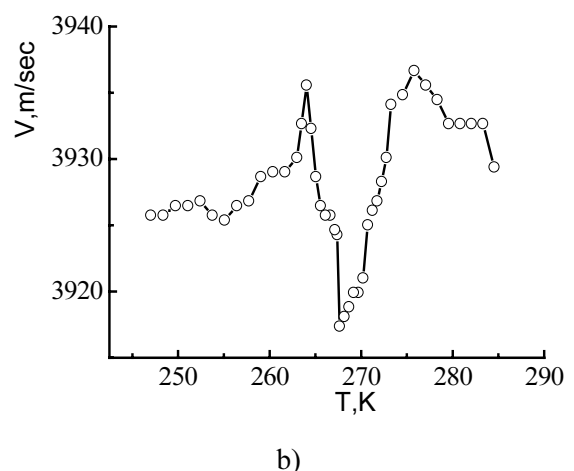


Fig.3. Temperature dependence of the ultrasonic velocity in $\text{Cu}_6\text{PS}_5\text{J}_x\text{Br}_{1-x}$ mixed crystals around T_C for the $\langle 110 \rangle$ direction: (a) $x=0$, (b) $x=0.25$.

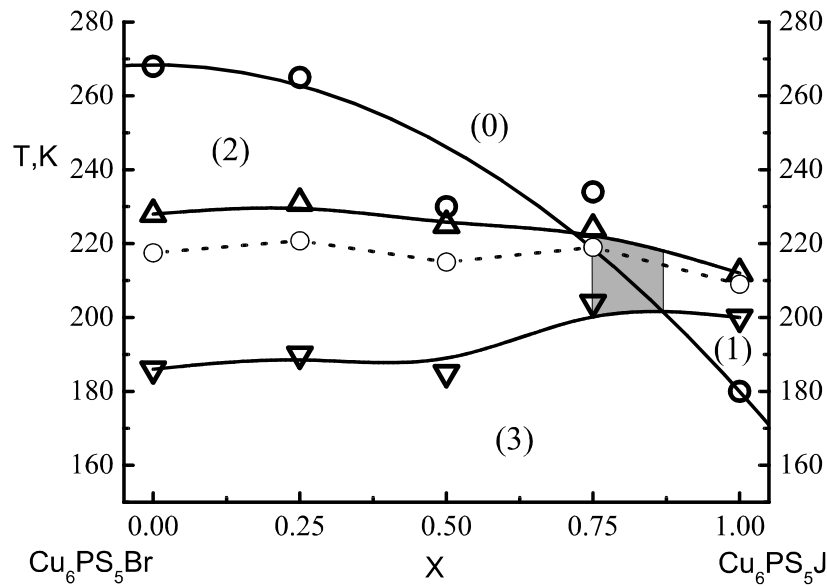


Fig.4. x, T -phase diagram of the $\text{Cu}_6\text{PS}_5\text{J}_x\text{Br}_{1-x}$ mixed crystals: (0) - paraelectric-paraelastic-SI phase (symmetry $\bar{4}3m$), (1) - paraelectric-paraelastic-nonSI ($\bar{4}3m$), (2) - FF-SI (m), and (3) - FF-nonSI (m). The curve of FFPT is marked with open circles; the upper and lower triangles indicate the curves of SI PT at heating and cooling, respectively; the dashed curve indicates the Curie temperature of the SI PT.

the two curves that correspond to the temperatures of T_S at cooling and heating. The temperature of T_S slowly increases with decreasing x , while the hysteresis width decreases. It follows from thermodynamic theory of the first-order PTs (see, e.g., [11]) that

$$T_{s,c} = T_{\max} - \frac{1}{4} \Delta T_h,$$

where $T_{s,c}$ is the Curie temperature of the SI PT and T_{\max} the SI PT temperature at heating. The $T_{s,c}$ values calculated with the mentioned above formula are presented as a dashed curve in Figure 4. The crossing of this curve with the curve of FFPTs would determine the coordinates of the polycritical point. Namely, we have $(x; T) = (0.76; 217\text{K})$.

Conclusions

Using the studies for temperature dependences of the domain structure, thermal expansion and the ultrasonic velocity, the x, T -phase diagram of the $\text{Cu}_6\text{PS}_5\text{J}_x\text{Br}_{1-x}$ mixed crystals is obtained. It is shown that all the compounds possess the first-order SI PTs, the temperatures of which are determined on the basis of thermal expansion measurements. The mixed crystals with the concentrations $x=0 \div 1$ manifest the second-order

structural PTs into the FF phase. The temperatures of these PTs are determined with the domain structure observations, the ultrasonic velocity study and the thermal expansion measurements. We conclude from our results that the FFPT occurs in the $\text{Cu}_6\text{PS}_5\text{J}$ crystals at $T_C = 180\text{K}$. In the composition range of $x=0 \div 0.75$, the temperature of structural PT slowly decreases and the line of T_C crosses the line of T_S approximately at $x=0.75$ (at heating) and at $x=0.9$ (at cooling). Due to a wide temperature hysteresis of T_S in the range $\Delta x=0.75 \div 0.9$, the sequence of PTs should depend on the temperature scan process, being different at cooling and heating. The polycritical point exist in this range of compositions, at which the crossed curves of PTs separate the following phases: paraelectric-paraelastic-SI (symmetry $\bar{4}3m$); paraelectric-paraelastic-nonSI ($\bar{4}3m$); FF-SI (m) and FF-nonSI (m). The coordinates of the polycritical point are determined as $(x; T) = (0.76; 217\text{K})$.

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