Optical Observation of Ferroelastic Domains in Cu_6PS_5X (X=I,Br,Cl) Crystals

D.I. Kaynts, I.P. Studenyak, I.I.Nebola, A.A.Horvat

Institution for Solid State Physics and Chemistry, Uzhgorod National University, 46 Pidhirna St., Uzhgorod, 88000, Ukraine

Received: 14.10.2002
After revision: 12.12.2002

Abstract

The ferroelectric-ferroelastic domain structure in Cu_6PS_5Br and $Cu_6PS_5I_{0.8}Cl_{0.2}$ crystals is investigated using a polarizing microscope. Four types of domain walls are found. These domain walls separate at least six orientation states. The domain walls are classified as W and W` walls. The $Cu_6PS_5I_{0.8}Cl_{0.2}$ ferroelastic phase transition temperature point is detected on the base of birefringence temperature dependence.

Key words: ferroelastic and superionic crystals, domain structure.

PACS: 77.80Dj ; 42.25Lc

Introduction

Cu_6PS_5Br crystals belong to the argyrodite-type structures, being characterized by dense tetrahedral packing of phosphorus and sulfur atoms as well as partial occupation of equivalent copper sites. Their crystal structure is characterized by a high concentration of disordered vacancies and they are known as fast-ion conductors and ferroelastics [1,2]. At room temperature they belong to cubic symmetry ($F\bar{4}3m$ space group of symmetry). In Cu_6PS_5Br a sequence of the ferroelastic and superionic phase transitions are realized at T_c=268K and T_s=169K respectively. The X-ray studies show that Cu_6PS_5Br crystals belong to a monoclinic syngony (*Cc* space group of symmetry) below the temperature of the superionic phase transition (PT), ($T\approx$100 K). But phase symmetry between ferroelastic and superionic phase transitions has not yet been determined, while the transition to superionic state seems to be an isostructural one [3]. The corresponding phase transition temperatures for pure Cu_6PS_5X (X=I,Br,Cl) crystals are listed in Tab.1. In the vicinity of the PT an anomalous behavior of the electrical conductivity, specific heat, dielectric constants, elastic and optical properties are observed in Cu_6PS_5X crystals [2, 4-7].

The possibility of the existence of an intermediate phase between known high- and low-temperature phases allows the investigation of real ferroelastic domain structure and its temperature behavior both in pure Cu_6PS_5Br crystals and the solid solutions on their base.

Table 1.

Temperatures of the ferroelastic (T_c) and superionic (T_s) phase transitions in the Cu_6PS_5X crystals.

Compound	T_c (K)	T_s (K)
Cu_6PS_5Br	268±2	173±7
Cu_6PS_5Cl	241±2	165±10

Experimental

The Cu_6PS_5Br and $Cu_6PS_5I_{0.8}Cl_{0.2}$ crystals were obtained by the conventional vapor-transport method. The crystals were grown from a mixture, enriched by CuX(X=I,Br,Cl)+Cu_2S. The temperature at the «hot» zone of the vessel was kept between 550…750^{o}C, and at the «cool» one – 500…650 ^{o}C, depending on the crystal composition. To determine the ferroelastic PT temperature point in the $Cu_6PS_5I_{0.8}Cl_{0.2}$ mixed crystals, the variation of the birefringence as the function of temperature was studied. The measurements were carried out at λ=0.63 μm in the temperature range of 77 to 295 K. The samples were oriented at room temperature so that the light beam propagated along its [100] crystallographic direction (in the cubic phase). The birefringence Δn was measured by the interference of polarized light. Temperature stabilization is provided by UTREKS cryostat. The error in the Δn determination did not exceed $\pm 5\times 10^{-5}$. Ferroelastic domain studies were carried out using a polarizing microscope.

Results and discussion

The investigations of the domain structure using a polarizing microscope in pure crystals were carried out in Cu_6PS_5Br and $Cu_6PS_5I_{0.8}Cl_{0.2}$ crystals. The domain structure formation in the Cu_6PS_5Br begins at the ferroelastic phase transition temperature T_c =(268±2)K. In the samples oriented along $\bar{4}$ cubic axis the seeding of the domains and their transformation with

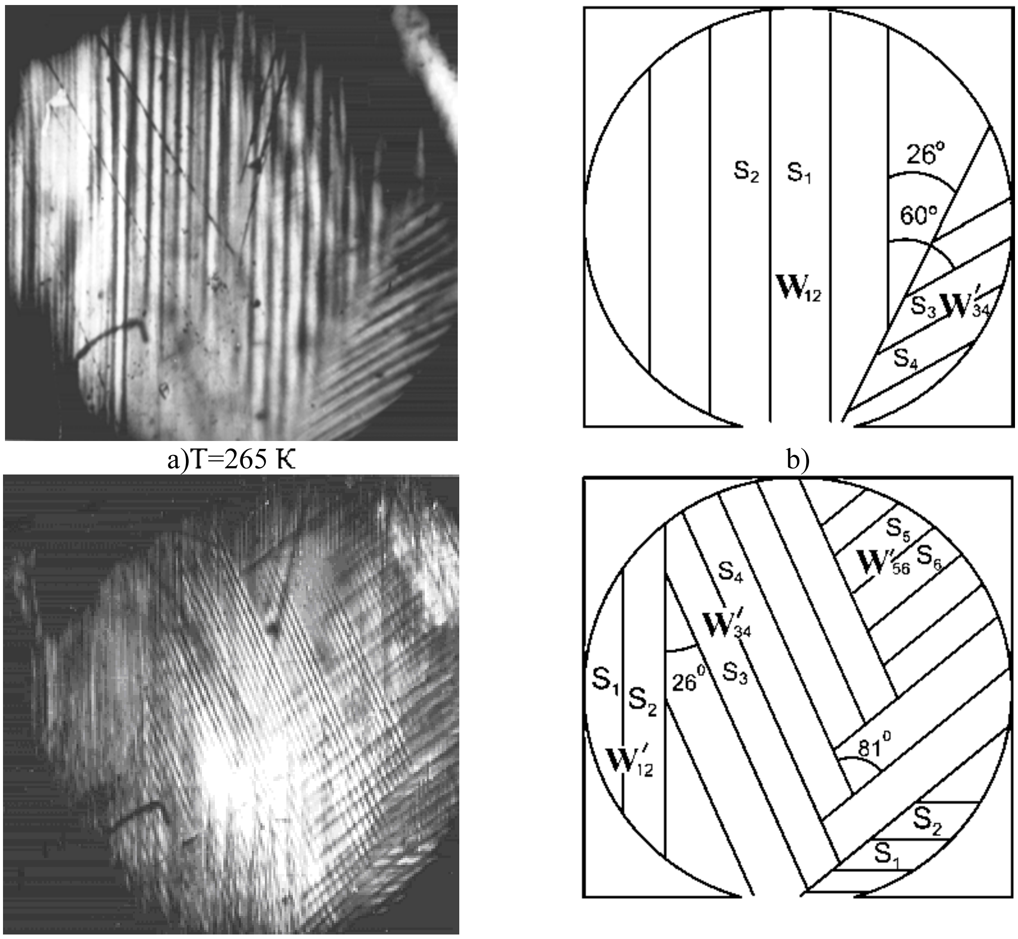

Fig.1. Domain structure observed using a polarizing microscope in the Cu_6PS_5Br crystals (a,c), schematical views (b,d).

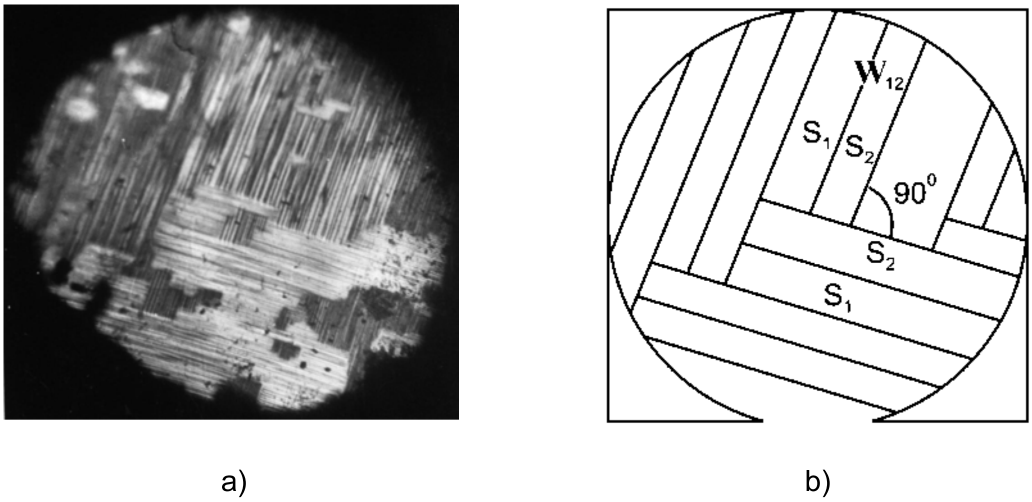

Fig.2. Domain structure observed using a polarizing microscope in the $Cu_6PS_5I_{0.8}Cl_{0.2}$ crystals (a), schematical views (b).

temperature were observed using a polarizing microscope. In Cu_6PS_5Br crystals at ferroelastic PT ($\bar{4}3mFm$ symmetry change) 12 orientation states and 45 different kinds of domain walls could exist as it was predicted in [8]. In our case only a few of them were observed.

In the low-symmetry phase ($T<T_c$) in the (100) plane one can distinguish six types of domains and four different orientations of domain wall traces on (100) plane (Fig. 1). On Figure 1a,b types of domain walls are clearly visible that probably separates four orientation states. The angle between traces of these walls on the (100)-plane is equal 60°. Since one of these walls is W - wall that separates S1 and S2 orientation states as well as the other one W` - wall separates S5 and S6 orientation states. This domain wall can be described by the relation $ey+dz=0$. On Figure 1c,d two pairs of traces of the walls are visible (four walls). One pair of walls possess orthogonality. The angle between them is equal 90°. These walls separate two orientation states S1 and S2 and are W - walls. The second pair of walls separates other

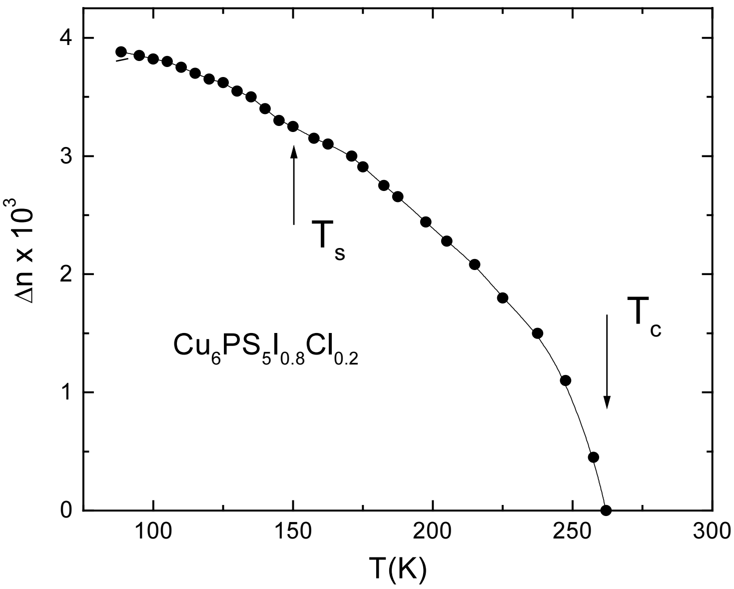

Fig.3. Temperature dependence of the birefringence for$Cu_6PS_5I_{0.8}Cl_{0.2}$ crystals

orientation states. This pair is "quasiorthogonal". The angle between traces of the walls is equal 81°. More probably these walls do not belong to one mutually perpendicular pair. They are W` walls and separate S3, S4 and S5, S6 orientation states.

In Figure 2 the domain structure of $Cu_6PS_5I_{0.8}Cl_{0.2}$ mixed crystals is presented. As it is visible from Figure 2 a,b in the sample with 570μm thickness two mutually perpendicular walls exist that separate two orientation states S1 and S2. In the more thin sample (d=87μm) domain configuration becomes more complicated. Two of the domain walls are mutually perpendicular (W - walls). They separate two orientation states S1 and S2. Probably they do not penetrate through all the sample and perhaps it is the reason why these walls are smeared. Two other traces of the walls are inclined to the angle 60°. These walls do not form the pair since they separate four different domains S3, S4, S5 and S6. At temperatures lower than superionic PT temperature point ($T<T_s$) no changing in domain wall orientation nor formation of new ones were observed.

The birefringence temperature dependence was measured to determine the order of ferroelastic phase transition and its temperature point. These results for $Cu_6PS_5I_{0.8}Cl_{0.2}$ crystal are presented in Fig. 3 and are rather similar to Δn *vs* T dependence obtained in the pure Cu_6PS_5Br crystals [2,9]. As a result we obtained the temperature of ferroelastic PT T_c=(261±1)K. In the temperature interval 170<T<240K the $|\Delta n|$ increase occurs with the temperature decreasing. At the 140<T<170K negligible anomaly inspired by superionic PT is observed, and its temperature interval becomes wider than in pure Cu_6PS_5I crystal as a result of structure disordering.

Conclusions

The Cu_6PS_5Br crystals possess both ferroelastic and superionic phase transitions. The ferroelectric-ferroelastic domain structure in Cu_6PS_5Br and $Cu_6PS_5I_{0.8}Cl_{0.2}$ crystals is investigated using a polarizing microscope. Four types of domain walls have been found. These domain walls separate at least six orientation states. The domain walls found are classified as W and W` walls. The $Cu_6PS_5I_{0.8}Cl_{0.2}$ ferroelastic phase transition temperature point is detected on the base of birefringence temperature dependence.

References

1. Kuhs W. F., Nitsche R. and Scheunemann K. , Mater. Res. Bull. **14** (1979) 241.
2. Studenyak I. P. , Kovacs Gy. Sh. , Orliukas A. S. and Kovacs Ye. T. News of Acad.Sc. Phys.is. **56** (1992) 86 (in Russian).
3. Haznar A., Pietraszko A. and Studenyak I.P. Solid State Ionics **119** (1999) 31.
4. Fiechter S. and Gmelin E., Thermochim. Acta. **85** (1985) 155.
5. Studenyak I. P. , Vaytkus R.A., Dyordyay V.S., Kezhenis A.P., Mikuchenis V.F., Panko V.V., Kovacs Gy. Sh., Stefanovich V. O., Orliukas A.S., Borets A.N., Slivka.V.Yu. Phys.Stat.Sol. **28** (1986) 2555 (in Russian).
6. Samulionis V., Valevičius V., Studenyak I. P., Kovač D.S., Ultragarsas **25** (1993) 129.
7. Studenyak I.P., Stefanovich V. O., Kranjčec M., Desnica D.I., Azhnyuk Yu.M., Kovacs Gy.Sh., PankoV.V. Solid State Ionics **95** (1997) 221.
8. Sapriel J., Phys.Rev.B. 12 (1975) 5128.
9. Studenyak I.P., Kranjčec M., Suslikov L.M., Kovacs Gy. Sh., Hagymashi Z.P., Ukr.J.Phys. **47** (2002) 447 (in Ukrainian).