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# Natural polarization in $Cu_3In_5S_9$ single crystals

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**Abstract**

Natural polarization in $Cu_3In_5S_9$ single crystals was studied. Pyrocurrent curves were recorded under various conditions, including heating shorted and open current-carrying contacts. The natural polarization vector was determined from the area bounded by the pyrocurrent curves.

**Keywords**: $Cu_3In_5S_9$ single crystals, pyroelectric current, natural polarization.
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## 1. Introduction

It is known that in the $In_2Se_3$ structure [1], indium atoms occupy tetrahedral and 3/4 octahedral positions. By replacing these atoms with others, ternary analogs with the In2Se3 structure and qualitatively new physical properties were obtained. These studies revealed the possibility of forming $A_3^I B_5^{III} C_9^{VI}$-type ternary compounds, which are isostructural derivatives of the $In_2Se_3$ structure, with the only difference being that the tetrahedral indium cations are replaced by monovalent copper atoms, maintaining the overall valence balance of the compound. In this study, natural polarization in $Cu_3In_5S_9$ single crystals was used.

It is known that when an electric field is applied, some crystals become polarized, and their polarization is characterized by a vector P, which is equal to the sum of the electric moments of the molecules per unit volume. However, in some cases, in

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such crystals, without the application of an external electric field, the crystal transitions from a parametric state to a ferroelectric state Pυ, which is called natural polarization. It depends on external factors such as temperature and illumination. The magnitude of natural polarization is determined by the area of the pyroelectric current, which occurs during heating and cooling of the crystal.

## 2. Experimental technique

The crystals were grown by the Bridgmen method in an evacuated ($10^{-4}$ Torr) quartz tubes X-ray investigation measurements showed that the crystals belong to the $Cu_3In_5S_9$ and have has a monoclinic structure with parameters *a*=6.60; *b*=6.91; *c*=8.12 $A^0$; β=890; z=1.

The samples for measurements were cleaved from the single crystal boules in the direction perpendicular to the crystallographic z-axis. Electrical contact for measurements was provided by a silver paste. The samples were mounted on to the copper finger of the low-temperature liquid nitrogen cooled cryostat, which had two optical windows. Illumination was performed by 400 W lamps DRS-250.

Measurements of pyroelectric current were made by quasi-static method with a rate of temperature scanning ~ 3 K/min. Temperature of samples was changed at a rate of 0,14 K/sec. The sensitivity of the equipment used was ~ 0,2 pF and the measurements were perfomed at frequency 50 kHz.

## 3. Experimental results and their discussion

In our case, $Cu_3In_5S_9$ crystals were heated at a rate of 0.16 K/s, resulting in a complex pyroelectric current curve (Fig. 1). The pyroelectric current curves were recorded under various conditions (Fig. 1, curves 1, 2, 3). As can be seen from the figure, natural polarization changes depending on the temperature range. The pyrocurrent in a $Cu_3In_5S_9$ single crystal upon heating was measured as follows: 1 – the crystal is naturally polarized with shorted (curve 1 in Fig. 1) and open contacts (curve 2 in Fig. 1); 2 – the crystal is polarized in the ferroelectric phase upon application of a field E=300 V/cm (curve 3 in Fig. 1). Then, the pyrocurrent of the naturally polarized crystal was measured again with shorted contacts (curve 4 in Fig. 1).

During the above measurements, the following features of the pyrocurrent in $Cu_3In_5S_9$ crystals were revealed: The magnitude of the natural polarization and the shape of the pyrocurrent curves for the same crystal do not depend on how the crystal was cooled (with open or closed contacts). It should be noted that with open contacts, a maximum of about 210 K is more clearly manifested (Fig. 1, curves 1 and 2). If, between two pyrocurrent measurements, the crystal is polarized in the ferroelectric phase by a constant electric field and then heated to 300 K and then the pyrocurrent (respectively $P_0$) is measured, the $P_0$ value is almost restored, but the pyrocurrent curves differ from the original ones (Fig. 1, curves 1 and 4). With multiple measurement cycles, the pyroelectric current maxima shift to the low-temperature region and are located around 215 K, 204 K, 193 K.

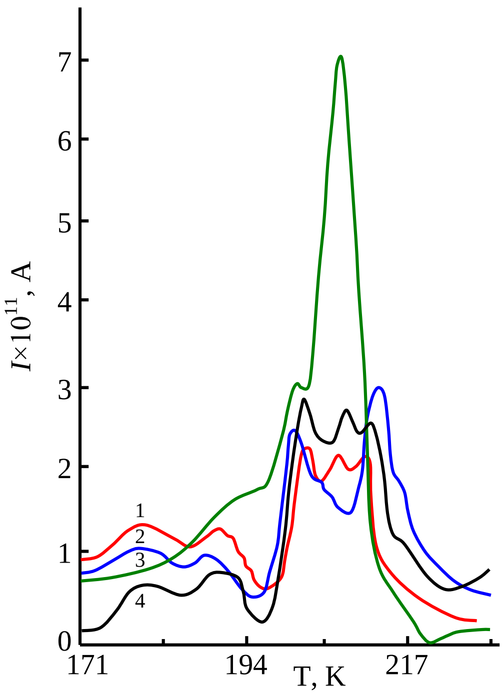


**Fig. 1.** Pyrocurrent curves during heating in $Cu_3In_5S_9$ single crystals. 1 – natural polarization with shorted contacts; 2 – natural polarization with open contacts; 3 – polarized by a 300 V/cm field in the $P_0$ direction; 4 – naturally polarized again.

As follows from a comparison of curves 1, 2 and 4, the polarization direction corresponding to the direction of the pyrocurrents (Fig. 1, curves 3, 4, 1) is the direction of preferential polarization, since the effect of the opposite field (Fig. 1, curve 3) is completely "erased" in the crystal during subsequent natural polarization. This to some extent demonstrates the unipolarity of the $Cu_3In_5S_9$ crystal. This phenomenon was discovered in SbSI crystals [2-6] and is explained by the fact that polarization charges are present on the crystal surface, compensated by external or internal charge carriers. If the domains in such crystals are depolarized by heating above the Curie point, then the charge distribution at the surface levels turns out to be such that it corresponds to the previous domain structure. If the crystal is cooled again before this charge distribution disappears, then the original domain structure appears, as the most favorable. As was pointed out in [7], in addition, any real crystal is imperfect, so there is a pinning of domain walls, which can also contribute to the formation of the initial domain structure. In SbSI, the equilibrium filling of surface levels mainly determines the magnitude of natural polarization, which, in our opinion, plays a significant role in $Cu_3In_5S_9$ crystals.

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