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Ultrasonic and piezoelectric studies of new layered ferroelectric compounds of $Sn_2P_2S_6$ family

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Abstract

Ultrasonic and piezoelectric studies of two-dimensional layered crystalline structures of $MM^1P_2X_6$ (M,M^1 = Cu, In, Sn, Cr; X = S, Se) are presented in this contribution. It was shown, that such materials: $CuInP_2S_6$, $CuCrP_2S_6$ and $CuInP_2Se_6$ undergo phase transitions (PT) and exhibit piezoelectric effect in low temperature phases. Anomalies of ultrasonic velocity and attenuation at phase transitions have been observed in these materials. Measurements of temperature dependencies of ultrasonic velocity and attenuation revealed the first order phase transition at $T_c \approx 312$ K in $CuInP_2S_6$; two successive phase transitions at $T_{c1} \approx 180$ K and $T_{c2} \approx 145$ K in $CuCrP_2S_6$; and two phase transitions at $T_{c1} \approx 235$ K and $T_{c2} \approx 228$ K in $CuInP_2Se_6$.

Keywords: Crystalline plates; Piezoelectric properties

1. Introduction

Tin hypotiodiphosphate $Sn_2P_2S_6$ is a ferroelectric-semiconductor material, exhibiting strong piezoelectric effect and suitable for applications in electroacoustics and electrooptics.[1–3] Substitution of chemical elements in this material allows obtaining new compounds exhibiting rich variety of physical properties, photosensitivity and ionic conductivity. Recently layered materials such as: $CuInP_2S_6$, $CuInP_2Se_6$, $CuCrP_2S_6$ and SnP_2S_6 were obtained in form of thin crystalline plates. $CuInP_2S_6$ crystals represent an example of a collinear two-sublattice ferrielectric system.[4] The first order phase transition (PT) of the order–disorder type from paraelectric to ferrielectric phase is realized at $T_c \approx 312$ K. The symmetry change at the PT (C2/c ↔ Cc) occurs due to ordering in cooper sublattice and displacement of cations from the centrosymmetric positions in the indium sublattice.[5] The spontaneous polarization arising at the PT is perpendicular to layer plane and directed along *c*-axis. The phase transition is accompanied by anomalous behaviour of physical properties.[6,7] According to calorimetric, dielectric and X-ray data,[8] $CuCrP_2S_6$ crystalline plates undergo two phase transitions at $T_{c1} \approx 190$ K and $T_{c2} \approx 150$ K, and have three phases: paraelectric ($T > T_{c1}$), antiferroelectric ($T < T_{c2}$) and intermediate quasi-antipolar in the temperature range ($T_{c2} < T < T_{c1}$). It was shown, that the paraelectric phase has symmetry C2/c and the antiferroelectric phase — Pc symmetry. The intermediate phase is characterized by incomplete antipolar ordering of the cooper cation sublattice and is treated as a kind of dipolar glass or incommensurate structure.[8,9] $CuInP_2Se_6$ layered crystals also are non-compensated ferrielectrics with two cation sublattices (indium and cooper).[10,11] In $CuInP_2Se_6$ compounds the first order PT at $T_{c2} \approx 236$ K and second order PT at $T_{c1} \approx 249$ K (the symmetry reduction P$\underline{3}$1c ↔ P31c at the PT) was observed.[12] The layered crystalline plates of SnP_2S_6 belong to R3 symmetry group, which is preserved until melting temperature. Hence, the ultrasonic and piezoelectric properties of these materials are almost unknown; the present contribution is aimed at studying the phase transitions, polarization processes in above described materials by temperature investigations of ultrasonic and piezoelectric properties.

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2. Experimental

Ultrasonic velocity and attenuation measurements were carried out by computer controlled pulse-echo equipment.[13] Ultrasonic system allowed us to measure delay intervals less than 0.2 ns, therefore the relative ultrasonic velocity measurements in very thin samples were possible. Piezoelectric measurements were performed on automatic resonance–antiresonance apparatus. Silicone oil was the material for making acoustic bonds. Silver paint electrodes were used for electric measurements.

3. Results and discussion

The ultrasonic and piezoelectric data of $CuInP_2S_6$ thin plates, prepared by solid-state reaction, were presented earlier.[7] Recently, better quality $CuInP_2S_6$ crystals of 0.4 cm × 0.6 cm × 0.6 cm dimensions were grown by Bridgman method. Therefore, it was possible to measure ultrasonic properties in two directions: across and along layers of the crystal. The crystallographic *c*-axis was perpendicular to layers. Measurements of the temperature dependencies of longitudinal ultrasonic velocity and attenuation coefficient revealed increase of attenuation and critical slowing down in velocity at the PT. Anomalies of ultrasonic velocities, measured in both directions, are shown in Fig. 1. Velocity dip at PT is considerably less for the ultrasonic wave propagating along layers. Such anisotropy arises from orientation dependence of corresponding elastic constants, which depend on appropriative electrostriction coefficients.[14] By direct measurements of electric signal from c-cut $CuInP_2S_6$ piezoelectric transducer, it was shown, that piezoelectric effect exists in ferrielectric phase below 312 K (Fig. 2). In this experiment, the exciting 10 MHz lithium niobate transducer was attached to one end of quartz buffer and to another end the thin $CuInP_2S_6$ plate was glued. The temperature dependence of detected by such transducer roughly represents the temperature dependence of electromechanical coupling coefficient of $CuInP_2S_6$ plate.

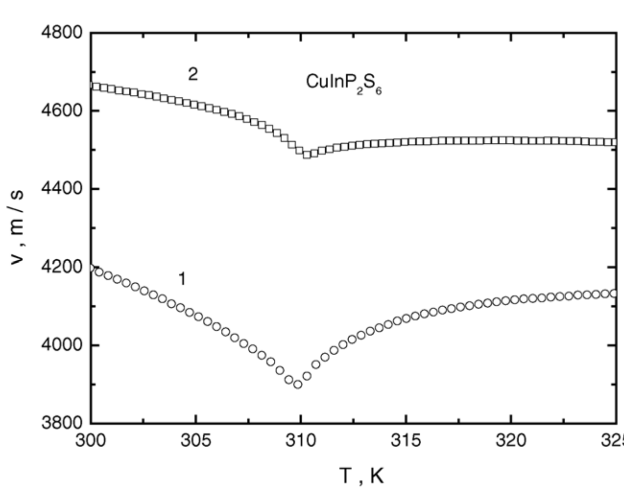

Fig. 1. The temperature dependencies of longitudinal ultrasonic velocity measured along (1) and (2) perpendicular to *c*-axis in $CuInP_2S_6$ crystal at 10 MHz frequency.

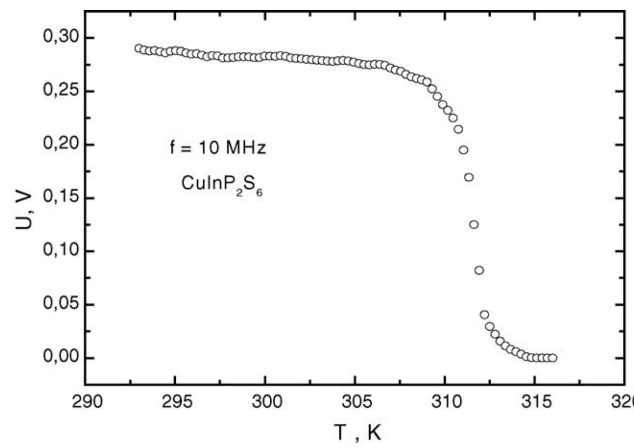

Fig. 2. The temperature dependence of electric signal detected by c-cut $CuInP_2S_6$ plate.

As it was described in introduction, two successive PT are expected to occur in $CuCrP_2S_6$ crystals. Indeed, the temperature dependencies of longitudinal ultrasonic velocity and attenuation measured along *c*-axis in $CuCrP_2S_6$ crystals show two anomalies near temperatures $T_1 = 180$ K and $T_2 = 145$ K (Fig. 3). Velocity minima correspond to the attenuation peaks. The attenuation has additional contribution, which increases with temperature increasing; it represents the influence of high ionic conductivity of $CuCrP_2S_6$ crystals.[15] In antiferroelectric phase below $T_2 = 145$ K we measured the frequency dependence of modulus of electric admittance Y for crystalline plate (thickness $d = 0.14$ mm). Electric field was applied along *c*-axis. The resonance and antiresonance character in admittance Y frequency dependence is clearly seen near 15 MHz frequency (see inset of Fig. 4). We attributed the antiresonance frequency f_a to the thickness

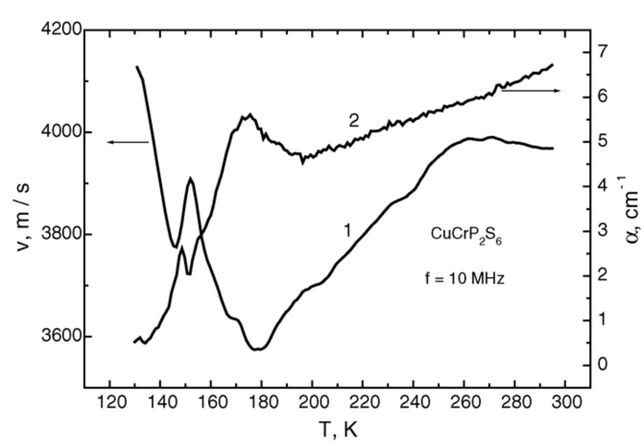

Fig. 3. The temperature dependence of longitudinal ultrasonic velocity (1) and attenuation coefficient (2) measured along *c*-axis in $CuCrP_2Se_6$ crystal at 10 MHz frequency.

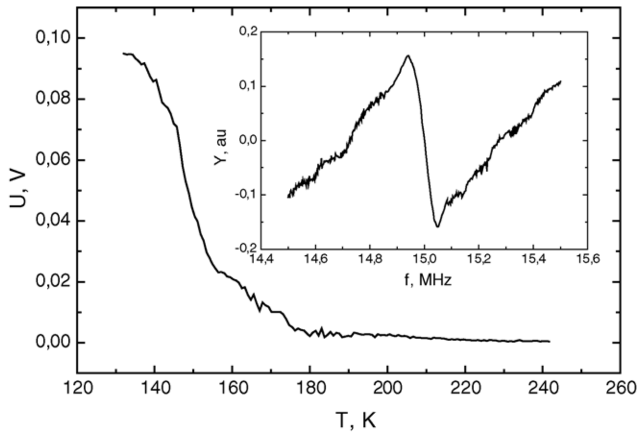

Fig. 4. The temperature dependence of electric signal detected by c-cut $CuCrP_2S_6$ plate. In the inset: the frequency dependence of electric admittance of c-cut $CuCrP_2S_6$ plate at 130 K temperature.

vibrations of the $CuCrP_2S_6$ plate. In this case the thickness of sample matches the half wavelength of longitudinal elastic wave: $f_a = V/2d$. Subsequently the ultrasonic velocity along *c*-direction have been calculated at temperature $T = 130$ K: $V_L = 4160 \pm 50$ m/s. This value we used for calibration of ultrasonic velocity measured by pulse echo method (Fig. 3). The square of the electromechanical coupling coefficient was calculated for this vibration mode from the equation:

$$K^2 = \frac{\pi f_r}{2 f_a} tg \left(\frac{\pi}{2} \frac{f_a - f_r}{f_a} \right). \quad (1)$$

The K_{33}^2 value of 2% has been obtained for the longitudinal mode of $CuCrP_2S_6$ crystal. The thin $CuCrP_2S_6$ (0.14 mm) plate quite efficiently worked as a piezoelectric transducer. The longitudinal ultrasonic wave was excited by $LiNbO_3$ transducer on 10 MHz frequency and was detected by $CuCrP_2S_6$ plate at $T = 130$ K temperature. The temperature dependence of detected by $CuCrP_2S_6$ transducer signal was measured (Fig. 4) and it was shown, that this signal drops down at $T_2 = 145$ K and completely disappears in the paraelectric phase (above $T_1 = 190$ K). It should be noted that small signal is observed and in the intermediate phase. This somewhat shows the polarisation of material, and we can conclude that, the intermediate phase ($145 < T < 180$ K) can be quasi-antipolar.

Similar results were obtained from ultrasonic velocity measurements, which were performed in layered $CuInP_2Se_6$ crystals. The temperature dependencies of longitudinal ultrasonic velocity have been measured along *c*-axis at 10 MHz frequency and anomalies at two PT have been observed (Fig. 5). Due to the small thickness of sample ($d = 0.16$ mm), it was impossible to obtain reliable ultrasonic attenuation data. The temperature dependence of ultrasonic velocity shows that there are two minima near temperatures $T_1 = 236$ K and $T_2 = 229$ K. There is some mismatch of transition temperatures from previous measurements,[11,12]

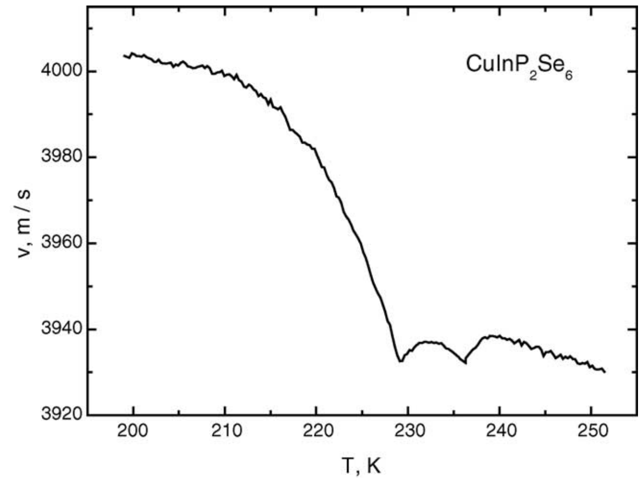

Fig. 5. The temperature dependencies of longitudinal ultrasonic velocity measured along *c*-axis in $CuInP_2Se_6$ crystal at 10 MHz frequency.

but it can be related to the different preparation conditions of $CuInP_2Se_6$ crystals. The steep increase of velocity in low temperature phase (below 125 K) is similar to that which was observed in DDSP, DMAAS and $CuInP_2S_6$ single crystals,[7,16] where the relaxation time of the order parameter was comparatively long. In this case, the temperature dependence of ultrasonic velocity in the low temperature phase is determined by elastic constant, which has additional contribution proportional to square of order parameter (see[16] for details). In order to confirm the existence of piezoeffect, we measured the frequency dependence of modulus of electric admittance *Y* along *c*-axis of the crystalline plate (thickness $d = 0.16$ mm). At 210 K temperature, the resonance and antiresonance were observed at 12.34 and 12.54 MHz frequencies correspondingly (inset of Fig. 6). If we consider the thickness vibrations of the $CuInP_2Se_6$

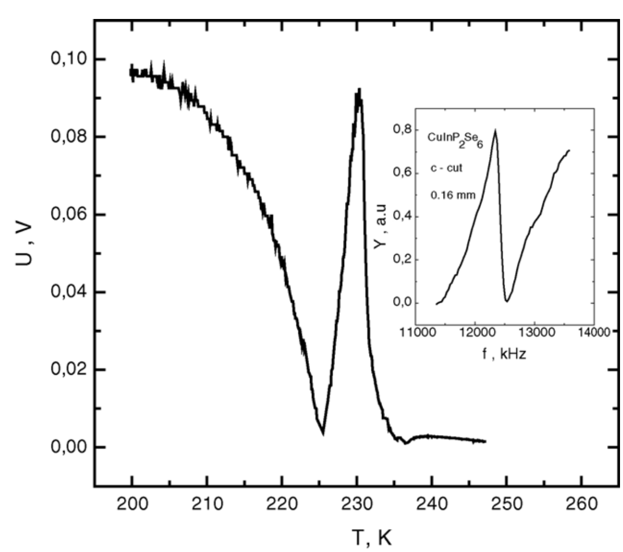

Fig. 6. The temperature dependence of electric signal detected by c-cut $CuInP_2Se_6$ plate. In the inset: the frequency dependence of electric admittance of c-cut $CuInP_2Se_6$ plate at 210 K temperature.

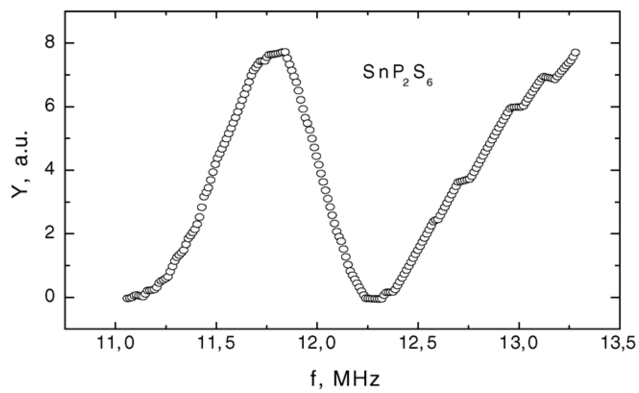

Fig. 7. The frequency dependence of electric admittance of c-cut SnP_2S_6 plate at room temperature.

plate, the value of ultrasonic velocity along *c*-axis can be calculated at temperature $T = 210\,K$: $V_L = 4000 \pm 50\,m/s$. The square of the electromechanical coupling coefficient for this vibration mode was found from the Eq. (1): $K_{33}^2 = 4\%$. In order to determine temperature interval of the existence of a piezoeffect in $CuInP_2Se_6$ we also made direct experiment on the same thin 0.16 mm plate vibrating as a piezoelectric transducer and attached to quartz buffer. The temperature dependence of detected by such $CuInP_2Se_6$ transducer signal is shown in Fig. 6. At low temperature we observed comparatively large signal. In heating cycle signal has a minimum at 226 K, increases in the intermediate phase ($T_2 < T < T_1$) then has another drop down and completely disappears in the paraelectric phase (above $T = 240\,K$). Of comparison to the same experimental data of $CuCrP_2S_6$ described above, we can conclude that the intermediate phase in $CuInP_2Se_6$ has no symmetry centre, i.e. it is also quasipolar phase.

We confirmed the existence of piezoeffect also in thin SnP_2S_6 plates. At room temperature, the mechanical resonance was observed in frequency dependence of an electric admittance *Y* (Fig. 7). Experimental value of the square of electromechanical coupling coefficient: $K_{33}^2 = 9\%$. The thin SnP_2S_6 plate also worked as piezoelectric transducer.

4. Conclusions

The piezoelectric effect was observed in new ferroelectric two-dimensional $CuInP_2S_6$, $CuInP_2Se_6$, and $CuCrP_2S_6$ layered crystals and the values of electromechanical coupling coefficients for longitudinal excitations were measured. The temperature dependencies of longitudinal ultrasonic velocity and attenuation revealed anomalies, which are indication of phase transitions in these materials. We have shown that thin plates of $CuInP_2S_6$, $CuInP_2Se_6$, $CuCrP_2S_6$ and SnP_2S_6 layered compounds can effectively excite and detect ultrasonic waves.

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