ANOMALIES OF LINEAR AND NONLINEAR ULTRASONIC PROPERTIES OF NEW PIEZOELECTRIC LAYERED CRYSTALS OF $Sn_2P_2S_6$ FAMILY

V.Samulionis* **and Yu.Vysochanskii+**
*Physics Faculty, Vilnius University, Vilnius, LITHUANIA
+Institute of Solid State Physics and Chemistry, Uzhgorod University, Uzhgorod, UKRAINE
vytautas.samulionis@ff.vu.lt

Abstract

Experimental results of ultrasonic and piezoelectric investigations of layered single crystals $CuInP_2S_6$, and $CuCrP_2S_6$ are presented. Ultrasonic measurements were performed in the frequency range 10-50 MHz. The anomalies of ultrasonic velocity and attenuation peaks near the first order phase transition (PT) temperature T_c=311 K in $CuInP_2S_6$ sample have been observed. With frequency increasing, attenuation peaks shift to lower temperatures showing the relaxation behavior. We also measured generation of the second ultrasonic harmonic arising at 20 MHz frequencies. It was shown, that the extremely large value of nonlinear elastic coefficient exists for longitudinal waves propagating across the layers. The unusual anomaly of the second harmonic amplitude in PT region is determined by increase of elastic nonlinearity near T_c. In $CuCrP_2S_6$ crystals the two critical anomalies of ultrasonic propagation at T_1=145 K and T_2=180 K exist. The piezoelectric effect has been measured in these crystals by resonance method.

Introduction

From the physical point of view, the anomalous behaviour of linear and nonlinear elastic properties near the phase transitions in ferroelectrics is important and has been widely studied [1,2]. The ferroelectric crystals of $Sn_2P_2S_6$ family are interesting due to their possible applications, because they exhibit strong piezoelectric effect, as well as semiconductive properties. Therefore, such materials could be used in acoustoelectronic and optoelectronic devices. The linear and nonlinear elastic properties of $Sn_2P_2S_6$ crystals we have investigated earlier [3,4]. Recently the new single crystals of this family were obtained. These are single crystals: $CuInP_2S_6$, $CuInP_2Se_6$ and $CuCrP_2S_6$, which also are wide energy band gap semiconductor materials exhibiting ionic conductivity, ferroelectric and piezoelectric properties [5-7]. These compounds crystallize as layered crystals. It is the main structural difference from $Sn_2P_2S_6$. Preliminary ultrasonic and piezoelectric studies were carried out in small, prepared by solid-state reactions, $CuInP_2S_6$ crystals [6]. Here we present the investigation of ultrasonic velocity, attenuation and second harmonic generation in large $CuInP_2S_6$ crystals grown by Bridgman method. It was shown, that the extremely large value of nonlinear elastic coefficient exists for longitudinal waves propagating across the layers. The ultrasonic and piezoelectric behaviour of $CuCrP_2S_6$ and $CuInP_2Se_6$ crystals near PT also is discussed.

Methods

The ultrasonic velocity and attenuation data were obtained from the phase shift and amplitude of the signal received by a computer controlled pulse-echo ultrasonic measurement system [8]. Lithium niobate transducers were used for excitation and detection of the longitudinal ultrasonic waves. The crystalline samples were carefully cut and polished. Both parallel faces of a sample were made perpendicular to the desired crystallographic axis. Silicone oil was the material for making acoustic bonds. The piezoelectric measurements were performed by automatic resonance-antiresonance analyzer. The calibration and regulation of the temperature was performed by a computer controlled device and copper constantane thermocouple as a sensor.

Results and discussion

The temperature dependence of longitudinal ultrasonic velocity along ferroelectric z-axis, which is directed across the layers, in Bridgman method grown $CuInP_2S_6$ sample exhibits large minimum near PT temperature (Fig. 1).

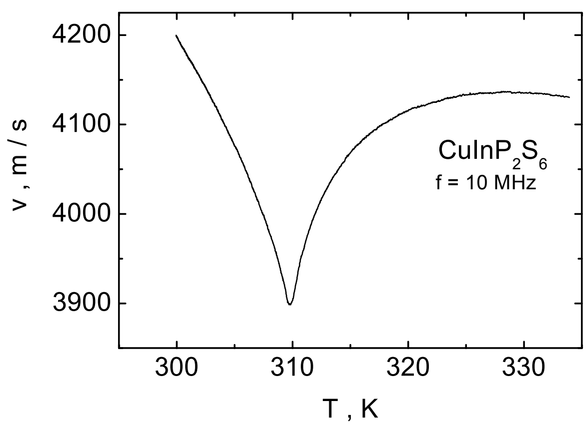

Figure 1: The temperature dependence of longitudinal ultrasonic velocity measured along *z*-axis in $CuInP_2S_6$ crystal at 10 MHz frequency

The data were collected in cooling cycle. It should be noted, that in heating cycle the thermal hysteresis of about 2 K is observed, which shows the first order nature of PT in $CuInP_2S_6$ compound [5]. The velocity minimum is accompanied by ultrasonic attenuation peaks. With frequency increasing from 10 to 50 MHz, attenuation maximum shifts to lower temperatures

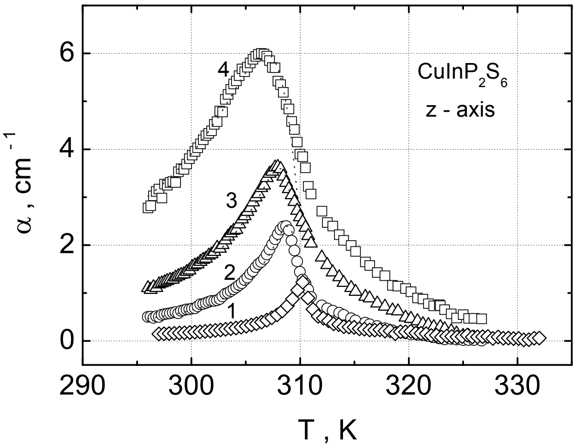

Figure 2 : The temperature dependencies of ultrasonic attenuation coefficient measured along *z*-axis in $CuInP_2S_6$ crystal at 10 (1), 20 (2), 30 (3) and 50 (4) MHz frequencies

(Fig. 2), showing the relaxation behaviour with relaxation time increasing when approaching the PT temperature.

Temperature and frequency dependencies of ultrasonic attenuation near PT in ferroelectric phase generally can be described by Landau-Chalatnikov theory [6,9]:

$$\alpha = 2\alpha_{\max}\frac{\omega\tau}{1+\omega^2\tau^2}; \qquad (1)$$

here α_{max} - the attenuation coefficient at maximum, ω - the angular frequency of elastic wave and $\tau = \tau_0/(T_c - T)$ - the polarisation relaxation time, which increases critically approaching T_c. The peak of ultrasonic

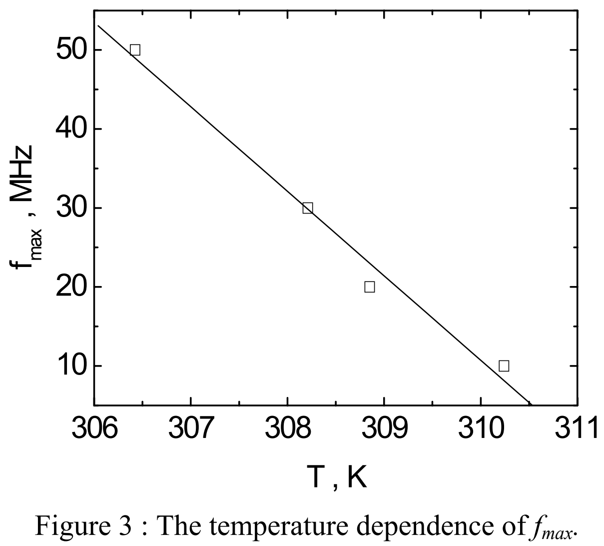

Figure 3 : The temperature dependence of f_{max}.

attenuation appears when condition $\omega\tau = 1$ fulfilled. In this case: $\omega\tau_o = T_c - T$. It means, that for higher frequencies α_{max} is reached at lower T. From the slope of the dependence $\omega_{max}/2\pi = f_{max} = f(T)$, the value of $\tau_0 = 1.4\times10^{-8}$ s K can be easily obtained (see Fig. 3). The intersection of this curve with abscise axis gives the value of T_c = 310.8 K. Using these parameters the theoretical dependencies $\alpha = f(T)$ were calculated for all frequencies and are shown in Fig. 2 by dot lines. In the paraelectric phase, long tails of anomalous ultrasonic attenuation were observed (see Fig. 2), what is determined by polar clusters existing far above phase transition point.

Very interesting results have been obtained in second longitudinal ultrasonic harmonic experiments in $CuInP_2S_6$ crystals. We measured the temperature dependencies of the second harmonic amplitude i.e. elastic displacement u_2 at 20 MHz frequency across and along the layers of the crystal. The values of elastic displacement u_2 were calculated from RF voltage appearing on receiving transducer similarly as in our previous papers [10,4]. It was shown, that the extremely large amplitude of the second harmonic was observed for longitudinal waves propagating across

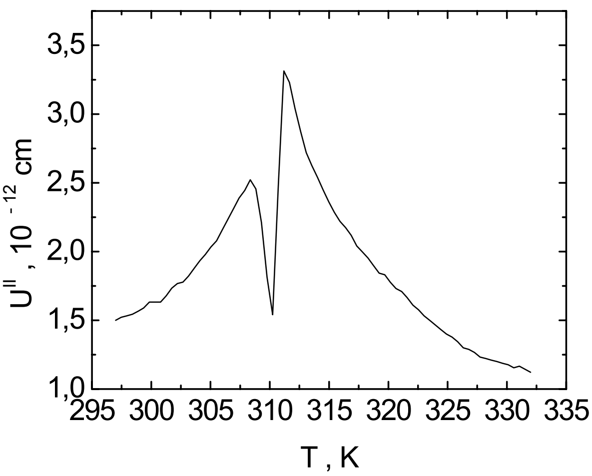

Figure 4 : The temperature dependence of the second longitudinal ultrasonic harmonic measured along *z*-axis in $CuInP_2S_6$ crystal

the layers (along *z*-axis) at room temperature. The amplitude u_2 was noticeably less when measured along the layers, normal to *z*-axis. The signal of second harmonic increased with temperature below T_c. The temperature dependence of the amplitude of the second ultrasonic harmonic measured on 20 MHz frequency is shown in Figure 4. There are two peaks of u_2. One is below PT temperature; another is in the paraelectric phase. The minimum is situated near the temperature where the peak of ultrasonic attenuation at input 10 MHz frequency exists (see Fig.2). The temperature dependence of nonlinear elastic parameter can be calculated from our obtained second harmonic and ultrasonic attenuation data. It is well known, that the amplitude of the second harmonic u_2 can be described by the following equation [11,12]:

$$u_2 = \frac{\Gamma \omega^2 u_1^2}{16 V^2 \alpha_1}[\exp(-2\alpha_1 x) - \exp(-4\alpha_1 x)] \ , \qquad (2)$$

where: x-length of the sample, Γ-nonlinear parameter, α_1- attenuation coefficient at the 10 MHz excitation frequency, u_1- the displacement amplitude at the input of the sample, V-velocity of the ultrasonic wave, ω-angular frequency. In our case: x = 0.49 cm, u_1 = 5×10^{-9} cm (this value was estimated from RF voltage on exciting 10 MHz transducer). According to above

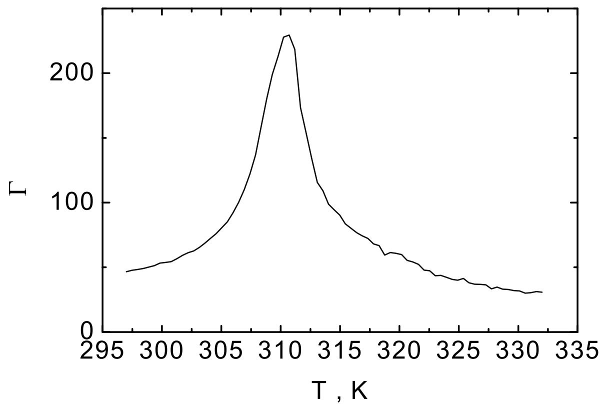

Figure 5 : The temperature dependence of nonlinear parameter for longitudinal waves along z-axis of $CuInP_2S_6$ crystal

written equation (2), using velocity, attenuation and the second harmonic amplitude data from Figs. 1, 2, 4 respectively, the temperature dependence of nonlinear parameter Γ was calculated. This dependence is shown in Figure 5. The value of nonlinear parameter at room temperature is about 50, what exceeds the nonlinear coefficient of other layered materials $KY(MoO_4)_2$ and $Si_{20}Te_{80}$ [13]. The peak of nonlinear parameter near PT can be explained by the soft mode, as in case of ferroelectric SbSI [10]. The anisotropy of nonlinear elastic properties arise from large anisotropy of bonding forces, determined by anharmonicity of appropriate longitudinal phonon modes.

Further, in this contribution, we present ultrasonic and piezoelectric investigations of layered $CuCrP_2S_6$. As it was described earlier [14], two successive phase transitions are expected to occur in these crystals. It was confirmed by our longitudinal ultrasonic velocity and attenuation measurements. The temperature dependencies of longitudinal ultrasonic velocity and attenuation have been measured along z-axis at 10 MHz frequencies in $CuCrP_2S_6$ crystals and anomalies at the phase transition have been observed (Fig.6 and 7). Due to the small thickness of a sample (d =0.14 mm) the data of ultrasonic attenuation and velocity are not very perfect. The temperature dependence of ultrasonic velocity shows, that there are two minima near temperatures T_1=180 K and T_2=145 K (Fig.6). Velocity minima correspond to the attenuation peaks

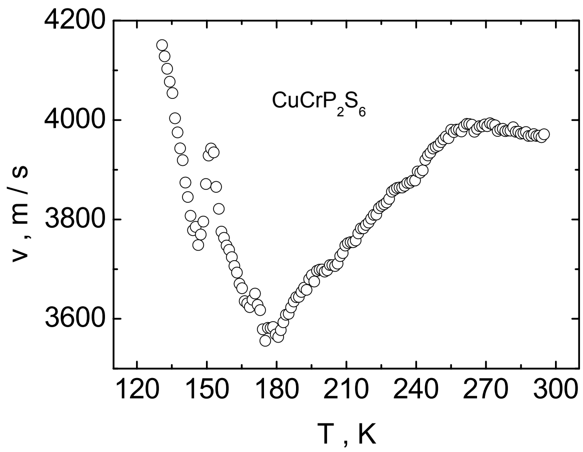

Figure 6 : The temperature dependence of longitudinal ultrasonic velocity measured along z-axis of the $CuCrP_2S_6$ crystal

(Fig.7). Such ultrasonic behaviour is in a good agreement with colorimetric data [14]. The attenuation has additional contribution, which increases with temperature increasing. It can be determined by the influence of high ionic conductivity of $CuCrP_2S_6$ crystals as in other fast ionic conductors [15]. Indeed, the ionic conductivity

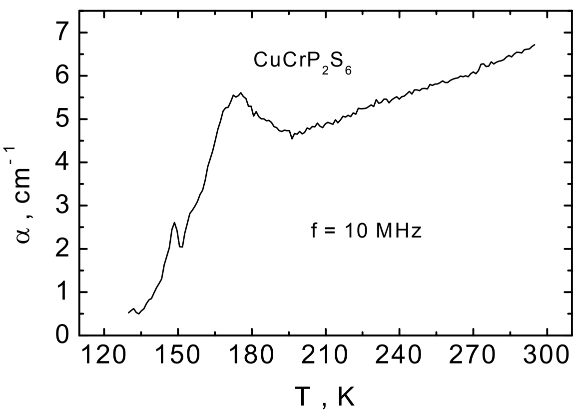

Figure 7 : The temperature dependence of ultrasonic attenuation measured along z-axis of $CuCrP_2S_6$ sample

according [5] is comparatively high for $CuCrP_2S_6$ and $CuInP_2S_6$ crystals. The long tail in ultrasonic velocity in the high temperature phase (T>180 K) of $CuCrP_2S_6$ as in case of $CuInP_2S_6$ may be caused by polar clusters, which were mentioned above. The critical contribution of defects is also possible in high temperature phase. The steep increase of velocity in antipolar phase (below 145 K) is similar to that which was observed in DDSP, DMAAS and $CuInP_2S_6$ single crystals [1,6,15], 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 must be proportional to square of order parameter. In order to confirm the existence of piezoeffect we measured the frequency dependence of modulus of electric admitance Y for thin crystalline plate (thickness d = 0.14 mm). The orientation of the sample was such, that ac electric field was directed along z - axis of the $CuCrP_2S_6$ crystal. The results are shown in inset of Fig. 7. The resonance and antiresonance character of admittance Y dependence is clearly seen near 15 MHz frequency. We attributed the antiresonance frequency f_a to the thickness vibrations of the $CuCrP_2S_6$ plate. The antiresonance is observed at frequency, when the thickness of a sample matches half wavelength of longitudinal elastic wave: $f_a = V/2d$. From this equation the value of ultrasonic velocity along z-direction have been calculated at temperature T=130 K: V_L = 4160 ± 50 m/s. This value we used for calibration of ultrasonic velocity data measured by pulse echo method (see Fig.6). The square of the electromechanical coupling coefficient was calculated for this vibration mode from the equation:

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

The K_{33}^2 value of 2 % has been obtained for the longitudinal mode of $CuCrP_2S_6$ crystal. This value is less than corresponding value K_{33}^2=8% for $CuInP_2S_6$ crystals. Nevertheless, $CuCrP_2S_6$ plate can be used for

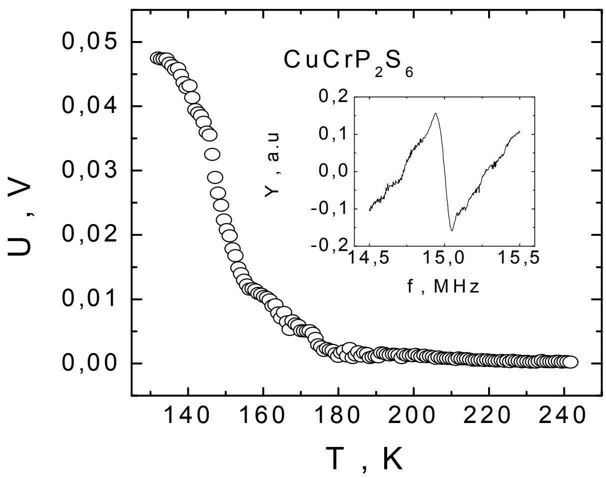

Figure 8 : The temperature dependence of electric signal detected by $CuCrP_2S_6$ plate. In the inset: the frequency dependence of electric admittance of the $CuCrP_2S_6$ plate at 130 K temperature. The linear background is subtracted.

excitation and detection of ultrasonic waves. We made direct pulse-echo experiment on the same thin 0.14 mm z-cut plate working as a piezoelectric transducer. Longitudinal ultrasonic wave was excited by $LiNbO_3$ transducer on 10 MHz frequency and was detected by $CuCrP_2S_6$ plate. The efficiency of such transducer was quite good. The temperature dependence of detected by $CuCrP_2S_6$ transducer signal was measured (Fig.8) and it was shown, that this signal drops down at T=145 K and completely disappears in the paraelectric phase (above T = 190 K). If we assume that the amplitude of detected by ultrasonic transducer signal is proportional to the square of electromechanical coupling coefficient, which somewhat shows the polarisation of material, we can conclude that, below T=145 K the antipolar phase exists and in intermediate phase (145<T<180 K) the polarisation does not vanish in $CuCrP_2S_6$ crystal [14]. Similar ultrasonic excitation was observed at temperatures below 235 K and in thin plates of $CuInP_2Se_6$ crystals, but the signal was very small due to very high ionic conductivity.

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