J Electroceram (2009) 22:192–197
DOI 10.1007/s10832-007-9397-7

Piezoelectric and elastic properties of layered materials of Cu(In,Cr)P_2(S,Se)$_6$ system

V. Samulionis · J. Banys · Yu. Vysochanskii

Received: 15 March 2007 / Accepted: 11 December 2007 / Published online: 23 December 2007
© Springer Science + Business Media, LLC 2007

Abstract In this contribution, we present new results of ultrasonic and piezoelectric investigation in layered materials of Cu(In,Cr)P_2(S,Se)$_6$ system including the phase transitions points. It was shown, that in low temperature phase the electromechanical coupling parameters substantially increased after polarization of the material. The large anisotropy of linear and nonlinear elastic properties was observed. The largest critical ultrasonic attenuation anomalies appeared for ultrasonic wave propagating normal to layers: i.e. along polarization direction. From measurements of the amplitude of second longitudinal ultrasonic harmonic we showed that these layered crystals have extremely high elastic nonlinearity in the direction normal to layers. DC bias electric field induced piezoelectricity due to electrostiction was observed in the paraelectric phase of pure materials and their solid solutions. The piezoelectric memory was observed after samples were kept for long time in DC electric field along polar axis at fixed temperature in the paraelectric phase.

Keywords Ferroelectrics · Piezoelectric properties · Elastic properties

1 Introduction

$CuInP_2S_6$ layered crystals represent an interesting example of a collinear two-sublattice ferrielectric system [1, 2]. This crystal illustrates the general features of cooperative dipole effects within a lamellar chalcogenophosphate. Here a first-order phase transition of the "order–disorder" type from the paraelectric to the ferrielectric phase is realized (T_c=315 K). The symmetry reduction at the phase transition (C2/c → Cc) occurs due to ordering in the copper sublattice and displacement of cations from the centrosymmetric positions in the indium sublattice. The spontaneous polarization arising along *c*-axis at the phase transition to the ferrielectric phase is perpendicular to the layer planes. Structure consists of lamellae defined by a sulphur framework in which the metal cations and P–P pairs fill the octahedral voids; within a layer, the Cu, In, and P–P form triangular patterns [3]. The cation off-centering, 1.6 Å for Cu^I and 0.2 Å for In^{III}, can be attributed to a second-order Jahn-Teller instability associated with the d^{10} electronic configuration. The lamellar matrix absorbs the structural deformations via the flexible P_2S_6 groups while restricting the cations to antiparallel displacements that minimize the energy costs of dipole ordering. Each Cu ion can occupy two different positions. The Cu, In or Cr ions and P–P groups form triangular patterns within the layer.

In $CuCrP_2S_6$ the Cu^I sublattice is off centered below 150 K; it coexists with an In^{III} sublattice of equal and opposite polarity [4]. So the $CuCrP_2S_6$ crystals can be defined as antiferroelectric system. At low temperature the space group changes to Cc or Pc as in $CuInP_2S_6$ material. In addition, the intermediate phase has been observed by neutron powder diffraction, calorimetric [5], ultrasonic and piezoelectric studies [6]. The phase transition sequence is very close to that of $Sn_2P_2Se_6$ where the existence of an incommensurate phase is well known. From calorimetric studies it was suggested that in $CuCrP_2S_6$ the incommensurate phase exists also [5]. This intermediate quasi-antipolar phase can be interpreted in terms of occasionally flipping dipoles in an otherwise antipolar phase, or static

V. Samulionis (✉) · J. Banys
Physics Faculty of Vilnius University,
Sauletekio 9/3,
10222 Vilnius, Lithuania
e-mail: vytautas.samulionis@ff.vu.lt

Y. Vysochanskii
Institute of Solid State Physics and Chemistry,
Uzhgorod University,
Uzhgorod, Ukraine

clusters of up and down dipoles that form “glassy” precursor to long-range order.

The $CuInP_2Se_6$ crystal also belongs to this class of chalcogenophosphate materials. Calorimetric evidence for the occurrence of a broad phase transition between 220 and 240 K in this compound was given in [7]. A single-crystal X-ray diffraction study showed that the high- and low-temperature structures of $CuInP_2Se_6$ (trigonal space group $P\text{-}31c$ and $P31c$, respectively) are very similar to those of $CuInP_2S_6$ in the paraelectric and ferrielectric phases, with the Cu^I off-centering shift being smaller in the former than in the latter [7]. Both cell parameters a and c slightly increase on cooling, only at $T=226$ K a parameters show a local minimum. This behaviour is quite different from the anomalous increases found in the cell parameters of $CuInP_2S_6$ when heating through the transition. The important feature of selenides is the higher covalence degree of their bonds. Evidently, for this reason the copper ion sites in the low-temperature phase of $CuInP_2Se_6$ are displaced only by 1.17 Å from the middle of the structure layers in comparison with the corresponding displacement 1.58 Å for $CuInP_2S_6$ [1]. These facts enable to assume the potential well for copper ions in $CuInP_2Se_6$ to be shallower than for its sulphide analog. Presumably, for this reason the structural phase transition in the selenide compound is observed at lower temperature than for the sulphide compound. The results of dielectric investigations of $CuInP_2Se_6$ showed two phase transition: a second-order one at $T_i=248$ K and a first-order transition at $T_c=236$ K [8]. There a hypothesis was put that an incommensurate phase occurs between T_i and T_c, because of the existence of anomalies of piezoelectric and elastic properties [9]. The nonpolar phase in $CuInP_2S_6$, $CuInP_2Se_6$ and $CuCrP_2S_6$ also was shown to be not of the usual paraelectric type, but, because of relatively strong dipole–dipole interactions, has polar clusters even at temperatures far above the transition [4].

With substitution of In to Cr and S to Se the solid solutions can be obtained. Therefore, it is of interest to study this polar-layered $CuInP_2S_6$ family system in order to obtain information about ultrasonic and piezoelectric behaviour near phase transitions as well as to establish the phase diagram. In this contribution, we summarize the results of extended experimental investigation piezoelectric sensitivity, linear and nonlinear elastic properties in this new family of $CuInP_2S_6$ crystals. The investigations of temperature dependencies of ultrasonic attenuation, second ultrasonic harmonic and piezoelectric properties revealed the anomalies at phase transitions. The large anisotropy of ultrasonic attenuation and harmonic generation was observed. The DC electric field induced piezoelectric effect had been found in the paraelectric phase of layered crystalline plates.

2 Experimental procedure

The crystalline samples of $Cu(In,Cr)P_2(S,Se)_6$ system were prepared by the chemical transportation reactions using the elements in the stoichiometric proportions and had the form of thin plates with c-axis normal to the plate surfaces. Large $CuInP_2S_6$ crystals were grown by Bridgeman method. The ultrasonic and piezoelectric measurements were carried out by the methods, which we previously used for such measurements in previous experiments [10,11]. Longitudinal ultrasonic velocity and attenuation measurements were carried out by automatic computer controlled pulse-echo ultrasonic system. This equipment allowed us to measure time delay changes less than 0.2 ns; therefore the relative ultrasonic velocity measurements on very thin samples were possible. In the same pulse-echo ultrasonic system simple piezoelectric measurements can be also performed. The simplified experimental set up is shown in Fig. 1. Here radio frequency pulse excites lithium niobate ultrasonic transducer T_1. Ultrasonic wave passes fused quartz buffer (QB) and excites $CuInP_2S_6$ plate. The electric signal appears only if plate is piezoelectric or in paraelectric phase piezoelectricity can be induced by applied DC voltage (U_{DC}) due to electrostriction. For calibration, the electric admittance frequency measurements of the same $CuInP_2S_6$ plate were also performed on homemade automatic resonance–antiresonance apparatus. Therefore the values of absolute sound velocity and electromechanical coupling factor at required stabilized temperature were obtained by measurements of electromechanical antiresonance frequencies. Silicone oil was the material for making acoustic bonds. Silver paint electrodes were used for electric measurements. The temperature stabilization and measurement accuracy was better than 0.03 K.

3 Results and discussion

Our former investigations of virgin $CuInP_2S_6$ layered crystalline plates [10] have shown, that in low temperature

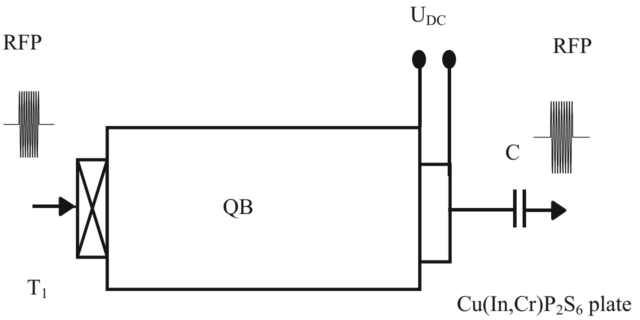


Fig. 1 Experimental set up for piezoelectric test using pulse-echo ultrasonic system. *RFP* Radio frequency pulse, T_1 lithium niobate ultrasonic transducer, *QB* quartz buffer

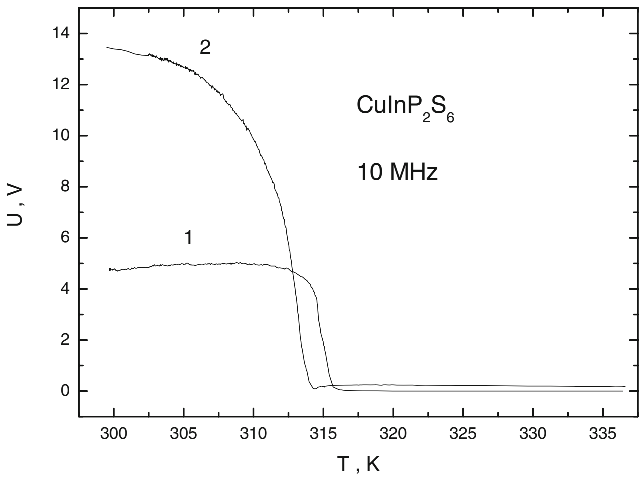


Fig. 2 The temperature dependences of ultrasonically detected piezoelectric signal in $CuInP_2S_6$ c-cut plate in heating run (*1*) and in the same plate in cooling run, when 4 kV/cm DC bias field was applied (*2*)

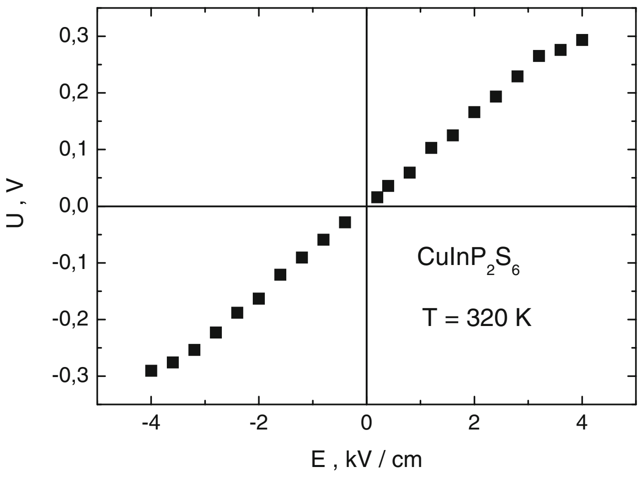


Fig. 3 The variation of longitudinal ultrasonic signal detected by $CuInP_2S_6$ plate on DC bias electric field in the paraelectric phase *T*= 320 K

phase the electromechanical coupling parameter for thickness vibrations is of order 9%. After polarizing crystal in DC bias field of 4 kV/cm along *c*-axis the signal on receiving plate increased, which is the indication of the increase of the electromechanical coupling constant. In Fig. 2 temperature dependencies of ultrasonically detected signals of virgin and polarized sample are shown. At room temperature the amplitude of received signal increased more than twice. Therefore in polarized $CuInP_2S_6$ c-cut plate the electromechanical coupling coefficient for thickness vibrations could be of order 30%. The hysteresis shows that phase transition is of the first order. The preliminary investigations by resonance method have shown that electromechanical coupling parameter increases and for shear vibrations in polarized c-cut $CuInP_2S_6$ plates. In the paraelectric phase the detected by $CuInP_2S_6$ c-cut transducer signal also was observed in experiment when DC bias field was applied Fig. 1 (curve 2). Such behaviour is determined by DC bias field induced piezoelectricity due to electrostriction. In this case after reversing of DC field polarity, the AC detected signal changed phase by 180° what was seen in the screen of the scope. The DC bias field dependence of the amplitude of ultrasonically detected signal is shown in Fig. 3 in the paraelectric phase at *T*= 320 K. The decrease of detected signal approaching the phase transition temperature is associated with the critical anomalies of ultrasonic attenuation and velocity observed earlier [10]. As it was mentioned in introduction, $CuInP_2S_6$ crystals are highly anisotropic, therefore ultrasonic attenuation peaks is much less when measured along layers. In Fig. 4 the temperature dependencies of longitudinal ultrasonic attenuation coefficient are shown for different propagation directions. The longitudinal wave attenuation peak in *c*-axis direction is more than by order larger than in the direction across layers. Usually, the ultrasonic behaviour near the ferroelectric phase transition in crystals is described by interaction of the order parameter (polarization) with the ultrasonic waves according to the relaxation theory of Landau-Chalatnikov [12], which implies piezoelectric coupling of elastic wave with order parameter and a critical increase of the polarization relaxation time. For crystals without piezoeffect in paraelectric phase the attenuation peak value is proportional to the square of electrostriction coefficient [13]. So it could be concluded that electrostriction parameters along layers are very small in comparison to that of across layers. The same orientation dependence was obtained for the second longitudinal ultrasonic harmonic amplitude. Across layers the second harmonic amplitude is very large because of extremely

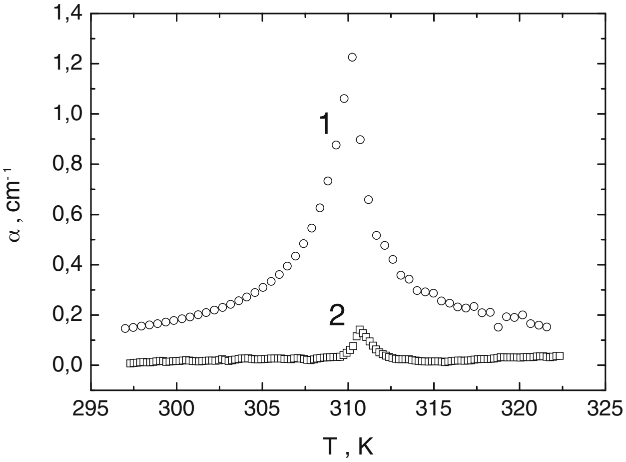


Fig. 4 The temperature dependences of longitudinal ultrasonic attenuation along (*1*) *c*-axis and normal (*2*) to *c*-axis in $CuInP_2S_6$ crystal

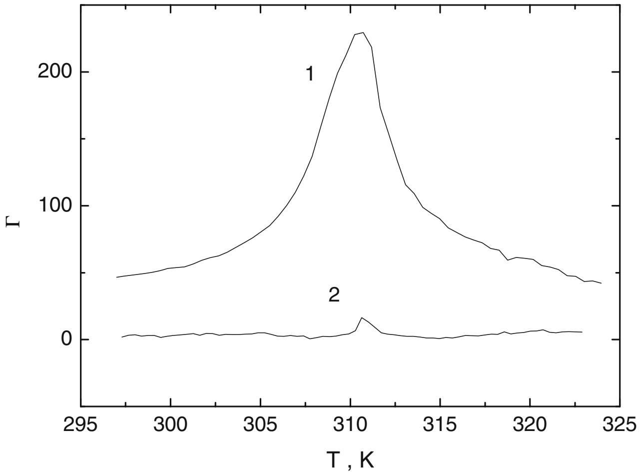


Fig. 5 The temperature dependences of nonlinear elastic parameter for longitudinal ultrasonic waves propagating along *c*-axis (*1*) and normal to *c*-axis (*2*) in $CuInP_2S_6$ crystal

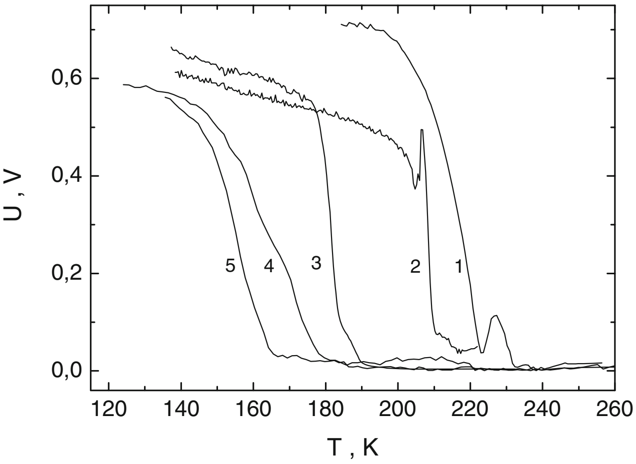


Fig. 6 The temperature dependences of ultrasonically detected piezoelectric signal in polarised $CuInP_2(S_xSe_{1-x})_6$ c-cut plates: $x=0$ (*1*), 0.05 (*2*), 0.1 (*3*), 0.2 (*4*) and 0.25 (*5*)

large acoustic nonlinearity [14], whereas along layers the second harmonic amplitude was much smaller. The nonlinear elastic parameters were calculated from ultrasonic attenuation and second harmonic amplitude u_2 temperature dependencies according to equation [14, 15]:

$$u_2 = \frac{\Gamma \varpi^2 u_1^2}{16 v \alpha_1}\left[\exp(-2\alpha_1 x) - \exp(-4\alpha_1 x)\right],$$

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. The temperature dependencies of nonlinear elastic parameter are shown in Fig. 5. As one can see from picture the value of nonlinear parameter in the direction normal to layers at room temperature is about 50, which exceeds the nonlinear coefficient of other known nonlinear layered materials $KY(MoO_4)_2$ and $Si_{20}Te_{80}$ [16]. The peak of nonlinear parameters near transition can be explained by the soft mode as in case of ferroelectric SbSI [17]. The high anisotropy of nonlinear elastic properties arises from high anisotropy of bonding forces anharmonicity of appropriate longitudinal phonon modes.

After substitution In to Cr or S to Se the solid solutions were obtained by the method of solid-state transport reactions. The piezoelectric test investigations were performed in these solid solutions. In Fig. 6 the temperature dependencies of ultrasonically detected AC signal are shown for $CuInP_2(S,Se)_6$ system. The piezoelectric signal vanishes in the paraelectric phase what is the indication that in this phase is centrosymetric in these materials. The phase transition temperature decreases when S content increases. Such behaviour also was confirmed by dielectric measurements. With higher S content >0.25 the appearance of glassy state was observed in dielectric investigations [18]. The additional anomaly in the temperature dependencies of piezoelectric signal can be attributed to the existence of intermediate phase [8]. The origin of such intermediate phase is not clear yet and the structural investigations are necessary. In solid solutions with Cr also the decrease of phase transition temperature and anomalies of piezoelectric signal in the low temperature phase were observed Fig. 7. In order to obtain full phase diagram of $Cu(In,Cr)P_2S_6$ system the investigations of solid solutions with content of Cr >0.4 are in progress. The DC electric field induced piezoelectricity was observed and in the layered crystals of $Cu(In,Cr)P_2S_6$ system. As an example the frequency dependencies of electric admittance are shown for $CuIn_{0.8}Cr_{0.2}P_2S_6$ plate in paraelectric centrosymetric phase. In the electric admittance *Y* frequency dependencies resonance–antiresonance character is clearly seen when

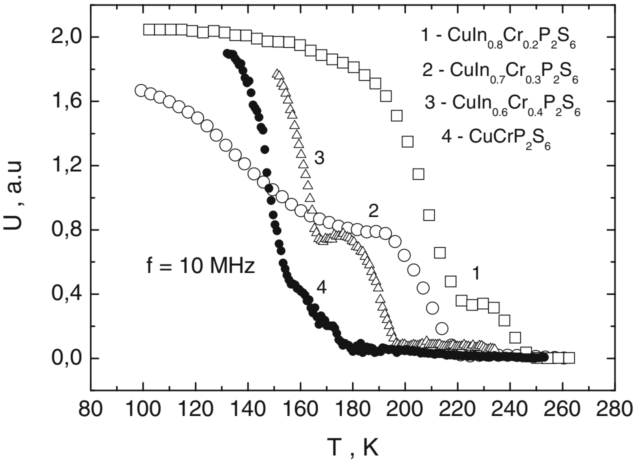


Fig. 7 The temperature dependences of ultrasonically detected piezoelectric signal in $CuIn_{1-x}Cr_xP_2S_6$ c-cut polarised plates. $x=0.2$ (*1*), 0.3 (*2*), 0.4 (*3*) and 1 (*4*)

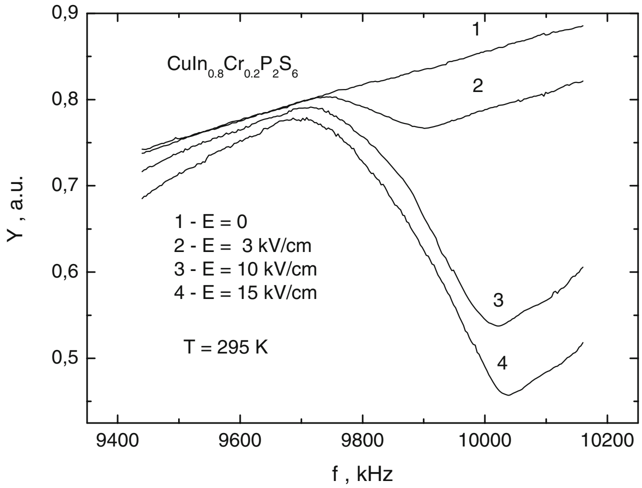


Fig. 8 The frequency dependences of electric admittance of the $CuIn_{0.8}Cr_{0.2}P_2S_6$ plate at room temperature, measured in various DC electric fields applied along *c*-axis

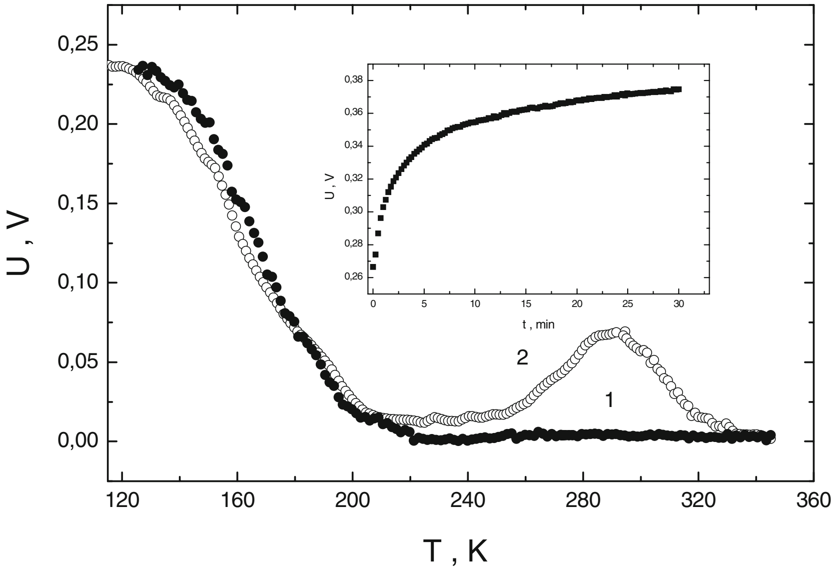
DC bias field is increased (Fig. 8). In this case, it was possible to obtain the elastic and electromechanical parameters of such electrostrictive ultrasonic transducers by measuring the resonance and antireresonance frequencies [19]. The calculated values of electromechanical coupling coefficient were of order 0.2–0.3 in DC electric field of order 15 kV/cm. It is necessary to note that such DC field induced piezoelectricity was observed in all layered crystals of $Cu(In,Cr)P_2(S,Se)_6$ system.

The interesting result was obtained after long-term exposure of the solid solutions in strong DC electric field at room temperature. It was shown that the peak of piezoelectric response signal appeared at this temperature in cooling/heating cycling and close to this temperature, when DC electric field was removed. As an example of such behaviour is shown for $CuInP_2\ (S_{0.25}Se_{0.75})_6$ sample in Fig. 9. To our opinion, this kind of a memory is related to the time dependencies of piezoelectric signal in DC electric field. Indeed, detected by our layered ultrasonic transducer signal in DC electric field depends on time and increases with time (see inset of Fig. 9). Such behaviour can be caused by ionic transport. Due to the high voltage applied to the sample, mobile Cu ions can move to surface area and redistribution of electric field can change effective DC field, which is responsible for the electrostriction induced piezoelectric effect. The similar time dependencies and memory phenomena we observed earlier in BT-LMT ceramic system [20]. Consequently, the migration and reorientation of Cu^+ ions, Cu vacancies and free electronic carriers in deep energy levels can be a possible mechanism of observed memory effects.

4 Conclusions

It was shown that layered crystals of $Cu(In,Cr)P_2(S,Se)_6$ system have very interesting elastic and piezoelectric properties. In low temperature the electromechanical coupling parameters substantially increased after polarization of the material. At the phase transition ultrasonic attenuation peaks and corresponding to them velocity minima were observed. The largest critical ultrasonic anomalies appeared for ultrasonic wave propagating normal to layers: i.e. along polarization direction. It was shown, from measurements of the amplitude of second longitudinal ultrasonic harmonic, that these layered crystals have extremely high elastic nonlinearity in the direction normal to layers. DC bias electric field induced piezoelectricity due to electrostiction was observed in the paraelectric phase. The piezoelectric

Fig. 9 The temperature dependences of ultrasonically detected piezoelectric signal in annealed $CuInP_2\ (S_{0.25}Se_{0.75})_6$ sample at zero electric field (*1*) and in the same sample after 20 kV/cm DC electric field was applied for 24 h and removed. *In the inset*: the time dependence after application of DC bias field



memory was observed after samples were kept for long time in DC electric field along polar axis at fixed temperature.

Acknowledgement Support of Lithuanian State Science and Studies Foundation under the project T-18/07 is gratefully acknowledged.

References

1. V.B. Cajipe, J. Ravez, V. Maisonneuve, A. Simon, C. Payen, R. Von der Muhll, J.E. Fischer, Ferroelectrics **223**, 43 (1999)
2. V. Maisonneuve, V.B. Cajipe, A. Simon, R. Von der Muhll, J. Ravez, Phys. Rev. B. **56**, 10860 (1997)
3. V. Maisonneuve, M. Evain, C. Payen, V.B. Cajipe, P. Molinie, J. Alloys Compd. **218**, 157 (1995)
4. V.B. Cajipe, J. Ravez, V. Maisonneuve, A. Simon, C. Payen, R. Von der Muhll, J.E. Fischer, Ferroelectrics **185**, 135 (1996)
5. K. Moriya, N. Kariya, A. Inaba, T. Matsuo, I. Pritz, Yu. M. Vysochanskii, Solid State Commun **136**, 173 (2005)
6. V. Samulionis, Yu. Vysochanskii, V. Cajipe, Ferroelectrics **295**, 21 (2003)
7. X. Bourdon, V. Maisonneuve, V.B. Cajipe, C. Payen, J.E. Fischer, J. Alloys Compd. **283**, 122 (1999)
8. Yu. M. Vysochanskii, A.A. Molnar, M.I. Gurzan, V.B. Cajipe, X. Bourdon, Solid State Commun. **115**, 13 (2000)
9. V. Samulionis, J. Banys, J. Europ. Cer. Soc. **25**, 2543 (2005)
10. V. Samulionis, J. Banys, Yu. Vysochanskii, V. Cajipe, Ferroelectrics **257**, 113 (2001)
11. V. Valevicius, V. Samulionis, J. Banys, A. Brilingas, J. Physique IV **6**, C8–C405 (1996)
12. L.D. Landau, I.M. Khalatnikov, Sov. Phys. Dokl. **96**, 459 (1954) (in Russian)
13. V. Valevicius, V. Samulionis, J. Banys, J. Alloys Compd. **211/212**, 369 (1994)
14. J. Banys, J. Macutkevic, V. Samulionis, A. Brilingas, Yu. Vysochanskii, Phase Transit. **77**, 345 (2004)
15. L.K. Zarembo, V.A. Krasilnikov, Usp. Fiz. Nauk. **102**, 549 (1970) (in Russian)
16. L.A. Kulakova, Fiz. Tverd. Tela. **43**, 1409 (2001)(in Russian)
17. V. Samulionis, V. Kunigelis, Zh Girshovicius, Zh. Eks. Teor. Fiz. **61**, 1941 (1971)(in Russian)
18. J. Banys, R. Grigalaitis, J. Macutkevic, A. Brilingas, V. Samulionis, J. Grigas, Yu. Vysochanskii, Ferroelectrics **318**, 163 (2005)
19. V. Samulionis, J. Banys, Yu. Vysochanskii, Mat. Sci. Forum. **514**, 230(2005)()
20. J. Banys, V. Samulionis, A. Salak, V.M. Ferreira, P. Keburis· Book of abstracts "ELECTROCERAMICS Toledo 06" (2006) p.87