Dielectric and ultrasonic studies of new $Ag_{0.1}Cu_{0.9}InP_2S_6$ layered ferroelectric compound

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Abstract

The dielectric properties of newly synthesized $Ag_{0.1}Cu_{0.9}InP_2S_6$ crystals were investigated in broad frequency (20 Hz – 1 MHz) and temperature range (110 K – 350 K). Anomaly in the temperature dependence of a complex dielectric permittivity indicating the polar phase transition was detected at the temperature 283 K . The dielectric properties of the presented crystal are mainly caused by conductivity and phase transition. The frequency spectra of the conductivity obey the Almond-West power law. The activation energy of the conductivity was found to be $E_{A/k}$= 6381 K. A suggestion is given that the electric conductivity in these crystals can be interpreted by ionic mechanism. The piezoelectric sensitivity was observed only when DC bias electric field was applied along direction normal to layers. In this case the piezoelectric sensitivity appeared due to electrostriction.

Keywords: Ionic conductivity, Electric modulus, Phase transition, $CuInP_2S_6$.

Introduction

Layered crystals of $CuInP_2S_6$ family are promising materials for functional electronics, because they exhibit ferroelectric and piezoelectric properties, have a mixed electronic – ionic conductivity [1-3]. They crystallize in a layered two-dimensional structure of the $Cu^I M^{III} P_2 S_6$ (M=In, Cr) type. At elevated temperatures, the smeared out copper electronic distribution perpendicular to the layer can be satisfactorily modeled by two vertically disposed positions, one distinctly (Cu1) and the other (Cu2) slightly shifted from the octahedral center where the crystal structure has a centro symmetric space group C2/c. The incomplete occupancy of these sites may be interpreted as a static or dynamic kind of disorder. A very interesting feature of these crystals is that they involve antiparallel shifts of Cu and In cations away from the midplane of a layer along c-axis. The Cu^I sublattice is polar in $CuInP_2S_6$ at T < 312 K and coexists with an In^{III} sublattice of unequal and opposite polarity [1]. So the $CuInP_2S_6$ can be defined as a ferrielectric system below T_c = 312 K. At low temperature the space group changes to the polar group Cc. In $CuInP_2Se_6$ compound the ferroelectric PT at $T_c \approx$ 236 K (the symmetry reduction $P\bar{3}1c \leftrightarrow P31c$ at the PT) was observed [4]. Additionally in $Cu1nP_2Se_6$ the intermediate phase has been observed by ultrasonic and piezoelectric studies [5]. By substitution Se for S, the mixed layered crystals of $CuInP_2(S_xSe_{1-x})_6$ were obtained. The phase diagram of $CuInP_2(S_xSe_{1-x})_6$ crystals according to [3] is complicated including possible morphotropic phase boundary, intermediate phases and glassy state at low temperatures. We have shown that the layered $CuInP_2(S_xSe_{1-x})_6$ crystals can be used for excitation and detection of ultrasonic waves [6]. Recently the new layered crystals of this family were grown when substituting Cu to Ag. The properties of pure $AgInP_2S_6$ and $AgInP_2Se_6$ crystals are completely unknown. Therefore it is of interest to study this new system with different Ag and Se content. In this contribution, we present the results of experimental studies of ultrasonic and piezoelectric properties in pure and mixed (Cu,Ag) $InP_2(Se,S)_6$ crystals. The investigations of temperature dependencies of ultrasonic attenuation, velocity and piezoelectric properties revealed the anomalies at phase transitions in this new family of $CuInP_2S_6$ crystals. After DC bias field was applied the piezoelectric effect due to electrostriction had been found in crystalline plates of pure compounds and in the paraelectric phase of solid solutions.

Experiment

The crystalline samples of $Ag_{0.1}Cu_{0.9}InP_2S_6$ solid solutions were prepared by solid chemical transport reactions and had the form of thin plates with c-axis normal to the plate surfaces. For the impedance spectroscopy single crystals were used. All measurements were performed in the direction perpendicular to the layers. The complex dielectric permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ was measured by the capacitance bridge HP4284A in the frequency range 20 Hz – 1 MHz. The sample was placed in the cryostat between the two copper conductors (contacts), the conductors where fresh polished for each measurement for a better electrical contact. The sample was covered by a silver paste for better contacting. Typical dimensions of the samples were ≈ 10 mm² area and ≈ 0.2 mm thickness. The $Ag_{0.1}Cu_{0.9}InP_2S_6$ system has been established using the X-ray diffraction and differential thermal analysis. The ultrasonic and piezoelectric measurements were carried out using the methods, which we previously developed for such measurements for $CuInP_2S_6$ and $CuCrP_2S_6$ crystals [7-9]. Ultrasonic velocity and attenuation measurements were carried out using the automatic time-of-flight technique. This equipment allowed us to measure time delay changes less than 0.2 ns; therefore the relative ultrasonic velocity measurements on very thin (0.2 – 0.4 mm) samples were possible. The piezoelectric studies were performed by direct measurement of electric signal arising on a thin plate used as a ultrasonic transducer in an usual pulse-echo ultrasonic experimental setup (see [6,10] for details). The lithium

niobate transducer for excitation of longitudinal ultrasonic wave was attached to one end of a quartz buffer and to another end of the quartz buffer a thin *c*-cut (Cu,Ag) $InP_2(Se,S)_6$ plate was fixed. Silicone oil was used to make acoustic bonds and silver paste electrodes were used in electric measurements.

Results and discussion

At first we investigated the $Ag_{0.1}Cu_{0.9}InP_2S_6$ crystal, which is not far of pure $CuInP_2S_6$ in the phase diagram.
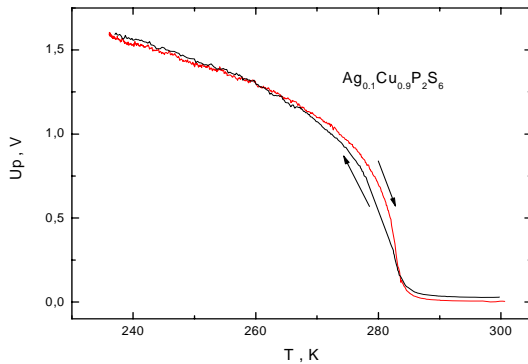
Fig. 1. **The temperature dependencies of ultrasonically detected piezoelectric signal in Ag0.1Cu0.9InP2S6 crystal. In cooling the 10 kV/cm bias field was applied.**

The temperature dependencies of the piezoelectric signal appearing on the sample plate were measured similarly to our former ultrasonic investigations of a piezoelectric sensitivity. At room a temperature no signal was detected, showing that the crystal was not piezoelectric. In cooling down the signal was observed at about 285 K and increased with temperature decreasing. So, the piezoelectricity was observed. In the virgin crystal the piezoelectric sensitivity was small. Due to a well-known fact, that the piezoelectric effect substantially increases when ferroelectric is polarized in a DC field, we performed the same experiment when the DC electric field was applied and the sample was cooled down below 283 K. In the heating run the DC field was removed. In this case the signal increased of about order at low temperatures and the polar state remained when heating. The results are shown in Fig. 1. As one can see the behaviour of the piezoelectric response is similar to that of spontaneous polarization. The absence of a temperature hysteresis shows that the phase transition at T_c=283.4 K is close to the second order. The increase of the dielectric permittivity at around T=283 K at various frequencies we can see in Fig. 2 from dielectric permittivity measurements. Here we can distinguish two regions of the dielectric dispersion. At the temperatures $T > 290$ K and the frequencies $f < 573$ Hz the dielectric dispersion is mainly caused by the high Cu^+ and Ag^+ ions conductivity. The dielectric dispersion at lower temperatures ($T < 283$ K) is caused by a phase transition.

The electrical conductivity σ has been calculated according to the formula $\sigma = \omega \varepsilon_0 \varepsilon''$. The obtained results are presented in Fig.3. We can expect that the conductivity of

$Ag_{0.1}Cu_{0.9}InP_2S_6$ crystals can be ionic (Ag^+ ions). Nevertheless, this hypothesis must confirmed by other experiments. At low frequencies, random distribution of the ionic charge carriers via activated hopping gives rise to a frequency independent conductivity (DC conductivity). At higher frequencies, the conductivity exhibits dispersion, increasing roughly in a power law fashion and eventually becoming almost linear at even higher frequencies. The high-temperature conductivity spectra of the Ag^+ and Cu^+ ion conducting materials are characterized by an additional low-frequency dispersion region due to electrode effects. The frequency behavior of σ has been fitted according to the Almond-West equation [10] $\sigma = \sigma_{DC} + A\omega^s$, where σ_{DC} is the DC conductivity and $A\omega^s$ is AC conductivity.
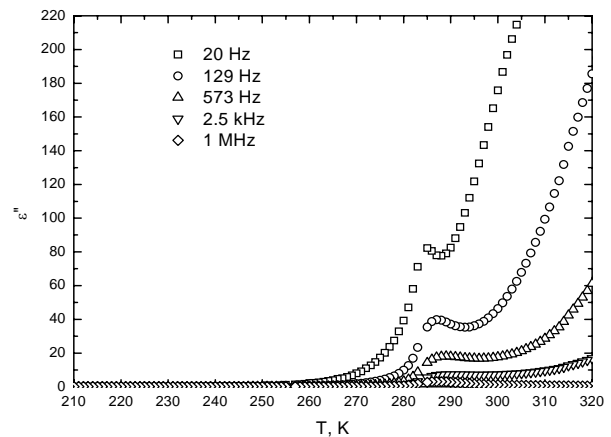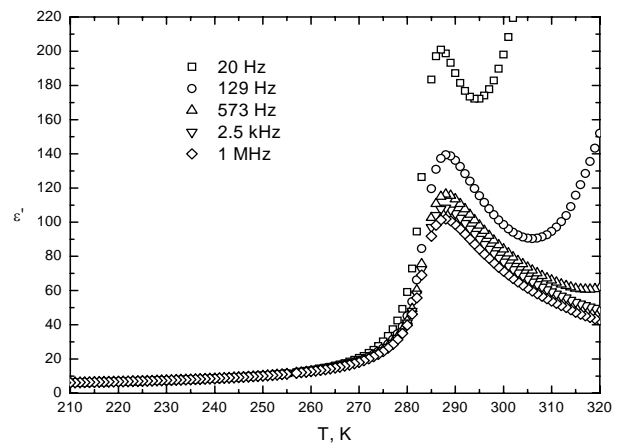

Fig. 2. **Temperature dependence of real part and imaginary part of the complex dielectric permittivity of $Ag_{0.1}Cu_{0.9}InP_2S_6$.**

Two formalisms such as electric conductivity and electric modulus [10] have been employed to study the ion dynamics in solids under AC electric field. However, there is a debate on which of these formalisms provides better insights into the phenomena of ion dynamics. Both formalisms are compared in this paper. The complex electric modulus spectra represent a measure of distribution of ion energies or configurations in the disordered structure and also describe the electrical relaxation of ionic solids as a microscopic property of these materials. The electric modulus M^* can easily be calculated from complex dielctric permittivity:

$$M^*(\omega) = \frac{1}{\varepsilon^*(\omega)} = \frac{\varepsilon' - j\varepsilon''}{|\varepsilon|^2} = M + jM'' = M_\infty \left(1 - \int_0^\infty e^{-j\omega t} \left(-\frac{d\varphi}{dt}\right) dt'\right)$$

The function $\varphi(t)$ gives the time evolution of the electric field within the materials. The obtained frequencies dependencies $M^*(\nu)$ are presented in Fig. 3. The real modulus M' shows dispersion as the frequency increased and tends to saturate at M_∞ at higher frequencies. The imaginary modulus M'' exhibits a maximum M''_{max} centered at the dispersion region of M'.
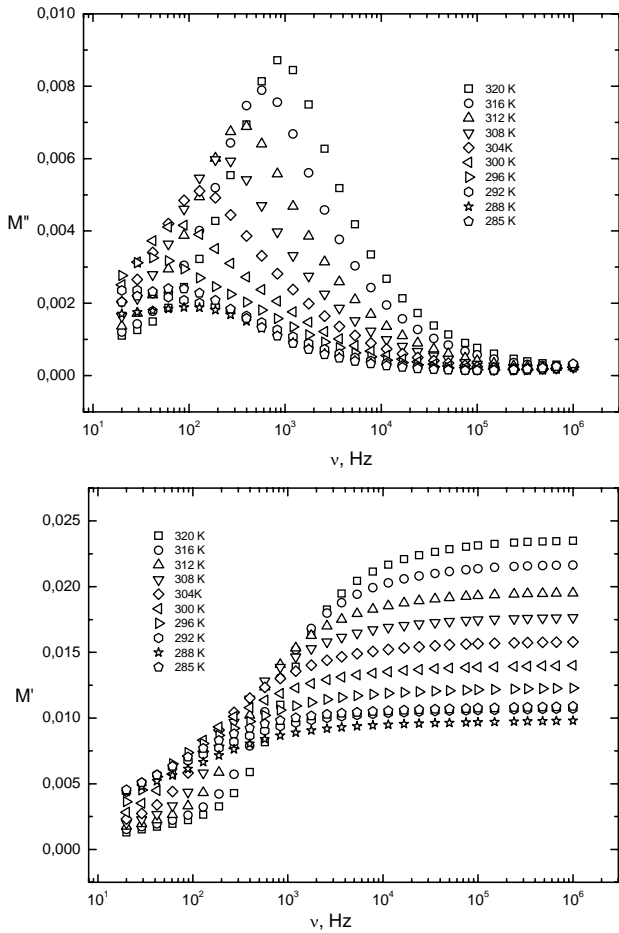

Fig. 4. **$1/T$ dependence of σ_{DC} Ag$_{0.1}$Cu$_{0.9}$InP$_2$S$_6$ crystal**

In Fig. 5 the peaks position of M'' was plotted versus the temperature. Using this plot we have calculated the activation energy $E_B/k_B = 11596$ K.

Fig. 5. **Peaks position of M'' versus the 1/T**

In a low temperature phase quite nice dependencies of piezoelectric signal on DC electric field were obtained (Fig. 6). In this case the DC field was changed in steps and the sample was at the constant field for two minutes.

Fig. 3 **Plots of the isothermal frequency spectra of M' and M'' of Ag$_{0.1}$Cu$_{0.9}$InP$_2$S$_6$ crystal**

The temperature dependence of $\ln(\sigma_{DC})$ is presented in Fig. 4. From this dependencies it was possible to calculate the activation energy E_A and σ_0 of the conductivity according to the Arrhenius law: $\sigma = \sigma_0 \exp(E_A/kT)$. The calculated parameters are: $E_A/k = 6381$ K, $\sigma_0 = 6{,}7$ S/m.
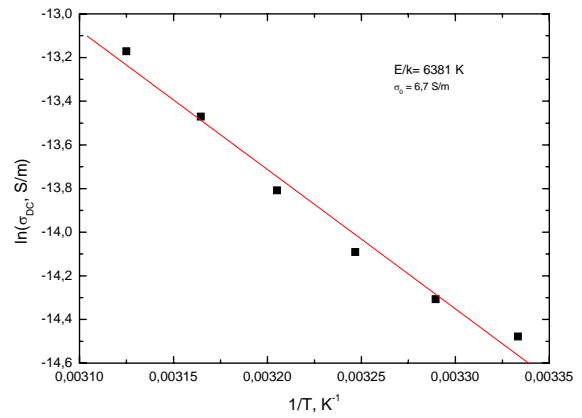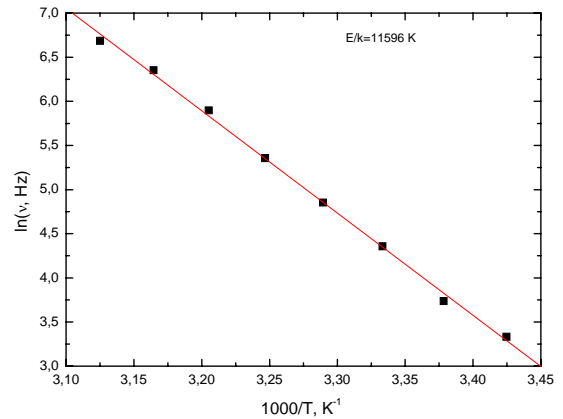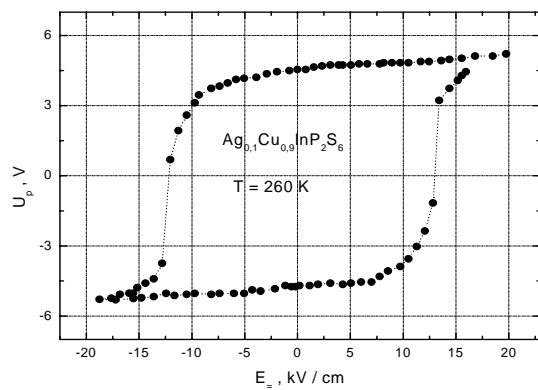

Fig. 6. **The DC field dependence of the piezoelectric signal in Ag$_{0.1}$Cu$_{0.9}$InP$_2$S$_6$ crystal.**

The coercive field is about 12 kV/cm and it is smaller as for pure CuInP$_2$S$_6$ (in [1] coercive field was obtained 77 kV/cm in AC field of 50 Hz frequency). Our measurements are in almost static field and of course the

coercive field is smaller. It is interesting to note that at fields near coercive the amplitude of piezoelectric signal changes with time, when the time increases the coercive field decreases. Therefore, the existence of a ferroelectric phase transition (PT) was established for $Ag_{0.1}Cu_{0.9}InP_2S_6$ crystal. The transition temperature is lower than in a pure $CuInP_2S_6$ crystal by 30 K. Also the order of PT as seen from Fig. 1, changes from the first to the second order. The existence of PT was confirmed and by ultrasonic attenuation and velocity measurements. The layered samples were thin and for reliable ultrasonic measurements the samples were made as stacks from 8-10 plates glued in such way that longitudinal ultrasonic wave can propagate across layers. At the PT clear ultrasonic anomalies were observed (Fig.7). The anomalies were similar to that which were described in pure $CuInP_2S_6$ crystals and could be explained by the interaction of elastic wave with polarization [11-12]. In this case the relaxation time increases approaching the T_c according to the Landau theory [13] and ultrasonic attenuation peak with downwards velocity step can be observed. Increase of the velocity in the ferroelectric phase can be attributed to the contribution of the fourth order term in the Landau free energy expansion. In this case velocity changes are proportional to the order parameter square [11]. Also influence of polarization fluctuations must be considered especially in the paraelectric phase.
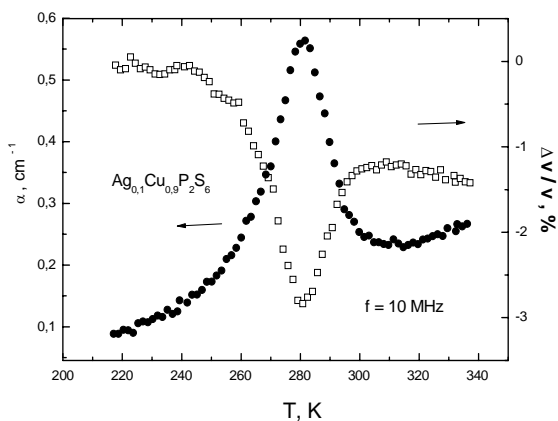

Fig. 7. **The temperature dependencies of longitudinal ultrasonic attenuation and velocity in $Ag_{0.1}Cu_{0.9}InP_2S_6$ crystal along c-axis**

Conclusion

We reported the first characterization of newly synthesized $Ag_{0.1}Cu_{0.9}InP_2S_6$ crystals by means of dielectric and conductivity spectroscopy. The anomaly in the temperature dependence of the complex dielectric permittivity of $Ag_{0.1}Cu_{0.9}InP_2S_6$ crystal indicating a polar phase transition at temperature 283 K was observed. The dielectric properties of the investigated crystals are caused by conductivity and phase transition. The temperature dependencies of the piezoelectric response, longitudinal ultrasonic velocity and attenuation along *c*-axis in new layered $Ag_{0.1}Cu_{0.9}InP_2S_6$ crystals were measured. The ultrasonic attenuation, velocity and piezoelectric sensitivity anomalies were observed at phase transitions in this new compound.

References

1. **Maisonneuve V., Cajipe V. B., Simon A., VonderMuhl R. and Ravez J.** Ferrielectric ordering in lamellar CuInP2S6. Phys.Rev. 1997. Vol.B 56. P. 10860-10867.

2. **Maisonneuve V., Evain M., Payen C., Cajipe V.B. and Molinie P.** Room temperature crystal structure of the layered phase CuInP2S6. J. Alloys and Compounds. 1995. Vol.218. P. 1574-1580.

3. **Vysochanskii Yu. M., Molnar A. A., Gurzan M. I and Cajipe V. B.** Phase transitions in CuInP2(SexS1-x)6 layered crystals. Ferroelectrics. 2001. Vol. 257. P. 147-154.

4. **Studenyak I. P., Mykajlo O. A., Stephanovich V. O., Gurzan M. I., Vysochanskii Yu. M. and Cajipe V. B.** Phase transitions and optical absorption edge in CuInP2Se6 layered ferrielectrics. Phys. stat. sol. (a). 2003. Vol.198. P. 487– 494.

5. **Samulionis V. and Banys J.** Ultrasonic and piezoelectric studies of new layered ferroelectric compounds of Sn2P2S6 family. J. Europ. Cer. Soc. 2005. Vol. 25. P. 2543 – 2546.

6. **Samulionis V., Banys J. and Vysochanskii Yu.** The characterization of two dimensional electrostrictive CuInP2S6 materials for transducers. Materials Science Forum. 2005. Vol. 514. P.230-234.

7. **Samulionis V., Vysochanskii Yu. and Cajipe V.** Ultrasonic and piezoelectric investigation of Sn2P2S6 type photosensitive ferroelectric-semiconductor crystals. Ferroelectrics. 2003. Vol. 295. P.21-30.

8. **Samulionis V., Banys J., Vysochanskii Yu. and Cajipe V.** Elastic and electromechanical properties of new ferroelectric-semiconductor materials of Sn2P2S6 family. Ferroelectrics. 2001. Vol. 257. P.113-123.

9. **Valevičius V., Samulionis V. Banys J. and Brilingas A.** Ultrasonic studies of incommen-surate phase transitions. J. de Physique IV, 6, C8-405-C8-408, 1996.

10. **Joncher A. K.** Dielectric relaxation in solids. Celsea Dielectric Press, London. 1983.

11. **Valevičius V., Samulionis V., Banys J., Grigas J. and Yagi T.** Ultrasonic study of ferroelectric phase transition in DDSP. Ferroelectrics. 1994. Vol. 156. P. 365-370.

12. **Valevičius V., Samulionis V. and Banys J.** Ultrasonic dispersion in the phase transition region of ferroelectric materials. J. Alloys and Compounds. 1994. Vol. 211/212. P. 369-373.

13. **Landau L. D., Khalatnikov I. M.** About anomalous sound attenuation near the phase transition of second order (in Russian). Sov.Phys.(Doklady). 1954. Vol. 96. P. 459-466.

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Sluoksninio $Ag_{0.1}Cu_{0.9}InP_2S_6$ feroelektriko dielektriniai ir ultragarsiniai tyrimai

Reziumė

Ištirtos dielektrinės ir ultragarsinės $Ag_{0.1}Cu_{0.9}InP_2S_6$ kristalo savybės. Dielektrinės skvarbos spektrai buvo matuojami žemųjų (20-106 Hz) srityse. Matuota kristalą šaldant nuo 350 K iki 110 K temperatūros. Kompleksinės dielektrinės skvarbos ε* realiosios ir menamosios dalių priklausomybės nuo temperatūros parodo, kad kristale reiškiasi dielektrinė dispersija – dielektrinės skvarbos priklausomybė nuo elektrinio lauko kitimo dažnio. Tiek iš realiosios, tiek iš menamosios dielektrinės skvarbos temperatūrinių priklausomybių galima išskirti dvi būdingąsias sritis: joninio laidumo ir fazinio virsmo sąlygotas dielektrinės skvarbos dispersijas. Žemojo dažnio srityje ir aukštoje temperatūroje (T > 290 K) dispersiją sąlygoja tūrinis kristalo laidumas. Dėl fazinio virsmo atsirandanti dispersija matyti visoje matuotų dažnių srityje ir temperatūroje, artimoje fazinio virsmo temperatūrai (T ≈ 283 K).