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Diffusion phase transitions in $(Pb_ySn_{1-y})_2P_2(Se_xS_{1-x})_6$ solid solutions

M.M.Maior, Sh.B.Molnar, V.T.Vrabel, M.I.Gurzan, S.F.Motrja, Yu.M.Vysochanskii

Institute for Solid State Physics and Chemistry,
Uzhgorod National University, Uzhgorod, Ukraine

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The dielectric properties of $(Pb_ySn_{1-y})_2P_2(Se_xS_{1-x})_6$ mixed crystals in the vicinity of the incommensurate phase transition have been studied. It has been found that due to the defect action, the dielectric anomalies at the phase transitions are smeared and instead of two anomalies bounding the incommensurate phase there is observed a single broad peak. The character of the dielectric dispersion as well as nonlinear dielectric behavior in the crystals studied suggest that in the chaotic state due to the action of the defect on the IC phase, the crystals possess the properties of ferroelectrics relaxors.

Key words: *diffusion phase transition, relaxors, dielectric properties*

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1. Introduction

$Sn_2P_2Se_6$ crystal exhibits a sequence of phase transitions: at $T_{\mathrm{i}} \approx 220$ K, from the paraelectric to the incommensurate phase, and at $T_{\mathrm{c}} \approx 192$ K, from the incommensurate phase to the ferroelectric phase. The substitution of tin by lead atoms in the cation sublattice of $Sn_2P_2Se_6$ leads to a decrease of the incommensurate phase transition temperatures. At the same time, the region of the occurrence of the incommensurate phase increases [1].

With an increase of lead content in the solid solutions, the ε' peak at paraelectric-incommensurate phase gets gradually smeared and, at $y > 0.4\varepsilon'(T)$ dependence, demonstrates only one very broad maximum. The $(Pb_ySn_1-y)_2P_2Se_6$ solid solutions with $y > 0.4$ exhibit only a paraelectric-incommensurate phase transition with the incommensurate phase extending down to 0 K.

When substitution is made simultaneously in both cation and anion sublattices, the effect of phase transition smearing is substantially enhanced.

At a relatively high concentration of the substituted component in the mixed crystals of $(Pb_ySn_{1-y})_2P_2(Se_xS_{1-x})_6$, the temperature dependence of the dielectric

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constant shows a single broad peak instead of two anomalies bounding the incommensurate phase [1]. In the vicinity of the maxima, the pronounced dielectric dispersion with a broad spectrum of relaxation times occurs. This makes the phase transition very similar to the phase transition observed in the so-called ferroelectrics-relaxors.

2. Experimental

$(Pb_ySn_{1-y})_2P_2(Se_xS_{1-x})_6$ mixed crystals were grown using vapor transport technique [2]. The samples in the form of platelets perpendicular to [100] polar direction with a typical size of $3 \times 3 \times 1$ mm were used. Dielectric measurements were performed in a liquid helium cryostat (UTRECS) operated in a quasistatic regime (with a temperature variation rate ≈ 0.5 K/min) using a capacitance bridge.

3. Results and discussion

Temperature dependence of the dielectric constant for mixed crystals $(Pb_ySn_{1-y})_2P_2(Se_xS_{1-x})_6$ with various compositions is represented in figure 1.

In the crystals with $x, y > 0.2$ at the paraelectric-incommensurate phase transition there occurs only a weak kink on the temperature dependence of ε'. At the dielectric losses, this phase transition manifests itself as a beginning of a sharp increase below T_{i}. As shown in figures 2 and 3, the dielectric constant demonstrates a pronounced dielectric dispersion in the vicinity of the smeared peak. From the high temperature side the dielectric response becomes frequency dependent below the temperature corresponding to the kink on $\varepsilon'(T)$ and $\varepsilon''(T)$. The character of the dielectric dispersion observed in $(Pb_ySn_{1-y})_2P_2(Se_xS_{1-x})_6$ crystals is as follows: smooth decrease of ε' and increase of ε'' with increase in frequency, which is very similar to the dispersion found in $(Pb_ySn_{1-y})_2P_2Se_6$ at low temperatures [3]. In the latter, the dispersion is related to the freezing of the activation dynamics of the incommensurate modulation pinned by defects.

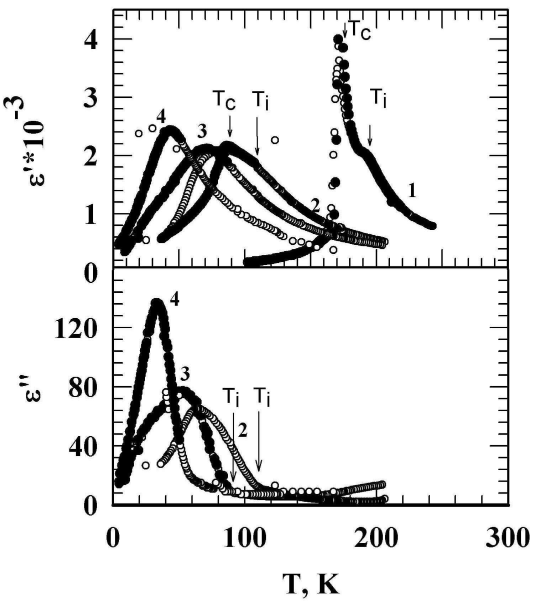

Figure 1. Temperature dependence of real and imaginary part of the dielectric constant for $(Pb_ySn_{1-y})_2P_2(Se_xS_{1-x})_6$ solid solutions: $1 - y = 0.1$, $x = 0.1$; $2 - y = 0.25$, $x = 0.25$; $3 - y = 0.3$, $x = 0.3$; $4 - y = 0.5$, $x = 0.2$.

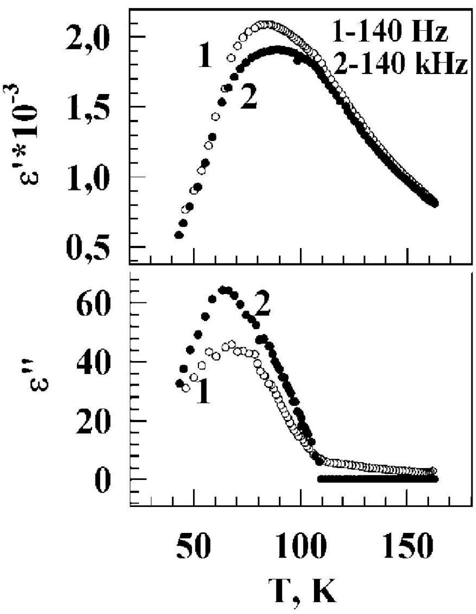

Figure 2. Temperature dependence of the dielectric constant for $(Pb_{0.25}Sn_{0.75})_2P_2(Se_{0.75}S_{0.25})_6$ solid solution at various frequencies.

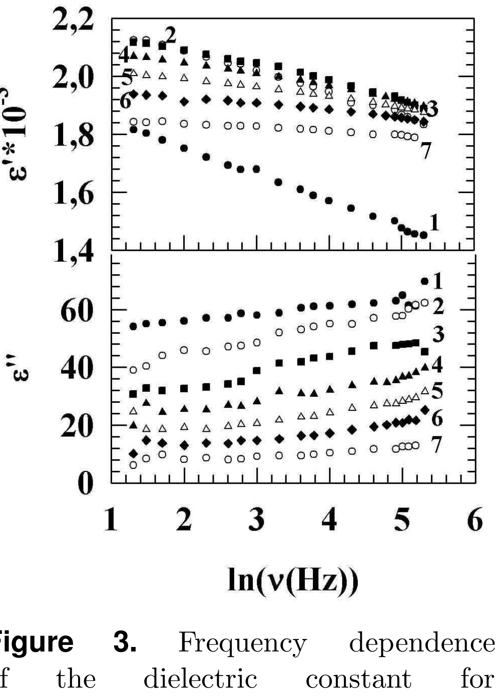

Figure 3. Frequency dependence of the dielectric constant for $(Pb_{0.25}Sn_{0.75})_2P_2(Se_{0.75}S_{0.25})_6$ solid solution at various temperatures: 1 – 68.7 K; 2 – 76.5 K; 3 – 89.8 K; 4 – 95.1 K; 5 – 100.2 K; 6 – 104.5 K; 7 – 109.4 K.

It seems likely that the dispersion in $(Pb_ySn_{1-y})_2P_2(Se_xS_{1-x})_6$ crystals is also caused by the relaxation dynamics of the incommensurate structure and ferroelectric domain walls (since the dispersion occurs in the ferroelectric phase as well).

It is evident from the structural data performed for $Sn_2P_2Se_6$ crystals [4] that there are no higher harmonics in the polarization distribution of the incommensurate phase. Therefore, there is no soliton structure in these crystals. Thus, in respect to coupling with the defects, the incommensurate modulation could be imagined as a sequence of broad domain walls separating the area with an opposite direction of polarization.

In the presence of high density of the defects, the broad domain walls are pinned by fluctuation in the defect density. This kind of pinning is considered to be weak [5]. In the weak pinning regime, there is a minimal length scale at which the domain walls or solitons feel the potential barrier between metastable states. In such systems the relaxation time is a function of the length scale. The minimal length scale in which domain walls are pinned depend on time and temperature [5]:

$$L_{\mathrm{c}} \propto \left[1 + \frac{T}{T + T_{\varepsilon}} \ln\left(\frac{t}{t_0}\right)\right]^{1/\theta},$$

where T_ε corresponds to the height of the barriers between metastable states E_{B}, θ is an exponent depending on the system dimension and the character of coupling of the wall with the defects of random field or random-bond type and t_0 is a time constant for the relaxation of domain walls in length scale $L(\tau(L) = t_0 \exp(-E_{\mathrm{B}}(L)/k_{\mathrm{B}}T)$.

Dielectric response for such disordered systems is defined by the scale in

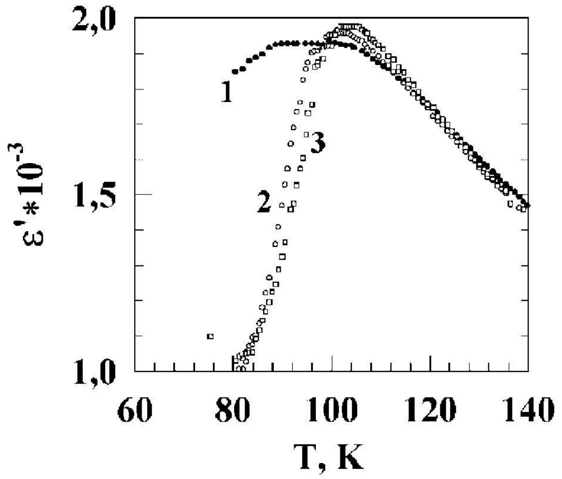

Figure 4. Temperature dependence of the dielectric constant for $(Pb_{0.25}Sn_{0.75})_2P_2(Se_{0.75}S_{0.25})_6$ solid solution under bc fields: 1 – 0 V/cm; 2 – 900 V/cm; 3 – 1800 V/cm.

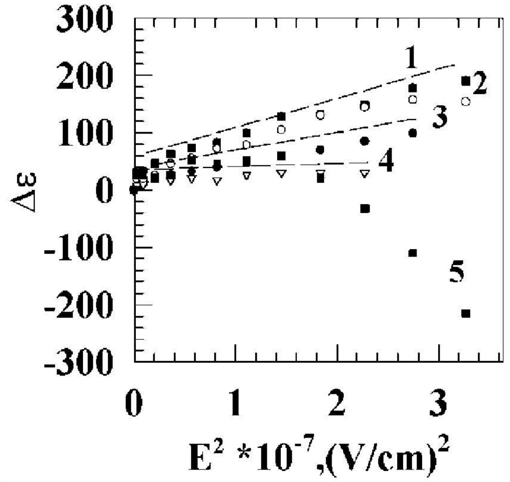

Figure 5. Field dependence of $\Delta\varepsilon$ for $(Pb_{0.25}Sn_{0.75})_2P_2(Se_{0.75}S_{0.25})_6$ solid solution at various temperatures: 1 – 109.4 K, 2 – 104.0 K, 3 – 114.7 K, 4 – 124.5 K, 5 – 98.3 K.

which domain walls can relax and ε is expected to have logarithmic frequency dependence. The theory prediction correlate well with the experimentally observed frequency behavior of the dielectric constant (figure 3).

Temperature dependence of ε for $(Pb_ySn_{1-y})_2P_2(Se_xS_{1-x})_6$ crystals is shown in figure 4 at various bias voltages. With lowering temperature in the intermediate phase, the effect of the bias field increases (figure 5). Nonlinear dielectric contribution $\Delta\varepsilon = \varepsilon(E) - \varepsilon(0)$ has a quadratic field dependence. In the low temperature region of the intermediate phase starting from a certain value of the bias, the field dependence changes from growing to diminishing. This is an indication of the presence of the polar state induced by an external electric field.

Dielectric measurements demonstrate the occurrence of positive nonlinear dielectric contribution in the IC phase under the effect of the external bias field [6]. It should be mentioned that the positive nonlinear dielectric contribution occurs in $Sn_2P_2Se_6$ throughout the temperature range of the existence of incommensurate phase.

At the same time, in $(Pb_ySn_{1-y})_2P_2Se_6$, solid solutions $\Delta\varepsilon$ have a positive sign in the IC phase only close T_i of the temperatures of phase transition from the paraelectric to the IC phase. At low temperature boundary of IC phase, $\Delta\varepsilon$ changes a sign to negative, which is manifested in suppression of $\varepsilon'(T)$ maxima at lock-in phase transition under the effect of the bias field. The latter suggests that in the low temperature region of the IC phase in such solid solutions under the action of the defects induced by substitutions in a cation sublattice, the polar areas appear which are increased with the increase of the external bias.

On the contrary, the character of the bias field effect in $(Pb_ySn_{1-y})_2P_2(Se_xS_{1-x})_6$ solid solutions (nonlinear dielectric effect is positive throughout the intermediate phase) testifies to the absence of macroscopic polar region.

Considering the substituted atoms in solid solutions as the defects, the interaction of IC polarization wave with these defects could be interpreted as a weak pinning, characteristic of a large defect concentration [5].

In $(Pb_ySn_{1-y})_2P_2Se_6$ solid solutions, both IC phase transitions remain reasonably sharp [1]. This means that the defects induced by substitutions in a cation sublattice, can be considered as the defects saving symmetry. At the same time, even at a relatively small concentration of sulfur atoms in an anion sublattice, the phase transition from the paraelectric to the IC phase in $(Pb_ySn_{1-y})_2P_2(Se_xS_{1-x})_6$ becomes hardly distinguishable considering a temperature dependence of the dielectric properties. It should be mentioned that in $Sn_2P_2(Se_xS_{1-x})_6$ solid solutions, this phase transition is not sharp as well. These facts make it possible to assume that the defects induced by substitutions in the anion sublattice can be considered as the defects destroying the symmetry.

The fact that the wave vector of the IC modulation in $Sn_2P_2(S_{0.2}Se_{0.8})_6$ solid solution shows a temperature independent behavior due to the pinning effect [4] in several temperature ranges, is a considerable evidence in favor of this suggestion. Thus, one can assume that mainly the defects induced by substitutions in an anion sublattice destroy the long-range order in the IC phase in solid solutions $(Pb_ySn_{1-y})_2P_2(Se_xS_{1-x})_6$ resulting in the formation of the so-called chaotic state.

The positive nonlinear dielectric contribution under the effect of the bias field was observed in $K_{1-x}(NH_4)_xH_2PO_4$ crystals, in which, in the intermediate phase between the paraelectric and the polar phase, the existence of a "structural glass" state is suggested [7]. The similar behavior under the effect of the bias field was also found in PMN crystals for a crystallographic direction [111] [8]. At the same time, for the direction [100], the nonlinear dielectric contribution is negative. Such orientation dependent nonlinear dielectric behavior in relaxors is related to the reorientation of polar regions [7].

The peculiarity of the solid solutions $(Pb_ySn_{1-y})_2P_2Se_6$ (at $y > 0.4$) with IC phase extended to very low temperatures is that the amplitude of the nonlinear dielectric effect steeply decreases below 50 K. The effect is essentially negligible below the temperature corresponding to the peak of the dielectric losses which is related to the freezing of the relaxation dynamics of IC modulation. This phenomenon is an argument in favor of the suggestion that nonlinear dielectric effect in the IC phase in the crystals studied is associated with the variation of configuration state of IC modulation pinned by the defects. In conclusion, one can mention that the character of the dielectric dispersion as well as nonlinear dielectric behavior in the crystals studied suggest that in the chaotic state due to the action of the defect on the IC phase, the crystals possess the properties of ferroelectrics relaxors.

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Розмиті фазові переходи в твердих розчинах $(Pb_ySn_{1-y})_2P_2(Se_xS_{1-x})_6$

М.М.Майор, Ш.Б.Молнар, В.Т.Врабель, М.І.Гурзан,
С.Ф.Мотря, Юл.М.Височанський

Ужгородський Національний Університет, Ужгород

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В роботі досліджувалися діелектричні властивості змішаних кристалів типу $(Pb_ySn_{1-y})_2P_2(Se_xS_{1-x})_6$ в околі неспівмірних фазових переходів. Було встановлено, що під впливом дефектів, індукованих заміщеннями, діелектричні аномалії при фазових переходах розмиваються і замість двох аномалій, що обмежують неспівмірну фазу, спостерігається один розмитий пік. Характер діелектричної дисперсії і нелінійна діелектрична поведінка в досліджуваних кристалах свідчать про те, що хаотичний стан, який виникає внаслідок впливу дефектів на неспівмірну фазу, володіє властивостями сегнетоелектриків-релаксорів.

Ключові слова: *розмитий фазовий перехід, релаксори, діелектричні властивості*

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