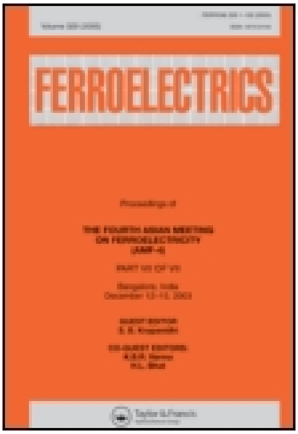

Ferroelectrics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gfer20

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Published online: 09 Mar 2011.

Ferroelectrics, 1999, Vol. 223, pp. 19-26
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Influence of Defects and Conductivity on the Phase Transitions and the Domain Structure Properties in Ferroelectric-Semiconductors $Sn_2P_2S(Se)_6$

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(Received August 23, 1998; In final form September 17, 1998)

The influence of the static defects and charge carriers on the dielectric permeability temperature anomalies at the phase transitions (PT) from paraelectric phase to incommensurate (IC) phase and from IC phase to ferroelectric one has been determined for $Sn_2P_2S(Se)_6$ crystals. For these crystals with controlled content of impurities the memory effect recording in IC phase was compared with the dielectric output of the domain walls in ferroelectric phase. The experimental data are analyzed in the mean-field approximation.

Keywords: Ferroelectrics-semiconductors, domains, incommensurate phase, thermal memory.

INTRODUCTION

It is interesting to compare the influence of static and dynamic defects on the nonequilibrium behavior of proper ferroelectrics-semiconductors in the incommensurate and ferroelectric phases. For this aim we investigated the dielectric properties of $Sn_2P_2Se_6$ crystals with different impurities and the efficiency of the recording of a thermal memory effect in the IC phase of these crystals. As the impurities the atoms of Pb, S, and Mn were used.

The $Sn_2P_2Se_6$ crystals at cooling have consecutive phase transitions from paraelectric to IC phase at T_i and from IC phase to ferroelectric one at T_c [1]. The Pb atoms in the structure of $Sn_2P_2Se_6$ play the role of the impurities of a «random temperature» type and atoms of sulfur in the structure of $Sn_2P_2Se_6$ serve as defects of a «random field» type [2]. The Mn^{2+} ions in crystal $Sn_2P_2Se_6$ serve as impurities of impression. They occupy free places in the elementary cell of crystal, which coincides with the center inversion in the paraelectric phase [3]. Introduction of Mn in the $Sn_2P_2Se_6$ structure strongly destroys the electro-neutrality and changes the electro-conductivity of the crystals.

EXPERIMENTAL RESULTS

The vapor-transport and Bridgeman methods where used for the crystals growing [1]. The crystals $Sn_2P_2Se_6$ obtained by Bridgeman method had the specific resistance of $\rho \sim 5 \cdot 10^{10}$ $\Omega \cdot$m. For $(Pb_{0.05}Sn_{0.95})_2P_2Se_6$ crystals obtained by vapor-transport method the specific resistance was $\rho \sim 3 \cdot 10^{10}$ $\Omega \cdot$m. Nominally clear $Sn_2P_2Se_6$ crystals obtained by vapor-transport had $\rho \sim 4.2 \cdot 10^{8}$ $\Omega \cdot$m, and for $Sn_2P_2(Se_{0.005}S_{0.995})_6$ crystals with impurity of Mn prepared by last method $\rho \sim 5.5 \cdot 10^{7}$ $\Omega \cdot$m. The specimens had the dimensions near $4 \times 3 \times 1$ mm^3. On the normal to polar direction [100] faces the gold was evaporated for preparing the electric contacts. The temperature dependences of the dielectric permeability were measured by computer controlled equipment [4].

We observe the Curie Weiss like $\varepsilon'(T)$ dependence in the paraelectric phase of Bridgeman type $Sn_2P_2Se_6$ crystal (Fig. 1). In the case of vapor transport $Sn_2P_2Se_6$ crystal the electric conductivity strongly influences the $\varepsilon'(T)$ behavior (Fig. 2). Big difference appears in the ferroelectric phase - here we can see a very strong dielectric output from the domain walls.

For Bridgeman type crystal the memory effect does not appear at temperature stabilization in darkness for 12 hours. This effect arises with small amplitude only at the same time temperature stabilization at white light illumination (Fig.1). The memory effect is very distinctly pronounced for the vapor-transport type crystal already after a two hours exposure in darkness. The amplitude and temperature interval of memory effect increase if we illuminate the sample with a white light at the process of temperature stabilization. The spectral sensitivity of memory recording also has been observed (Fig.2).

The substitution of Sn by Pb significantly smears the anomaly of $\varepsilon'(T)$ at T_i, increases the hysteresis of the temperature T_c of PT from IC phase to ferroelectric one and decreases the dielectric output of the domain walls in the ferroelectric phase (Fig. 3). For $(Pb_{0.05}Sn_{0.95})_2P_2Se_6$ crystals at the temperature stabilization in the IC phase for 5 hours upon white light illumination of the sample the memory effect does not appear (Fig. 3).

Partial substitution of Se by S slightly increases the anomalous hysteresis of $\varepsilon'(T)$ in IC phase and hysteresis T_c. The introduction of the impurity atoms into the anion sublattice also decreases the dielectric output of domain walls in the ferroelectric phase. At the same time, the introduction of Mn impurity into the array of $Sn_2P_2Se_6$ significantly rises the electro-conductivity of specimens. For this reason we even don't observe the anomaly at T_i on the temperature dependence of dielectric constant (Fig. 4).

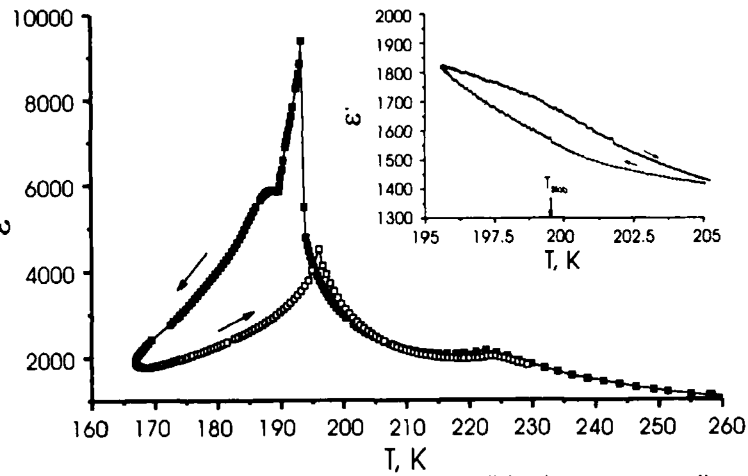

FIGURE 1 The temperature dependences of the dielectric constant at cooling and heating for $Sn_2P_2Se_6$ crystal with low electric conductivity (grown by Bridgeman method). On insert: the thermal memory recording in the IC phase at white light illumination during the temperature stabilization at 12 hours.

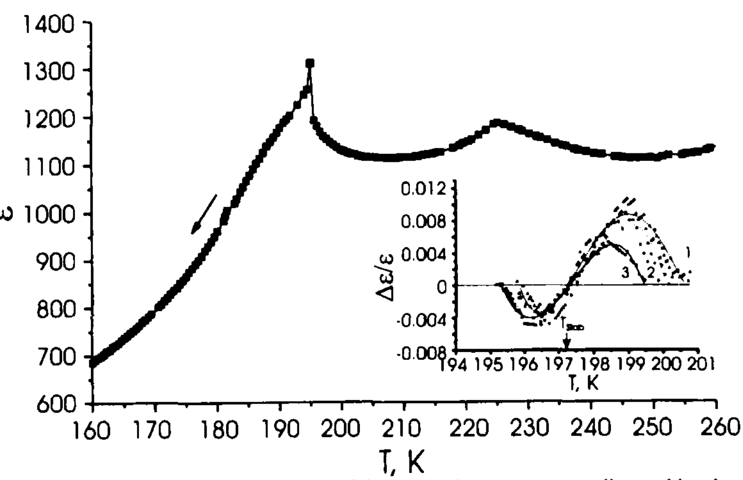

FIGURE 2 The temperature dependence of the dielectric constant at cooling and heating for $Sn_2P_2Se_6$ crystal with high electric conductivity (grown by vapor transport method). On insert: the reduced anomalous part Δε/ε of the dielectric constant related to the thermal memory effect in the IC phase at the temperature stabilization time of 2 hours under illumination by the light with different wave length (1 - 1.000 μm, 2 - 0.560 μm, 3 - 0.666 μm).

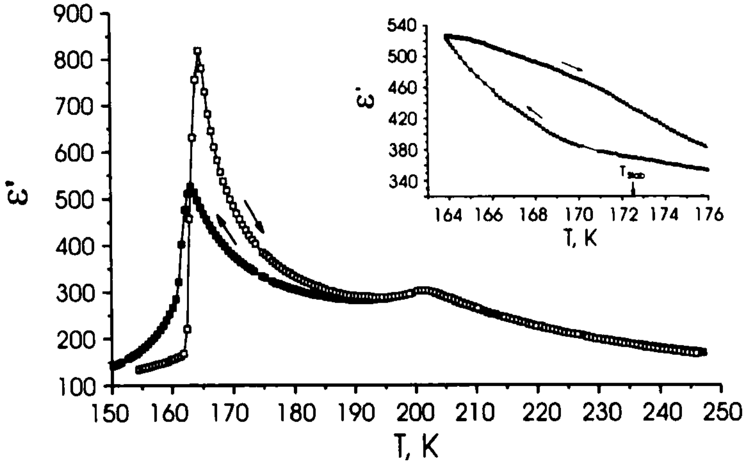

FIGURE 3 The temperature dependences of the dielectric constant at cooling and heating for $(Pb_{0.05}Sn_{0.95})_2P_2Se_6$ crystal. On insert: the result of the thermal memory recording in the IC phase at white light illumination during the temperature stabilization at 5 hours.

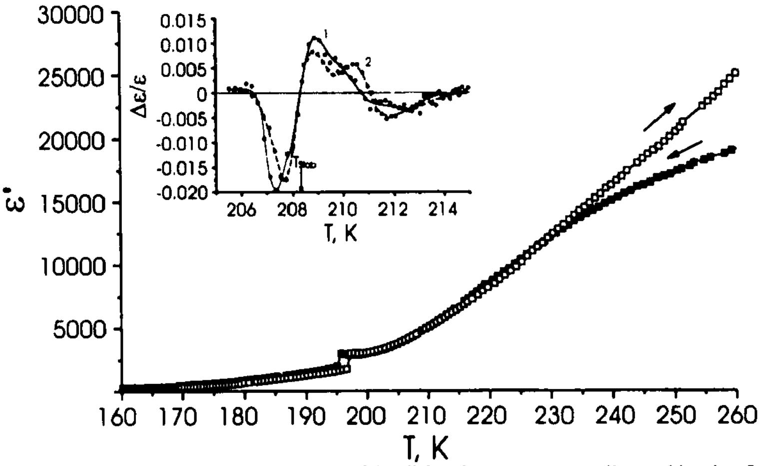

FIGURE 4 The temperature dependences of the dielectric constant at cooling and heating for $Sn_2P_2(S_{0.005}Se_{0.995})_6$ crystal with impurity of Mn. On insert: the reduced anomalous part $\Delta\varepsilon/\varepsilon$ of the dielectric constant that is related to the thermal memory effect in the IC phase at the temperature stabilization time 2 hours in darkness (1) and under white light illumination (2).

Along with this the dielectric output of domain walls in the ferroelectric phase is strongly suppressed. In $Sn_2P_2(Se_{0.995}S_{0.005})_6$ crystals with impurity of Mn the «memory» is revealed most strongly. For these crystals the illumination at the temperature stabilization significantly refines the recording of the named effect (Fig. 4).

DISCUSSION OF RESULTS

It was determined that the static defects concentration increment (Pb in $Sn_2P_2Se_6$) makes the recording of the memory effect impossible. At an increase of the free charge carriers concentration (crystals $Sn_2P_2(Se_{0.995}S_{0.005})_6$ with impurity of Mn) the recording of «memory» becomes better. At the same time, the static defects smear the anomaly ε'(T) at T_i, they significantly amplify the anomalous hysteresis and deform the anomaly of ε'(T) in the vicinity of T_c. But even at high concentration of the static defects the lock-in PT at T_c looks like a sharp first-order transition – upon heating the clear jump on ε'(T) dependence at T_c is observed. The increase of the free charge carriers concentration decreases the dielectric output of the domain walls in the ferroelectric phase more effectively than that of a number of static defects. At high concentration of free carriers the first order PT at T_c clearly appears in ε'(T) dependences, the anomalous hysteresis slightly increases.

The crystals $Sn_2P_2S(Se)_6$ are proper uniaxial ferroelectrics with the symmetry changing $P2_1/c$ - Pc at phase transition from paraelectric to ferroelectric phase. The 180^0 domains with anti-collinear orientation of the spontaneous polarization vector $\vec{P}_s$ exist in the ferroelectric phase. According to the data of [5] on the directed light scattering by the domain walls in the ferroelectric phase of $Sn_2P_2S_6$ these walls are oriented at some angle relatively to $\vec{P}_s$ and, consequently, they are charged.

The analysis of the properties of domain structures in uniaxial ferroelectrics in the mean-field approximation has been performed by many authors [6-8]. Following these works we will use the thermodynamic potential density

$$F = F_0 + \frac{\alpha}{2}\cdot P^2 + \frac{\beta}{4}\cdot P^4 + \frac{\gamma}{6}\cdot P^6 + \frac{\delta}{2}\cdot\left(\frac{\partial P}{\partial z}\right)^2 + \dots , \tag{1}$$

where $\alpha = \alpha_T(T - T_0)$. In the presence of the intermediate IC phase in proper uniaxial ferroelectrics in the expression (1) for the thermodynamic potential density the coefficient is $\delta < 0$ and we must also take in to account the invariants

$$\frac{g}{2}\left(\frac{\partial^2 P}{\partial z^2}\right)^2+\frac{\lambda}{2}\cdot P^2\left(\frac{\partial P}{\partial z}\right)^2. \qquad (2)$$

For $Sn_2P_2Se_6$ two coefficients are negative (δ and β) and all other coefficients in (1) and (2) are positive [9]. In such case we can find the solution for the space distribution of the spontaneous polarization in the form [7] $P = P_0 \cdot thK \cdot z$. Then, from (1) and (2) we obtain

$$P_0^2=-\frac{\beta}{2\cdot\gamma}\cdot\left(1+\sqrt{1-\frac{4\cdot\gamma\cdot\alpha}{\beta^2}}\right) \qquad (3)$$

and

$$K^2=\frac{k_i^2}{8}\left[\left(1-\frac{\lambda}{2\cdot\delta}\cdot P_0^2\right)+\left\{\left(1-\frac{\lambda\cdot P_0^2}{2\cdot\delta}\right)^2-\frac{4\cdot\alpha}{\alpha_i}\right\}^{0.5}\right], \qquad (4)$$

where $k_i^2=-\dfrac{\delta}{2\cdot g}$, $\alpha_i=\alpha+\dfrac{\delta^2}{4\cdot g}$. The domain wall width is $r_c = K^{-1}$.

In the approximation of small value of γ we find next expression for the specific surface energy of the domain wall: $\sigma_0=\dfrac{4\cdot\delta\cdot P_0^2}{3\cdot r_c}$.

Taking into account the depolarization energy and the full energy of the domain walls in the specimen with the thickness l in the polar direction X, we can find the equilibrium width d of the domains in the ferroelectric phase of crystal: $d=\sqrt{\dfrac{\varepsilon_0\cdot l\cdot\sigma_0}{k\cdot P_0^2}}$. Here $k=\dfrac{3.4}{1+\sqrt{\varepsilon_x\cdot\varepsilon_z}}$, ε_x and ε_z - the dielectric permeability of crystal in longitudinal (polar) and transverse directions, respectively, dielectric constant is $\varepsilon_0 \approx 8.85\cdot10^{-12}$ F·m^{-1}.

We can estimate the characteristics of the domain walls in the ferroelectric phase of $Sn_2P_2S_6$. We will use the data for 300 K. Here P_0=0.15 C·m^{-2}, $\varepsilon_X \approx 200$ and $\varepsilon_Z \approx 50$. The coefficients of the thermodynamic potential (1) are $\alpha_T \sim 1.6\cdot10^6$ J·m·C^{-1}·K^{-1}, $\beta \sim 7.4\cdot10^8$ J·m^5·C^4, $\gamma \sim 3.5\cdot10^{10}$ J·m^9·C^5, $\delta \sim 1.5\cdot10^{-10}$ J·m^3·C^2 [9]. For the listed parameters using the above formulae we find: $r_c \approx 4.2\cdot10^{-9}$ m, $d \approx 1.6\cdot10^{-7}$ m.

According to the relations (4), the width of domain wall r_c under the cooling decreases from ~4.3·10^{-9} m at T$_0$-T= 20K to ~1.3 10^{-9} m at T$_0$-T =100K. So, at decreasing temperature the width of the domain walls decreases until it reaches the dimensions of the elementary cell of the crystal lattice. For this reason we observe the well known effect of the domain walls "freezing", which appears in $Sn_2P_2S_6$ as the maximum of the dielectric losses at T_0-T~100K and decrease of the domain contribution to dielectric permeability at T_0-T>100K [10].

In fact $Sn_2P_2S(Se)_6$ crystals are ferroelectrics-semiconductors. The change of the free charge carriers concentration and the variation of the density of donor or acceptor impurities states can change the configuration of the domain structure. So, the dimension of domains d depends on the concentration of the free charge carriers n and also depends on the density of impurities state on the surface of the sample N_i. At the critical concentrations [8] $n^{cr} = \frac{k_B \cdot T}{4 \cdot e^2 \cdot l} \cdot \sqrt{\frac{\pi \cdot \varepsilon_0 \cdot \varepsilon_Z}{\delta}}$ and $N_i^{cr} = \frac{\sqrt{\pi \cdot \varepsilon_0 \cdot \varepsilon_Z}}{16 \cdot e^2} \cdot \frac{\Delta E}{\sqrt{\delta}}$ the sample becomes monodomain ($d \to \infty$). For $Sn_2P_2S_6$ platelet sample with the thickness $l = 2 \cdot 10^{-3}$ m, using the earlier listed parameters and taking the energy of impurities level $\Delta E_i \approx$ 0.7eV [4] for temperature 330K we estimate $n^{cr} \approx 6.8 \cdot 10^{19}$ m^{-3} and $N_i^{cr} \approx 0.9 \cdot 10^{18}$ m^{-2}.

For the $Sn_2P_2Se_6$ and $Sn_2P_2S_6$ crystals both relaxation effects (the thermal memory in the incommensurate phase of $Sn_2P_2Se_6$ and the second order ferroelectric PT splitting after long term temperature stabilization near T_0 in paraelectric phase of $Sn_2P_2S_6$) are consistently explained with the use of the following set of the semiconductor parameters of these compounds: the conduction electron concentration $n \approx 10^{14}$-10^{16} m^{-3}; the attachment level concentration $N_a \approx 10^{24}$ m^{-3} [4]. From the named values of N_a the estimation of the concentration of surface impurities levels follows — $N_i \approx 10^{16}$ m^{-2}. As one can see, the values of concentrations n and N_i estimated on the basis of experimental data, are much smaller than their critical values n^{cr} and N_i^{cr}. In this case the mean domain width is probably close to earlier estimated value.

In the investigated samples the specific resistance ρ is changed from $5 \cdot 10^{10}$ Ω·m for the crystals $Sn_2P_2Se_6$ obtained by the Bridgeman method up to $5.5 \cdot 10^7$ Ω·m for prepared by vapor-transport method crystals $Sn_2P_2(Se_{0.005}S_{0.995})_6$ with impurity of Mn. For different investigated samples the conductivity differs by three orders. At the same time we have estimated the concentrations n of the charge carriers in the conduction zone for the mostly conductive specimens of $Sn_2P_2Se_6$. From this we can conclude that in all investigated specimens the charge carriers concentrations are quite smaller relatively to concentration n^{cr} at which the sample becomes monodomain. The decrease of the domain-walls dielectric contribution in the ferroelectric phase of $Sn_2P_2S(Se)_6$ crystals is obviously caused by the decreasing of the

domain walls mobility. The mobility decreases due to the charged domain walls compensation by free charge carriers.

CONCLUSION

For the ferroelectrics-semiconductors $Sn_2P_2S(Se)_6$ the increase of charge carriers concentration promotes the thermal memory recording in the IC phase and decreases the dielectric contribution of domain walls in the ferroelectric phase. Such influences of charge carriers on the memory effect and the dielectric output of domain walls obviously are connected with redistribution of the carriers in the field of the spontaneous polarization and their localization on the impurities levels. The static defects destroy the memory effect. They improve the anomalous temperature hysteresis in the IC phase and suppress the dielectric response of domain walls in the ferroelectric phase.

Acknowledgments
This work has been partially supported by the INTAS-93-3230-ext project.

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