Thermal characterization and critical behavior study of \((\Pb_{x}\Sn_{1-x})_2P_2\Se_6\)

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\textbf{ABSTRACT}
Thermal characterization of the ferroelectric family \((\Pb_{x}\Sn_{1-x})_2P_2\Se_6\) has been completed studying the thermal diffusivity of \(x = 0.1\) and \(x = 0.8\) by means of \(ac\) photopyroelectric calorimetry in the range 30–295K. Two phase transitions have been detected for \(x = 0.1\): II-order paraelectric-incommensurate and I-order incommensurate-ferroelectric. A critical behavior study of the continuous transition has been undertaken in the light of renormalization group theory. The critical parameters obtained (\(\alpha = -0.018, A^+/A^- = 0.99\)) allows the attribution of the 3D-XY universality class, in agreement with theory. The crystal with \(x = 0.8\) shows no transitions in a full temperature range measured.

\textbf{KEYWORDS}
Uniaxial ferroelectrics; thermal diffusivity; phase transition; critical behavior

\section{1. Introduction}
Pb(Sn)\textsubscript{2}P\textsubscript{2}Se\textsubscript{6} mixed compounds belong to a broad family of semiconductor ferroelectric crystals Pb(Sn)\textsubscript{2}P\textsubscript{2}S(Se)\textsubscript{6}, which possess promising photorefractive, acousto-optic and electro-optic properties [1–4]. In particular, Pb(Sn)\textsubscript{2}P\textsubscript{2}Se\textsubscript{6} crystals could find a practical interest in low temperature thermometry in a high magnetic field, due to their dielectric properties [5]. On the other hand, these materials are attractive from the solid state physics standpoint, because they have a quite complex phase diagram with the presence of a Lifshitz point, and where the different stable phases such as Ferroelectric, Incommensurate and Paraelectric are separated by the first-order and second-order phase transition lines [6]. This provides the possibility to study the behavior of the system across the different types of critical points. In previous publications related to these families, it was well established that the critical behavior of Sn\textsubscript{2}P\textsubscript{2}S\textsubscript{6} is well described by the combination of two physical mechanisms: first order fluctuations of the order parameter (polarization) and the presence of charged defects [7]. The substitution of S with Se in Sn\textsubscript{2}P\textsubscript{2}(Se\textsubscript{x}S\textsubscript{1-x})\textsubscript{6} series at concentrations close to the Lifshitz point (\(x = 0.28\)) modifies the critical behavior, which is better described by the Lifshitz universality class [8], while an isovalent replacement of Sn atoms by Pb provokes a crossover from the described behavior in the pure sample to a mean-field model [9]. Finally, the...
continuous paraelectric to incommensurate phase transition in \((Pb_xSn_{1-x})_2P_2Se_6\) \((x = 0, 0.05)\) was studied in our previous work \([10]\) and was attributed to belong to the 3D-XY universality class. This particular case of the Paraelectric-Incommensurate phase transition in ferroelectrics is extremely interesting because the order parameter associated with the irreducible representation of the cogroup of the modulation wave vector \(q\) is a complex variable; hence the Hamiltonian which describes the system has a two component order parameter \([11, 12]\). Renormalization group theory assesses that this transition must belong to the 3D-XY universality class \([11]\) for which the critical parameters for specific heat are \(\alpha = -0.014, \lambda = 1.06\) \([13]\). It is worth noting that the critical behavior analysis of \((Pb_xSn_{1-x})_2P_2Se_6\) family had been previously undertaken by other authors only for the undoped \(Sn_2P_2Se_6\) crystal, measuring optical birefringence \([14]\), neutron magnetic resonance (NMR) \([15]\) or thermal expansion coefficient \([16]\). In all cases, only information from one phase was used to extract the critical behavior and the results were not confronted with the theoretical predictions of renormalization group theory mentioned above.

The aim of the present paper is as follows: in the first place, we will complete the thermal characterization of \((Pb_xSn_{1-x})_2P_2Se_6\) mixed ferroelectrics measuring thermal diffusivity \(D\) for \(x = 0.1\) and 0.8 in a low temperature range, in order to better understand how heat is being propagated inside the material as Pb concentration is changed from \(x = 0\) to 1. The second step is focused on completing the critical behavior study for the paraelectric to incommensurate phase transition, after ref. \([10]\), for which we will be using information from both phases, above and below the critical temperature and compare it with the universality classes theorized by renormalization group theory. This will allow us to have a full view on how the isovalent atom substitutions \(S\) by \(Se\) and \(Sn\) by \(Pb\) in \(Pb(Sn)_2P_2Se_6\) ferroelectrics alter the behavior of the system in the vicinity of the second order phase transitions.

2. Samples and experimental techniques

\(Sn_2P_2Se_6\) monoclinic ferroelectric exhibits three phases; at room temperature it is paraelectric (P2_1/c) \([6]\), at \(T_1 \approx 221K\) a second order transition takes place to a modulated incommensurate phase, and at \(T_c \approx 193 K\) the crystal shows a first order transition to the ferroelectric phase (Pc) \([6]\). Single crystals \((Pb_xSn_{1-x})_2P_2Se_6\) with lead concentrations of \(x = 0.1\) and \(x = 0.8\) were grown in a quartz tube using vapour-transport method. Both samples have been checked by X-ray measurements confirming that the crystal \(x = 0.1\) has the same quality as the samples already studied in ref \([10]\) while the crystalline quality of \(x = 0.8\) was slightly worse than for the rest of them. For thermal diffusivity \(D\) investigations the samples have been prepared in a form of plane parallel slabs with thickness in a range of 520–550 \(\mu m\). In case of \(x = 0.1\) its face was cut in a direction perpendicular to [100] crystallographic axis, in order to better compare with data published in ref. \([10]\). For \(x = 0.8\) the only effective value of \(D\) was measured.

Thermal diffusivity measurements have been carried out using \(ac\) photopyroelectric calorimetry in the back detection configuration with \(LiTaO_3\) as a detector. This technique has been successfully employed for this kind of studies in a broad variety of materials \([7–10, 17–19]\). A detailed description of the experimental setup and procedure can be found in \([8]\) and references therein. The measurements were performed in two steps: the first was a quick run with a rate of 100 mK/min in order to cover a wide temperature range 30–295 K. The second one consisted of slow heating/cooling runs (10–20 mK/min) around the critical point retrieving
the precise shape of the transition (necessary for the critical behavior study) and checking the possible presence of thermal hysteresis. Using the constituent relation \( D = K/\rho c_p \), where \( K \) is the thermal diffusivity, \( \rho \) is the density of the material and \( c_p \) is the specific heat, and taking into account that \( K \) does not have any singularity at the second order transitions in these ferroelectric crystals [7, 20], we conclude that \( c_p \) and \( 1/D \) have the same critical behavior. Therefore, \( 1/D \) can be used instead of specific heat in further critical analysis.

3. Results and discussion

3.1. Phase transitions

Figure 1 presents the influence of Pb atoms on the I and II order phase transitions of \( \text{Sn}_2\text{P}_2\text{Se}_6 \) crystal. To better compare and see the full picture in detail we have included our previous thermal diffusivity data for \( x = 0 \) and \( x = 0.05 \) [10]. It is clearly seen from the graph that the shapes of both transitions are heavily altered while Pb content is increased. For \( x = 0.1 \) there is a strong downward temperature shifting with a simultaneous broadening of both II-order paraelectric-incommensurate transition (\( T_i \)) as well as I-order structural incommensurate-ferroelectric one (\( T_c \)) compared to the pure sample. At higher concentrations both transitions have already been shown to smear and, for particular Pb contents, disappear [10, 21, 22]. The continuous character (lack of hysteresis) of the upper transition at \( T_i \) for \( x = 0.1 \) has been checked by performing heating and cooling runs at slow rates. On the other hand, a temperature hysteresis accompanied with a distinct difference in shape for heating and cooling runs was found for \( T_c \); this temperature hysteresis increases from 0.45 K at \( x = 0 \) to about 2.1 K at \( x = 0.1 \). Besides, the temperature interval for the modulated phase existence is also extended from an initial 28 K for pure \( \text{Sn}_2\text{P}_2\text{Se}_6 \) to approximately 40 K for \( (\text{Pb}_{0.1}\text{Sn}_{0.9})_2\text{P}_2\text{Se}_6 \) crystal. This tendency is in agreement with data obtained by means of light transmission measurements [21]. The transition temperature lowering is related to the ionic radius difference, which is smaller for \( \text{Sn}^{2+} \) cations than that for \( \text{Pb}^{2+} \) ones. Thus, the introduction of Pb instead of Sn increases the space available for tin cations; as a result, the last

![Figure 1](image-url)
ones are able to move in the crystal lattice with smaller thermal energies [22]. No trace of any transition was found for $x = 0.8$ in the full temperature range measured, meaning that the crystal remains in the paraelectric phase, in agreement with literature [21, 22].

### 3.2. Thermal characterization

Let’s discuss Figure 2, which contains the temperature evolution of the thermal diffusivity curves for crystals with Pb content of $x = 0$, 0.05, 0.2, 0.47, and 1 [10] accompanied by $x = 0.1$ and $x = 0.8$ measured in this work. We consider the general trend omitting phase transition region. The graph displays an interval from 30 K up to approximately double the Debye temperature $\theta_D$ (for Pb$_2$P$_2$Se$_6$ and Sn$_2$P$_2$Se$_6$ crystals this values are about 65 K and 85 K respectively [6]). From then upwards there is a general monotonic background decrease in $D$, where the phase transitions are superimposed. In all cases in Fig. 2, $D$ rapidly increases with temperature lowering, specially for the extreme compounds, starting from their respective Debye temperatures, which is related to the fact that this is the temperature below which the lattice vibrations begin to be frozen out while above it all modes start to be excited, seriously modifying the phonon mean free path. The behavior with doping can be explained by the presence of two different species (Pb and Sn) with different sizes (Pb$^{2+}$ ionic radius is larger than that for Sn$^{2+}$) in the cation sublattice for mixed compositions. Thus, both atoms share the same space available, distorting the crystal lattice. As a result, it leads to a reduction in the phonon mean free path, hence, to a lower thermal diffusivity value. The same trace has been observed in the case of (Pb$_x$Sn$_{1-x}$)$_2$P$_2$Se$_6$ ferroelectrics [9], which in general is typical for the thermal insulator material, where phonons are mainly responsible for heat propagation.

### 3.3. Critical behavior

In order to complete our previous critical behavior analysis for (Pb$_x$Sn$_{1-x}$)$_2$P$_2$Se$_6$ mixed ferroelectrics $x = 0, 0.05$ [10] we have studied the continuous transition of (Pb$_{0.1}$Sn$_{0.9}$)$_2$P$_2$Se$_6$...
crystal. In order to do this we have simultaneously fitted both low and high temperature branches of $1/D$ in the vicinity of $T_i$ to the well known equation [8]

$$\frac{1}{D} = B + C t + A^\pm |t|^{-\alpha} (1 + E^\pm |t|^{0.5})$$

where $t = (T-T_C)/T_C$ is the reduced temperature, $\alpha$ the critical exponent, which has to be the same for both branches. $A^\pm$ are the critical coefficients, where superscripts ‘+’ and ‘−’ correspond to the high and low temperature phases, respectively. The factor in parenthesis is a small correction to the leading power. The linear term represents a background contribution while the nonlinear one describes the anomalous part.

The results of the fitting together with the deviation plot are displayed on Figure 3. The best fit gave the following results: critical exponent $\alpha = -0.018 \pm 0.007$, critical ratio $A^+/A^- = 0.99$. The quality of the fitting was confirmed by the high coefficient of determination $R^2 = 0.999$. The critical regions $t$ used for analysis were as follows: $2.21 \times 10^{-2} - 1.05 \times 10^{-1}$ for $T < T_C$ and $5.07 \times 10^{-3} - 9.63 \times 10^{-2}$ for $T > T_C$. These results agree quite well with the theoretical predictions for the 3D-XY model ($\alpha = -0.014$, $A^+/A^- = 1.06$), which has been theorized to be of application to the paraelectric to incommensurate phase transitions in ferroelectrics [11]. Moreover, the critical parameters for $x = 0.1$ are perfectly aligned with those found for $x = 0$ ($\alpha = -0.019 \pm 0.008$, $A^+/A^- = 1.00$) and for $x = 0.05$ ($\alpha = -0.026 \pm 0.018$, $A^+/A^- = 1.03$) [10], indicating that the continuous paraelectric to incommensurate phase transitions at $x = 0$, 0.05 and 0.1 add up to the list of the 3D-XY universality class.

4. Conclusions

Thermal diffusivity of $(\text{Pb}_{0.1}\text{Sn}_{0.9})_2\text{P}_2\text{Se}_6$ mixed ferroelectrics at $x = 0.1$ and $x = 0.8$ has been measured in the range 30–295 K using $ac$ photopyroelectric calorimetry and compared with the rest of the family. The evolution with temperature is the typical one for thermal insulator materials, where heat is mainly transported by crystal lattice vibrations. For the sample doped with $x = 0.1$ two phase transitions at about $T_i \approx 284$ K and at $T_c \approx 144$ K have been found. The critical behavior analysis performed for the continuous transition leads to the conclusion that the 3D-XY universality class is of application, as theory predicts for this

![Figure 3.](image-url)
kind of transitions. The crystal with $x = 0.8$ exhibits no transitions in the full temperature range.

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