FERROELECTRIC PHASE TRANSITION AND IMPURITY-LATTICE CORRELATIONS IN Pb$_{1-x}$Ge$_x$Te(Ga)

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The impedance of single-crystal samples of PbTe(Ga) and Pb$_{1-x}$Ge$_x$Te(Ga) (0 $\leq$ x $\leq$ 0.095) is investigated in the frequency range from 10$^2$ to 10$^6$ Hz and temperature range 4.2–300 K. The temperature dependence of the capacitance of all the Pb$_{1-x}$Ge$_x$Te(Ga) samples studied exhibited two types of features. These are a pronounced peak at a temperature $T \sim T_{ph}$, caused by a dielectric anomaly at the ferroelectric phase transition, and strong frequency dependent increase of the capacitance in the temperature region $T < 100$ K. The ferroelectric phase transition temperature for all the samples is found to be significantly higher than the characteristic temperatures of the long term relaxation process appearance. Thus these phenomena seem not to be correlated directly. The low temperature behavior of the capacitance may be caused by recharge processes in the impurity system accompanied by local reconstruction of the impurity center surrounding.

1. Introduction

The impurities characterized by mixed valence (In, Ga, Cr, Yb and some others) generate in lead telluride based solid solutions a system of deep energy levels, their position depending on the composition of the solution and the kind of a dopant. The Fermi level pinning, persistent photoconductivity at low temperatures, specific view of current-voltage characteristics, nonexponential relaxation of nonequilibrium carriers, unusual magnetic properties may be regarded as characteristic features of such doped solutions.

Most of the models developed to describe the impurity behavior consider the strong correlation of the impurity charge state and local distortion of the lattice nearby the impurity center [1]. Nevertheless the conception of ferroelectric phase transition induced by the doping was not still disproved by direct experiment.

Pb$_{1-x}$Ge$_x$Te(Ga) single crystals seem to be the mostly suitable object for such kind of investigation. Their electrophysical and photoelectric characteristics have been studied in detail [2-6]. The phase transition temperature $T_{ph}$ in undoped Pb$_{1-x}$Ge$_x$Te(Ga) is well known [7,8]. Doping with Ga leads to significant resistance growth due to the Fermi level pinning within the energy gap and persistent photoconductivity appearance at $T \leq T_c \approx 80$ K. Thus the opportunity to measure the impedance indicating the dielectric permittivity behavior for single crystal samples without specially prepared p-n junction appears.

2. Samples and Experimental Technique

Single-crystal samples of Pb$_{1-x}$Ge$_x$Te(Ga) (0 $\leq$ x $\leq$ 0.095) were obtained by sublimation from the vapor phase. An impurity of 1.5 mol. % GaTe was introduced directly into the growing melt. The composition of the samples was determined by the X-ray diffraction method. The values of the lattice constant are presented in the Table. The samples intended for impedance measurements were in the form of rectangular slabs with an area of $\sim 4 \times 4$ mm and thickness $\sim 1$ mm. The surface of the slabs was coated by a 95%In+4%Ag+1%Au alloy.
For the measurements the samples were placed in a chamber that shielded them from background radiation.

<table>
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<th>N</th>
<th>Lattice constant $a$, Å</th>
<th>$X$</th>
<th>$T_{ph}$, K (liter.)</th>
<th>$T_{ph}$, K (exper)</th>
<th>Energy gap $E_g$, meV</th>
<th>$E_A$, meV</th>
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The measurements were made with E7-12 and MIT 9216A ac current bridges at frequencies $f$ from $10^2$ to $10^6$ Hz in the temperature interval 4.2–300 K. The temperature dependence of the resistivity $\rho$ was measured in dc on samples 1x1x5 mm in size in darkness and under illumination by IR radiation sources.

3. Experimental Results

The typical view of the temperature curves of the resistivity $\rho$ measured in darkness and under illumination of a lightemitting diode at wavelength $\lambda = 1$ µm is shown in Fig.1 for the Pb$_{1-X}$Ge$_X$Te(Ga) sample with $x = 0.046$. Similar curves had been observed previously for solid solutions of various compositions [2–6]. The characteristic feature distinguishing the $\rho(T)$ curve for Pb$_{1-X}$Ge$_X$Te(Ga) from that for PbTe(Ga) is the presence of a maximum followed by rapid drop of the $\rho$ value at cooling even for the curve taken in darkness. In lead telluride containing gallium $\rho(T)$ increases monotonically with decreasing temperature all the way down the lowest temperatures of the experiment. Persistent photoconductivity is

![Fig.1](image-url)

Fig.1. Temperature dependence of the resistance $R$ for Pb$_{1-X}$Ge$_X$Te(Ga) sample ($x = 0.046$) in darkness and under illumination.
observed at $T<T_C = 80$ K, where $T_C$ is independent of the composition $x$ of the solid solution. In Refs. [2] and [4–6] a correlation was noted between the composition $x$ of the solid solution and the temperature $T_m$ corresponding to the maximum on the $\rho(T)$ curves obtained under conditions of shielding. This suggested that the maximum is due to a phase transition [4–6] the temperature of which is shifted by approximately 80 K downward on the temperature scale because of the presence of the dopant. However, the possibility of such a substantial change in phase transition temperature for such an insignificant impurity concentration has raised valid objections [2,3]. In the high-temperature region the $\rho(T)$ curves for all the samples studied exhibited a segment corresponding to an activational character of the conductivity. The activation energies $E_A$ calculated from the relation $\rho \sim \exp(E_A/kT)$ are given in the Table. It should be noted that the values of the activation energy obtained previously [2-6] are practically equal to the data of the present study and do not depend on the shape and size of the sample. At frequencies below $10^5$ Hz the real part of the impedance $Z'$ is practically equal to $\rho$. At a frequency of $10^6$ Hz the value of $Z'$ in the peak region is somewhat lower. An example of the typical temperature dependence of the capacitance $C$ for the Pb$_{1-x}$Ge$_x$Te(Ga) ($x = 0.095$) sample measured at different frequencies is shown in Fig. 2. Since the crystals studied were not completely isolated, especially in the high-temperature region, in the processing of the experimental data the capacitance of the crystals was calculated from the values of the real $Z'$ and imaginary $Z''$ parts of the impedance in the approximation of an equivalent circuit in the form of a parallel $R-C$ circuit. As is seen in Fig.2, for $T = T_{ph}$ the $C(T)$ curves clearly exhibit a peak with a position that is practically independent of frequency. The Table also gives the values of the phase transition temperature for undoped Pb$_{1-x}$Ge$_x$Te(Ga) crystals, according to published data ($T_{ph}$ liter.) and according to the experimental data of the present study ($T_{ph}$ exper.). The temperature at which the peak is observed on the $C(T)$ curve is somewhat lower than the temperature of the transition from the cubic to the rhombohedral phase for the undoped alloy of the same composition but is substantially higher than the temperature of the maximum on the $\rho(T)$ curves. It should be

![Fig.2. Temperature dependence of the capacitance for Pb$_{1-x}$Ge$_x$Te(Ga) ($x = 0.095$). The reference signal frequency is shown at the curves.](image)

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noted that the lowering of the phase transition temperature by an amount that is quite comparable with the data of the present study has also been observed upon doping of Pb$_{1-X}$Ge$_X$Te(Ga) alloys with indium [8]. It is important that the peak on the $C(T)$ curves is rather sharp, indicating good homogeneity of the samples in respect to composition. In the temperature region $T < T_{\text{cap}}$ ($T_{\text{cap}}$ is the temperature at which low-frequency anomalies appear) a strong frequency dependence of the capacitance is observed. At low frequencies ($f \sim 10^3$ Hz) one observes a sharp increase in the capacitance by almost an order of magnitude. With increasing $f$ the amplitude of the jump decreases, and at $f \sim 10^5$ Hz the $C(T)$ curve becomes rather smooth. In the temperature region $T < 70$ K the capacitance of PbTe(Ga) single crystals is practically independent of both temperature and the frequency $f$ (see Fig. 3).

Fig.3. Temperature dependence of the capacitance of PbTe(Ga) samples in relative units ($C_0$ is the capacitance of the vacuum condenser of the same configuration). The reference signal frequency is shown at the curves. Two curves corresponding to the same frequency of $10^6$ Hz are measured for samples with different shape and, consequently, $C_0$ values.

Figure 4 shows the temperature dependence of the ratio $C/C_0$ for Pb$_{1-X}$Ge$_X$Te(Ga) samples of various composition ($C_0$ is the geometric capacitance, defined as the ratio of the area of the contacts on the sample to the distance between them). If it is assumed that the sample is a flat capacitor, then the value of $C/C_0$ corresponds to the permittivity $\varepsilon$. For all the Pb$_{1-X}$Ge$_X$Te(Ga) samples studied we find $\varepsilon \sim 1300$ in the temperature interval $T_{\text{cap}} < T < T_{\text{ph}}$ for all $f < 10^5$ Hz and in the interval 4.2 K $< T < T_{\text{ph}}$ for $f > 10^5$ Hz. The additional contribution to the capacitance observed in Pb$_{1-X}$Ge$_X$Te(Ga) in the low-frequency range for $T < T_{\text{cap}}$ cannot be attributed to processes due to polarization or resonance effects of the crystal lattice itself. The characteristic frequencies of such effects are many orders of magnitude higher than $10^6$ Hz. The most probable cause of the increase in capacitance may be processes involving charge exchange between impurity centers. An analogous effect in the same frequency range has been observed previously in the heterojunctions of germanium-silicon diodes and was explained as being the contribution to the capacitance of the heterojunction from charge exchange between boundary states [9].
4. Conclusion

In this study we have established experimentally that the phase transition temperature $T_{ph}$ in Pb$_{1-x}$Ge$_x$Te(Ga) is substantially higher than the characteristic temperatures for the appearance of persistent photoconductivity ($T_c \sim 80$ K), the temperatures of the maximum on the $\rho(T)$ curves $T_m$, and the temperatures at which the low-frequency anomalies appear on the temperature curves of the capacitance ($T_{cap}$). The data show that processes involving charge exchange between impurities are characterized by only a local reconstruction of the lattice, unaccompanied by the frequency-independent dielectric anomalies observed at transitions to the ferrophase. This study was supported in part by Grants Nos. 04-02-16397, 05-02-16657 and 1786.2003.2 from the Russian Foundation for Basic Research and by INTAS Grant No. 2001-0184.

References