

NONSTOICHIOMETRY AND CONDUCTIVITY ANISOTROPY OF LEAD GERMANATE SINGLE CRYSTALS

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The conductivity of lead germanate single crystals with the stoichiometric composition, PbO deficiency, and PbO excess has been measured. A reduction of the PbO fraction in the initial blend leads to a considerable increase of the conductivity, because the fraction of lead ions which change their valency from Pb^{2+} to Pb^{3+} grows. The relative arrangement of lead ions, which are able to change their valency and trap holes, can be responsible for a significant anisotropy of conductivity.

1. Introduction

Lead germanate $Pb_5Ge_3O_{11}$ is a uniaxial ferroelectric with a phase transition of the second kind at 179 °C, at which the crystal symmetry changes from the hexagonal to trigonal one: $P\bar{6}(C_{3h}^1) \longleftrightarrow P3(C_3^1)$ [1, 2]. Owing to its pyroelectric and ferroelectric properties, lead germanate is a rather promising photorefractive substance. In work [3], the photorefractive effect, i.e. a variation of the refractive index under the light action in a nominally pure $Pb_5Ge_3O_{11}$, was demonstrated for the first time. By illuminating a photorefractive crystal with two

coherent light beams, one can record a phase hologram in it. Two types of diffraction gratings are observed in lead germanate at the hologram recording: a fast (with a time constant less than 1 s) and a slow one (the time constant falls within the interval from several minutes to hours) [4]; and each hologram type is associated with specific charge carriers. In works [5, 6], attempts to enhance photorefractive properties of the crystal were done by introducing impurity atoms into it, because impurities often considerably affect electro-optical properties and charge transfer. However, no appreciable result was achieved. Ultimately, it is the defect structure and electroconductivity of a crystal that play the crucial role in governing its photorefractive properties. In this connection, we aimed in this work at studying the anisotropy of conductivity and the influence of the lead sublattice on the electric conductivity of lead germanate (grown up with both a deficiency and an excess of PbO).

2. Results

Single crystals of lead germanate, $Pb_5Ge_3O_{11}$, were grown up for researches by the Czochralski method. The initial ratio between the PbO and GeO_2 oxide contents at the blend synthesis was $(5+x) : 3$, respectively, where $x = -0.05, 0.00$, and $+0.05$. Measurements were carried out by the bridge method (using a bridge E8-2) in the frequency range from 50 Hz to 18 kHz. Specimens 0.4–0.8 mm in thickness were cut out in the directions [100] and [001]. They were supplied with platinum electrodes deposited by cathode sputtering.

The experimental data were plotted in the plane of complex impedance $Z'' - Z'$ (Fig. 1). The corresponding hodograph curves are represented by semicircle arches. This means that a parallel RC circuit [7] is an equivalent scheme of the specimen in the given frequency range, which, in its turn, evidences for a dominating contribution of conductivity to dielectric properties of the crystal already at intermediate temperatures. Such rather high electroconductivity of lead germanate does not allow the dielectric relaxation to be studied directly in the

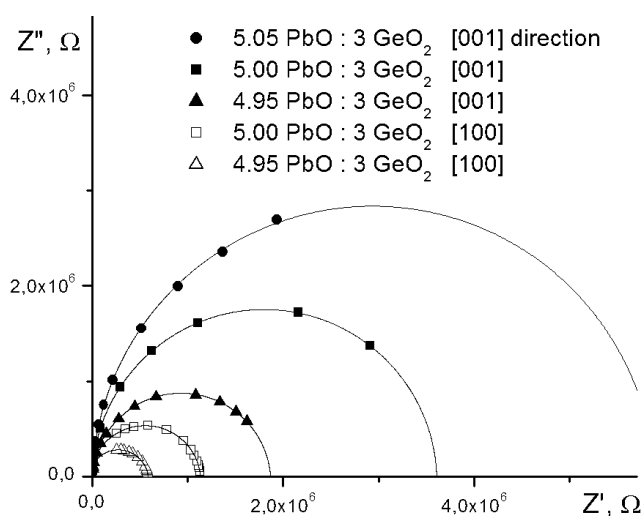


Fig. 1. Example of experimental data plotted in the complex impedance plane

$\epsilon'' - \epsilon'$ plane (except at low temperatures), because it smears the semicircle arches in these coordinates. The low-frequency point of arch intersection with the real Z' -axis (Fig. 1) corresponds to the total resistance of the specimen in the dc mode. Knowing the geometrical dimensions of the single crystal, we calculated its dc conductivity σ_{dc} . Then, the temperature dependences of specific electroconductance were plotted for various compositions and directions. The corresponding plots (Fig. 2) are straight lines in the coordinates $\ln \sigma_{dc}$ versus $1/T$, which testifies that the charge transfer in lead germanate crystals is thermally activated:

$$\sigma_{dc}(T) = A \exp\left(-\frac{E_a}{k_B T}\right), \quad (1)$$

where A is a preexponential factor, E_a the activation energy of the electroconductivity process, and k_B the Boltzmann constant.

In the studied temperature range, the conductivity grows with the reduction of x . The conductivity of stoichiometric single crystals $5.00\text{PbO} : 3\text{GeO}_2$ is slightly higher than that for the composition $5.05\text{PbO} : 3\text{GeO}_2$. At the same time, the relative difference between electric conductivities for $5.00\text{PbO} : 3\text{GeO}_2$ and $4.95\text{PbO} : 3\text{GeO}_2$ contents exceed 100% (in the crystal with PbO deficiency, the conductivity is higher).

Concerning the conductivity anisotropy, it is well pronounced in lead germanate single crystals. For instance, the conductivity in the direction [001] (the third-order axis) is 3 to 4 times as low as that in the direction [100]. In Table, the calculated values of the conductivity activation energy E_a of lead germanate single crystals with various nonstoichiometries in directions [100] and [001] are listed. The table testifies that, below the Curie point, the conductivity activation energy is approximately identical for all compositions and directions (within the experimental error limits), being of about 0.70 eV. In the paraphase, the activation energy decreases for almost all specimens, but the stoichiometric specimen in the direction [001], when the activation energy does not change.

Activation energy E_a

Initial blend content	Measurement direction	Activation energy E_a , eV	
		ferroelectric phase	paraphase
$5.05\text{PbO} : 3\text{GeO}_2$	[001]	–	0.70 ± 0.01
$5.00\text{PbO} : 3\text{GeO}_2$	[001]	0.71 ± 0.01	0.71 ± 0.01
$4.95\text{PbO} : 3\text{GeO}_2$	[001]	0.70 ± 0.03	0.63 ± 0.01
$5.00\text{PbO} : 3\text{GeO}_2$	[100]	0.68 ± 0.01	0.60 ± 0.01
$4.95\text{PbO} : 3\text{GeO}_2$	[100]	0.70 ± 0.01	0.60 ± 0.01

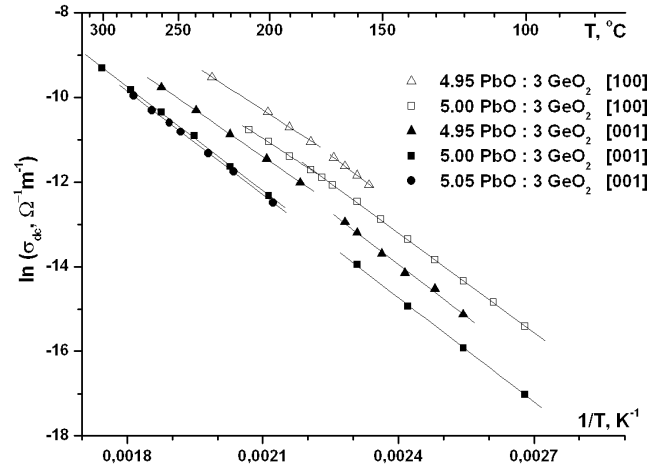


Fig. 2. Temperature dependences of specific conductance for lead germanate single crystals with various nonstoichiometries

3. Discussion

The electric conductivity of lead germanate has an ionic and an electronic component. The availability of ionic component (at least at high enough temperatures – more than 300 °C – in the direction [001]) is evidenced by a characteristic low-frequency section – a finite-length Warburg impedance – in the plots Z'' versus Z' [8], which testifies to a contribution to conductivity made by oxygen ions [9]. The crystalline structure of lead germanate consists of alternating layers with either the apatite or nasonite structure, which are oriented normally to the direction [001]. Tetrahedra GeO_4 and double tetrahedra Ge_2O_7 are connected with one another by strong Pb–O covalent bonds and form one-dimensional wide empty channels along the third-order axis [1]. Those channels are filled with univalent negative halogen or hydroxyl ions in ordinary apatites and with oxygen ions in oxyapatites [10]. In lead germanate, these channels can stimulate a considerable electric conductivity by means of oxygen ions at high enough temperatures. However, as Fig. 2 demonstrates, the conductivity along the direction [001] is several times lower than that in the direction [100]. That is, at temperatures below 300 °C, the contribution of the ionic component does not dominate. As was shown in work [8], a reduction of the partial pressure of oxygen in the surrounding atmosphere considerably reduces the conductivity of lead germanate, which testifies that holes are electronic charge carriers (the p -type of conductivity). Since the energy gap width in lead germanate is about 3 eV, the interband mechanism of conductivity is hardly

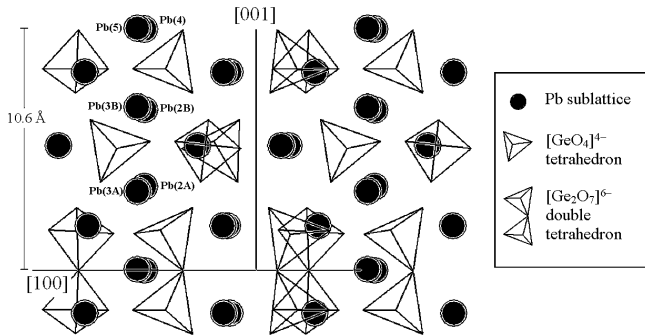
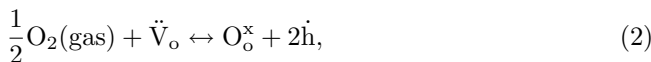


Fig. 3. Structure of lead germanate in the ferroelectric phase [1]

probable at high temperatures. The actual transport of charge carriers can occur by means of the hopping mechanism over localized states in the energy gap. Since the valency of germanium ions in the lead germanate structure is maximal, it is the lead ions that are the centers of hole localization. This conclusion was directly confirmed in work [11], where the electron paramagnetic resonance method was used to reveal Pb^{3+} ions. In addition, it was shown that only one of six atoms—Pb(2A), Pb(2B), Pb(3A), Pb(3B), Pb(4), or Pb(5) (in the notations of work [1])—in the lead germanate elementary cell (see Fig. 3) can change its valency.

At the blend synthesis and single-crystal growing which are executed at high temperatures, it is impossible to completely prevent partial losses of the volatile component, lead oxide PbO . The ratios between the oxide PbO and GeO_2 contents in the initial blend and the obtained single crystal are different, with the width of homogeneity range in oxides being able to reach several percent. Therefore, even in a nominally stoichiometric lead germanate, there exist the enough number of vacancies in the lead and oxygen sublattices. Taking into account a huge influence that the partial pressure of oxygen in the surrounding atmosphere exerts on the electric conductivity of $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ crystal [8], it is possible to suppose that oxygen enters into the crystalline matrix freely enough, according to the quasichemical reaction



where $\text{O}_{\text{O}}^{\times}$ is a neutral occupied site in the oxygen sublattice, and $\ddot{\text{V}}_{\text{O}}$ is the oxygen vacancy. Hence, there can be much more lead vacancies in the lead germanate lattice than oxygen ones. In such a situation, in order to provide the electroneutrality of the crystal as a whole, some lead ions change their valency: $\text{Pb}^{2+} \rightarrow \text{Pb}^{3+}$, which is the reason for the hole electroconductivity observed experimentally. Therefore, the conductivity of a lead ger-

manate single crystal grown up with a PbO deficiency ($4.95\text{PbO} : 3\text{GeO}_2$) is more than twice higher than that of nominally stoichiometric $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ (Fig. 2) in both directions. The more is the number of lead vacancies $\ddot{\text{V}}_{\text{Pb}}$ and the less is the number of oxygen ones $\ddot{\text{V}}_{\text{O}}$ in the lead germanate lattice, the more number of lead atoms change their valency to Pb^{3+} , providing the growth of electric conductivity in such a way.

At the same time, the conductivity of the crystal that was grown up with a PbO excess ($5.05\text{PbO} : 3\text{GeO}_2$) is only slightly lower than that for the $5.00\text{PbO} : 3\text{GeO}_2$ composition. We may suppose that a GeO_2 deficiency (or a PbO excess) at the blend synthesis does not affect the single crystal structure so strongly as a similar PbO deficiency, because germanium is included into the $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ lattice in the form of structural elements (germanium–oxygen tetrahedra).

As is seen from Fig. 2, there is a strong anisotropy of conductivity in lead germanate: the conductivity is much lower in the direction [001] than that in the [100] one. As was already pointed out, only one of six lead atoms with symmetry $C3$ in the elementary cells of $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ can change its valency to Pb^{3+} (Fig. 3). In this case, two Pb^{2+} ions are always located along the direction [001] and on a line that connects two nearest atoms, at which the hole can be localized. These ions, possessing a positive potential, can hamper the directed motion of a hole along the direction [001] over the localized states, by reducing the conductivity in this direction in such a way. At the same time, there are no obstacles between the potential Pb^{3+} ions in the direction [100]. It can result in a substantially higher conductivity in this direction within the given temperature interval.

The phase transition does not essentially vary the values of specific conductance and its activation energy, since relative displacements of atoms in the lead sublattice are minimal, when the symmetry changes. To some extent, the activation energy at the phase transition point – especially in the direction [100] – can be affected by a conspicuous motion of germanium–oxygen tetrahedra. But, in order to confirm this idea, it is necessary to study the conductivity in various directions in the vicinity of the phase transition point.

4. Conclusions

Lead germanate grown up from a blend with the deficiency of lead oxide PbO potentially possesses better photorefractive properties than the stoichiometric compound $\text{Pb}_5\text{Ge}_3\text{O}_{11}$, because it contains a larger number of photoactive centers Pb^{3+} in its matrix. Only a

small fraction of lead atoms can change their valency from Pb^{2+} to Pb^{3+} . The relative arrangement of such atoms, capable to trap holes, in the lattice can cause a substantial anisotropy of electric conductivity, which is observed experimentally.

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НЕСТЕХІОМЕТРІЯ
Й АНІЗОТРОПІЯ ЕЛЕКТРОПРОВІДНОСТІ
МОНОКРИСТАЛІВ ГЕРМАНАТУ СВИНЦЮ

О.С. Єрмаков, В.М. Дуда

Резюме

Проведено виміри електропровідності монокристалів германату свинцю стехіометричного складу та вирощених з нестатком та надлишком PbO. Зменшення PbO у вихідній шихті приводить до суттєвого зростання електропровідності, оскільки збільшується частка іонів свинцю, що змінюють свою валентність з Pb^{2+} на Pb^{3+} . Взаємне розташування іонів свинцю, що здатні змінити валентність та локалізувати на собі дірку, може зумовлювати наявну суттєву анізотропію електропровідності.