Electrogyration effect in lead germanate crystal family. 2. The case of crystals doped with Li, Eu, La, Nd and (Li, Bi)

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Abstract

Temperature dependences of spontaneous and induced electrogyration are studied for the crystals of lead germanate doped with Li, Eu, La, Nd and (Li, Bi). Critical fluctuations observed in the optical parameters near ferroelectric phase transition point are explained in frame of the first fluctuation correction to the Landau theory and the critical indices governing the order parameter are found. It is shown that the doped crystals may be promising for practical applications owing to their large induced electrogyration coefficients.

Keywords: lead germanate crystals, ferroelectric phase transition, optical activity, electrogyration, critical fluctuations

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1. Introduction

Lead germanate (LG) crystals, $Pb_5Ge_3O_{11}$, represent a wide-gap semiconductor characterised by the point symmetry class $\bar{6}$ at the room temperature. In spite of long-standing history of its studies, LG still attracts much attention of researchers (see, e.g., [1–5]). A transition to ferroelectric phase state with the symmetry change $\bar{6} \rightarrow 3$ occurs approximately at 450 K [6]. Below the Curie point the crystal becomes optically active as a result of effect called as electrogyration (EG) [7]. It is linearly dependent on the order parameter of the phase transition, spontaneous electric polarization. The fact that the order parameter and the optical activity are directly linked to each other facilitates studies of the phase transformation with reliable and sensitive optical techniques. It is the more so as the optical gyration manifests itself along the optic axis direction where the accompanying optical birefringence is absent and the experimental errors are the least.

It is known that the LG may serve as a basis for a large family of solid solutions and other structurally modified compounds (see, e.g., [7]). The influence of isovalent or het-

erovalent substitutions in the LG crystals or doping on their physical properties and, in particular, the phase transition characteristics represent an interesting subject for further researches [3–5]. Another aspect of our interest in structurally modified LG crystals is good EG characteristics of the basic compound, the pure LG. This represents a subject potentially important for construction and practical application in electrically operated optical and optoelectronic devices [8, 9]. In this respect one can hope that doping of the LG may result in still better EG parameters and so lower operating voltage.

In the first part of our studies [10] we have concentrated upon the EG properties of solid solutions based on the LG and formed due to the ionic substitutions $Ge^{4+} \rightarrow Si^{4+}$ and $Pb^{2+} \rightarrow Ba^{2+}$. The aim of this work is to study a number of doped compounds. Some preliminary data on the subject have been earlier reported in [11].

2. Experimental

Single LG crystals with different doping impurities had been grown at the laboratories of Dnipropetrovsk National University (Ukraine). In our studies we used crystals containing a number of dopants, in particular lithium, lanthanide elements (lanthanum, neodymium and europium) and a combination of lithium and bismuth. The corresponding compounds are abbreviated hereafter as LG:X, where X = Li, La, Nd, Eu and (Li, Bi). The impurity concentrations x (in weight per cents) were approximately equal to x = 0.005 and 0.010 % (Li), 0.020 % (La), 0.020 % (Nd), 0.021 % (Eu) and 0.152 % (Li and Bi). For the case of doping with bismuth some information is known about the heterovalent substitution $Pb^{2+} \rightarrow Bi^{3+}$ (see, e.g., [7, 12]). The exact character of locations of the other impurities in the lattice is not yet clear.

The optical properties under study were natural optical activity imposed in the ferroelectric phase by spontaneous electric polarization P_S in the absence of external field E (i.e., a spontaneous EG) and the effect strictly induced by that field in both ferroelectric and paraelectric phases (an induced EG). They were measured with a high-accuracy polarimeter, of which principles and construction were described elsewhere (see, e.g., [13, 14]).

It is known [11] that introducing of the impurities mentioned above into single crystals of LG manifests itself in a sharp increase of coercive electric field. This hinders experimental observation of hysteresis loops for the optical activity at the room temperature and makes difficulties in reaching completely single-domain state of LG:X crystals. As a practical step intended to achieve saturated polarization prior to the measurements, we heated the samples to the temperatures higher than the Curie one and then slowly cooled them down to the room temperature under dc voltage applied along the direction of optic axis ($E = E_z$).

All the measurements were carried out using intensity-stabilised He-Ne laser (the radiation wavelength $\lambda = 632.8$ nm) as a light source. The apparatus for controlling tem-

perature of samples enabled the typical accuracy of the order of 10^{-2} K. The sensitivity of the polarimetric setup for the angular rotation of light polarization plane was about 3×10^{-4} deg, while the final accuracy for the optical rotatory power was lower (5×10^{-2} deg/mm), being dependent additionally on temperature stabilization tolerance and thermo-optical coefficient.

3. Results and discussion

3.1. Spontaneous electrogyration

On the basis of our data for the specific optical rotatory power ρ ($\rho=(\pi g_{33})/(\lambda n_o)$, with g_{33} being the gyration tensor component relevant for the propagation direction along the optic axis and n_o the ordinary refractive index) we have calculated temperature dependences of the parameter g_{33} (Fig. 1). The latter is linked immediately with the spontaneous EG coefficient γ_{333} ($g_{33}=\gamma_{333}P_S$ – see [10]).

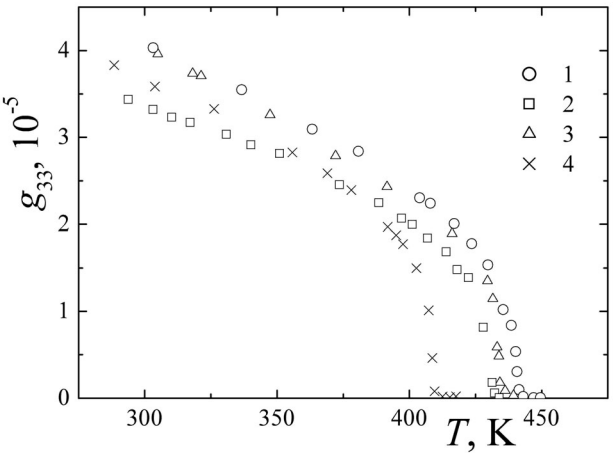

Fig. 1. Temperature dependences of gyration parameter g_{33} characterising spontaneous EG for the doped LG:X crystals: 1 – LG:Li1, 2 – LG:La, 3 – LG:Eu and 4 – LG:(Li,Bi).

As seen from Fig. 1, even small concentrations of dopants produce appreciable changes in the gyration parameter g_{33} and lower the phase transition temperature T_C (see Table 1). Notice that the crystals of LG:Li2 and LG:Nd have been studied only for the room temperature. The optical activity at the room temperature becomes somewhat lower when compare with the appropriate data for the pure LG crystal. However, it would be premature to state that the dopants under test diminish the effect in general, since the saturation for the doped crystals is still not reached at 290–300 K. Some smearing of the phase transition is also visible from Fig. 1.

In order to gain reliable information regarding the influence of the impurities on the phase transition in LG and the critical fluctuations accompanying the phase transition, we

have analysed the data of Fig. 1 using the technique described in our previous work [15]. According to [15], temperature derivative $\zeta_g = \mathrm{d}[g_{33}^2]/\mathrm{d}T$ in the region of relatively weak fluctuations (defined by the inequalities $G << |\tau| << G^{1/3}$, with $\tau = (T - T_C)/T_C$ being the relative temperature and *G* the Ginzburg number [16, 17]) should behave as

$$\begin{aligned} \zeta_g^+ &= \lambda^+ \tau^{-1/2} \qquad (\tau > 0), \\ \zeta_g^- &= \zeta_L + \lambda^- |\tau|^{-1/2} \qquad (\tau < 0), \end{aligned} \tag{1}$$

where $\lambda^{\pm}$ are the constants linked as $\lambda^- / \lambda^+ = 2\sqrt{2}$ and ζ_L denotes the so-called "Landau step" in the derivative ζ_g (see [17]). Only outside the temperature region where fluctuation phenomena are present one can describe the temperature behaviour of the gyration in frame of plane Landau theory that predicts the law $g_{33} \propto |\tau|^{1/2}$ for the ferroelectric phase. More generally, one can stay on the positions of the mean field theory ($g_{33} \propto |\tau|^{\beta}$, with β being the critical index of the order parameter of the phase transition) though the β parameter retains a clear physical meaning only if the fluctuations are absent or too weak to affect the optical activity.

Table 1. Characteristics of spontaneous EG for the doped LG:X crystals. The data for the pure LG crystal are taken from [11, 15].

Dopant notation X	Concentration x, weight %	Specific rotatory power ρ, deg/mm (at T = 300 K)	T_C, K	T_C, K [11]	Critical index β	Ginzburg number G	$\frac{\lambda^-}{2\sqrt{2}\lambda^+}$
–	0	5.7	447	451	0.43	0.010	2.9
Li1	0.005	5.6	440	441	0.36	0.004	2.4
Li2	0.010	5.4	–	436	–	–	–
La	0.020	4.6	428	429	0.32	0.015	*
Nd	0.020	5.6	–	429	–	–	–
Eu	0.021	5.0	432	432	0.43	0.006	0.3
(Li,Bi)	0.152	5.1	408	408	0.31	0.009	1.5

* Difficult to derive due to limited number of data points available for the paraelectric phase

It is seen from Fig. 2 that the temperature dependences $\zeta_g(T)$ have sharp divergences at the Curie point given by Eqs. (1), which should be related to the fluctuations. It is worthwhile that the divergence points may provide more exact phase transition temperatures than those derived earlier from the initial dependences $g_{33}(T)$ (see Table 1 and the data [11]). While moving away from T_C, the curves $\zeta_g(T)$ acquire almost constant

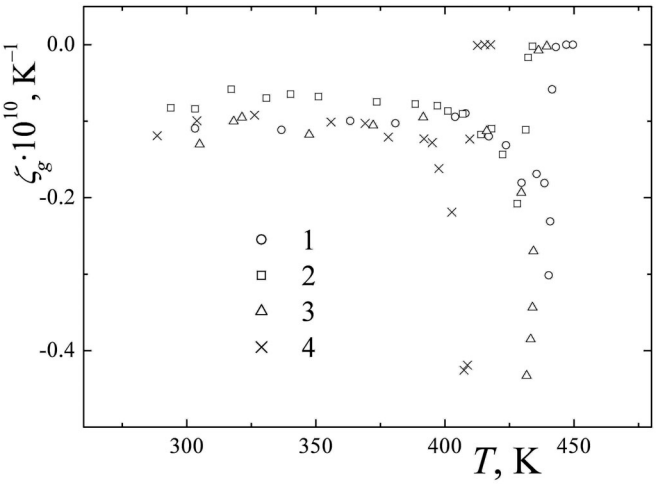

Fig. 2. Temperature dependences of derivatives $\zeta_g = \mathrm{d}[g_{33}^2]/\mathrm{d}T$ for the doped LG:X crystals: 1 – LG:Li1, 2 – LG:La, 3 – LG:Eu and 4 – LG:(Li,Bi).

values and the resulting differences between the values for the paraelectric and ferroelectric phases tend to the "Landau steps" ζ_L.

Quantitative approximation of the data of Fig. 2 with Eqs. (1) (details see in [15]) gives the results shown in Table 1. In particular, the ratio $\lambda^- / (2\sqrt{2}\lambda^+)$ is not far from its theoretical unit value, thus confirming fairly good agreement of our experimental data with Eqs. (1) and correctness of the first fluctuation correction approach [17]. The Ginzburg number has been calculated from the experimental curves $\zeta_g(\tau)$ using the technique suggested in [17]. The averaged Ginzburg numbers for all the crystals are of the order of 10^{-2}. Although it is difficult to deduce strict conclusions concerning the influence of dopants on the *G* parameter, the latter is seen to be slightly less than that for the pure LG. Therefore the doping of the LG crystals, most likely, results in decreasing Ginzburg number and so larger correlation length (see [16]). This should mean narrower fluctuation region and, according to Ginzburg-Levanyuk criterion [16], broader region of validity of the first fluctuation correction approach. However, in order to make definite conclusions, influence of defects should be properly analysed, which is outside the scope of the first fluctuation correction theory [17]. Anyway, it is known that one of the effects of structural defects may be deviation of λ^- / λ^+ ratio from the unity.

Fig. 3 illustrates on the example of crystal doped with Li and Bi how the critical indices β of the order parameter have been derived (see Table 1). It is essential here that the temperature region of notable fluctuations be excluded from the analysis. Then the corresponding accuracy for β has been equal to 10^{-2}. One can see from Table 1 that the doping tends to decrease the β parameter and so manifests itself in further deviation of

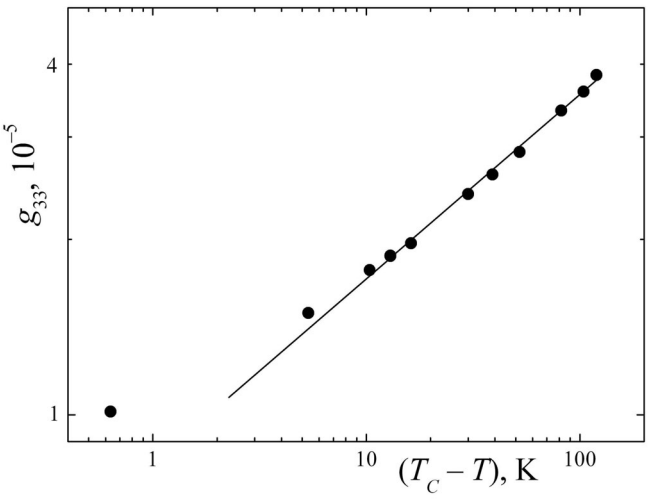

Fig. 3. Log-log scaled temperature dependence of gyration component g_{33} for the crystals LG:(Li,Bi).

thermodynamic behaviour of the crystals from that predicted by the Landau theory. Again, one of natural reasons is partial structural disordering due to interstitial lattice defects concerned with the doping. The only exception is the LG:Eu crystal, for which the decrease in β has not been observed, probably because of its smallness.

3.1. Induced electrogyration

Let us now consider the induced EG effect in the doped LG:X crystals appearing under external electric field. As seen from Fig. 4 (insert), the induced increment $\Delta\rho$ of the specific optical rotation depends linearly on the electric field, with a tendency for saturating in the highest fields. This correlates fairly well with simple phenomenological relationships quoted in the work [10]:

$$\Delta\rho = (\pi\Delta g_{33})/(\lambda n_o), \quad \Delta g_{33} = \gamma_{333} E_z, \tag{2}$$

where Δg_{33} means the induced change in the gyration component and γ_{333} the induced EG coefficient.

Temperature dependences of the γ_{333} coefficient in the vicinity of phase transition point (see Fig. 4) reveal anomalies very similar to those peculiar of the dielectric permittivity [12]. In particular, the temperature curves are somewhat smeared near T_C, the effect typical for diffused phase transitions [18, 19]. Some quantitative characteristics of the induced EG are collected in Table 2. Here the induced specific rotatory power parameter $\Delta\rho / E_z$ attributed to the unit field ($\Delta\rho / E_z = (\partial\rho / \partial E_z)_{E_z \to 0}$) characterises the EG coefficient at the Curie point. The average experimental error of its determination is less than 2×10^{-4} deg/V. However, the above coefficients have partly restricted significance when

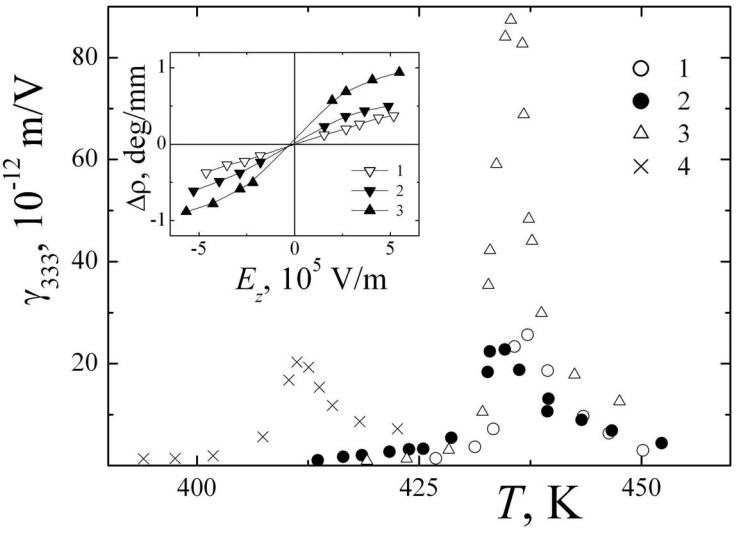

Fig. 4. Temperature dependences of the induced EG coefficient γ_{333} for the doped LG:X crystals near the phase transition point: 1 – LG:Li1, 2 – LG:Li2, 3 – LG:Eu and 4 – LG:(Li,Bi). The insert shows dependences of induced changes $\Delta\rho$ in the specific rotatory power of LG:Li1 crystals on the electric field E_z for different temperatures (1 – $T = T_C + 10.9$ K, 2 – $T_C + 7.3$ K, 3 – $T_C + 3.4$ K).

comparing the influence of different dopants. This is because the fields that saturate the $\Delta\rho(E_z)$ dependences differ for different crystals.

In the work [10] it has been explained in detail that the temperature dependences $\gamma_{333}(T)$ should strictly follow the corresponding behaviour of the dielectric permittivity, which is governed by the Curie-Weiss law (see Eqs. (8) and (9) from [10]). At the same time, the EG coefficient $\tilde{\gamma}_{333}$ related to the induced polarization P_z, which is defined as

$$\Delta g_{33} = \tilde{\gamma}_{333} P_z, \quad \gamma_{333} = \tilde{\gamma}_{333} \varepsilon_0 (\varepsilon_{33} - 1) \tag{3}$$

(with ε_{33} denoting the dielectric permittivity component and ε_0 the dielectric constant), should remain temperature independent. Furthermore, simple phenomenology predicts [10] that the relation $\gamma_{333} \propto \tilde{\gamma}_{333}/[\alpha(T - T_C)]$ should hold true, where α is the expansion coefficient appearing in the part of thermodynamic potential proportional to P_z^2. In Table 2 we present averaged values of the parameter $\tilde{\gamma}_{333}/\alpha$ for both the paraelectric and ferroelectric phases. In accordance with the theoretical consideration mentioned, the experimental dependences of the parameter $E_z/\Delta\rho \propto {\gamma_{333}}^{-1}$ on the relative temperature $T - T_C$ are very close to linear (Fig. 5), despite larger scattering of the data points, when compare with the lead germanate-silicate crystals [20].

Table 2. Characteristics of induced EG for the doped LG:X crystals. The data for the pure LG and LG:La crystals are taken respectively from [10] and [11].

Dopant notation X	Concentration x, weight %	$\Delta\rho/E_z$, 10^{-3} deg/V (at $T = T_C$)	γ_{333}/α, V/(m · deg · K)	
			$T < T_C$	$T > T_C$
–	0	1.0	–	–
Li1	0.005	3.2	–1.23	0.23
Li2	0.010	3.9	–0.49	0.16
La	0.020	1.8	–	–
Nd	0.020	–	–	–
Eu	0.021	10.6	–1.22	0.09
(Li,Bi)	0.152	2.7	–0.72	0.14

In order to verify the relation between the dependences $\gamma_{333}^{-1}(T)$ in the ferroelectric and paraelectric phases (see Eqs. (8) and (9) from [10]), let us use as a quantitative parameter the ratio of temperature slopes of the reciprocal EG coefficients taken for those phases. Even after averaging over all the doped crystals under study, we arrive at the result $\left|\mathrm{d}(E_z/\Delta\rho)/\mathrm{d}T\right|_{T<T_C} : \left|\mathrm{d}(E_z/\Delta\rho)/\mathrm{d}T\right|_{T>T_C} \approx 2.8:1$, instead of the ratio 2:1 predicted by the simplest thermodynamic theory for the second-order phase transitions. It is inter-

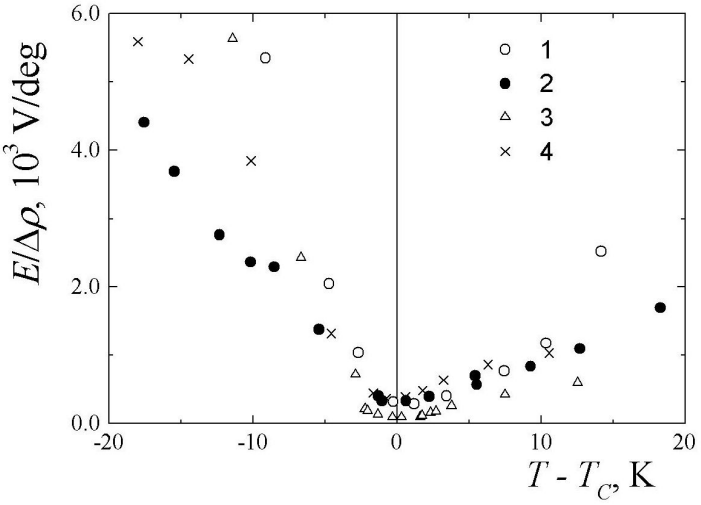

Fig. 5. Temperature dependences of the parameter $E_z/\Delta\rho$ proportional to the reciprocal induced EG coefficient γ_{333} for the doped LG:X crystals: 1 – LG:Li1, 2 – LG:Li2, 3 – LG:Eu and 4 – LG:(Li,Bi).

esting that some other physical properties demonstrate fair enough agreement with the theory. For instance, the corresponding ratio found following from the decrement coefficient for the neutron and Raman scattering [21] is close to 2:1, though the relative accuracy has not been high enough and, moreover, all the results have been concerned with the pure LG only. It is likely that the deviation from the theory observed for the EG in our crystals is associated with some influence of structural defects, similarly to the smearing of the phase transition.

It is obvious from Table 2 that the largest coefficient of induced EG is inherent to the crystals doped with Eu and Li. Notice for comparison that the optical rotation induced electrically in $PbMoO_4$ crystals (which have until recently been regarded as the most efficient EG material among insulators) under the same conditions is only ~ 0.3 deg.

4. Conclusions

In the present work we have studied spontaneous and induced EG effects in the doped LG. It has been shown that introduction of Li, La, Nd, Eu and (Li,Bi) dopants produces conspicuous effect upon the phase transition and alters its quantitative parameters. It shifts the Curie point towards lower temperatures and smears the phase transition. Spontaneous and electrically-induced gyrations turn out to be convenient tool in studying phase transformation in the LG crytals. In particular, the spontaneous EG reveal clear fluctuation phenomena in the vicinity of the Curie temperature, which can be satisfactorily explained in frame of the modified Landau theory, the first fluctuation correction approach. The influence of structural defects on the fluctuation phenomena in the LG-based solid solutions and the doped LG crystals will be elucidated in our forthcoming paper.

In general, the doping causes essential increase in the induced EG effect, when compare with the pure LG crystals. Though quantitative explanation of those peculiarities represents a cumbersome problem involving detailed structural studies of the doped LG and ascertaining the exact location of doping atoms in the crystalline lattice, the effect may prove important for many applications. Moreover, doping of the LG crystal suggests some additional practical conveniences such as lower Curie temperatures and so lower conductivity (see [11]).

A comparison with the other promising insulating EG material, bismuth germanate-silicate [22], testifies another practical advantage of the doped LG, much weaker nonlinearities in the $\Delta\rho(E_z)$ dependences. Perhaps, this is a reason for significantly larger specific optical rotation EG induced electrically. Since the optical saturation comes at certain electric field strength E_z and the induced optical rotation depends on the electric voltage alone, improving of operational performance of EG elements should imply usage of thicker crystal samples.

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Анотація. *У роботі вивчено температурні залежності спонтанної та індукованої електрогірації кристалів германату свинцю з домішками Li, Eu, La, Nd і (Li, Bi). Спостережувані в оптичних параметрах критичні флуктуації поблизу точки сегнетоелектричного фазового переходу пояснено в рамках підходу першої флуктуаційної поправки до теорії Ландау. Визначено критичні індекси параметра порядку. Показано, що леговані кристали перспективні для практичних застосувань завдяки великим коефіцієнтам індукованої електрогірації.*