
Optical studies of order parameter fluctuations in solid solutions based on lead germanate crystals

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Abstract

The approach for interpreting fluctuations seen in optical activity is suggested based on the first fluctuation correction to the Landau theory. Quantitative analyses of the fluctuation effects for Si-, Ba- and Bi-containing crystals of lead germanate family show applicability of the model. Critical indices governing temperature behaviour of the order parameter of ferroelectric phase transition are found for the crystals under study.

Keywords: lead germanate crystals, optical activity, ferroelectric phase transition, order parameter, fluctuations

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1. Introduction

Single crystals of lead germanate $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ manifest a proper ferroelectric phase transition (PT) with rather uncommon point symmetry change $\bar{6} \rightarrow 3$ occurred close to 450 K [1]. Lead germanate forms a broad family of structurally isomorphous compounds that represent solid solutions based on both isovalent and heterovalent ionic substitutions $\text{Ge}^{4+} \rightarrow \text{Si}^{4+}$, $\text{Pb}^{2+} \rightarrow \text{Ba}^{2+}$, $\text{Pb}^{2+} \rightarrow \text{Bi}^{3+}$, etc. PTs observed in those compounds are partly smeared [2], most likely, owing to spatial fluctuations of the chemical content. Similarly to the symmetry change at the PT, the crystals of the lead germanate family reveal very interesting physical properties, in particular dielectric, pyroelectric, optical and electrooptic ones (see, e.g., [3, 4]), which make them promising for utilising in various optoelectronic devices.

In spite of versatile knowledge on different physical properties of the lead germanate-based solid solutions and the changes of corresponding parameters in the course of the PT, characteristics of their critical behaviour and static and dynamical order parameter fluctuations have still not been elucidated in sufficient detail. As far as we know, ample information on the critical fluctuations is available only for one of the related compounds, lithium hepta-germanate [5, 6]. Moreover, some discrepancies still exist concerned with

the critical indices. In particular, Konak et al. [7] have found the critical exponent β of the order parameter for the pure lead germanate to be equal to 0.35, whereas most of the optical data (see, e.g., [3, 4, 8, 9] and the monograph [10]) assume the values very close to a classical one, $\beta = 0.5$. The recent studies [11–13] have also addressed this point. The authors of Ref. [12] have studied the concentration dependences of thermodynamic coefficients basing on the experimental data for electrogyration effects and have suggested that a hypothetical tricritical point might exist on the x, T -diagram of $(\text{Pb}_{1-x}\text{Ba}_x)_5\text{Ge}_3\text{O}_{11}$ system at $x > 0.05$. Those points are all the more interesting since they also touch a more general problem of influence of ionic substitutions upon the PT characteristics and the critical behaviour of lead germanate crystals.

Although the paraelectric phase of the lead germanate is acentric, it lacks optical activity, which appears only below the PT point. Furthermore, the optical activity is closely related to the spontaneous polarization and linearly depends on the latter inside the ferroelectric phase [10]. This enables one to interpret, at least conventionally, this optical quantity as a secondary order parameter [14] and investigate thermodynamic behaviour of the crystal using high-precision polarization-optical techniques. In this work we will develop a theoretical approach for studies of static fluctuation phenomena on the basis of temperature dependences of optical activity and will find the quantitative fluctuation characteristics and the critical indices of the order parameter for the solid solutions $(\text{Pb}_{1-x}\text{Ba}_x)_5\text{Ge}_3\text{O}_{11}$, $\text{Pb}_5(\text{Ge}_{1-x}\text{Si}_x)_3\text{O}_{11}$ and $(\text{Pb}_{1-x}\text{Bi}_x)_5\text{Ge}_3\text{O}_{11}$.

2. Theoretical Approach

It is well known that description of second-order PTs within the simplest Landau-like approach based on thermodynamic potential expressed in terms of the order parameter η ,

$$\Phi = \Phi_0 + \frac{A}{2}(T - T_C)\eta^2 + \frac{B}{4}\eta^4, \quad (1)$$

often appears to be too rough. Some of the reasons of violations of the mean-field theory are critical fluctuations and influence of structural defects.

A true critical behaviour is concerned with a scaling region around the PT point T_C , which is very difficult to study experimentally. Indeed, the scaling region for a wide variety of ferroelectrics is as small as $|\tau| < 10^{-4} \div 10^{-3}$ (with $\tau = (T - T_C)/T_C$ denoting the so-called relative temperature), or even much less. With T_C being not too far from the room temperature, we arrive at the estimation $|T - T_C| < 10^{-2} \div 10^{-1}$ K, thus requiring at least one order of magnitude better temperature stabilization and measurements.

On the other hand, a region of relatively weak fluctuations is easier to access. Really, it is determined by the inequality (see [15])

$$G \ll |\tau| \ll G^{1/3}, \quad (2)$$

where the Ginzburg number $G = B^2 T_C / (8\pi^2 AD^3)$ is defined by the Landau expansion coefficients A , B and the additional term $\Delta\Phi = \frac{D}{2}(\nabla\eta)^2$ in Eq. (1) that accounts for spatial inhomogeneity of the order parameter of isotropic nature. Further on we will address just the region given by Eq. (2), which permits utilization of the approach of small fluctuation corrections to the Landau theory.

Let us settle on the first fluctuation correction adopted in the work [16]. Then the optical gyration parameter g may be related to the inhomogeneous order parameter $\eta(r)$ as

$$g = g_B + a\eta(r) + b\eta^2(r) + \dots, \quad (3)$$

where g_B is the “background” gyration not associated with the effect of PT and a and b the optical susceptibilities. Using general symmetry considerations for the crystals under test, we have $g_B = 0$ and $b = 0$. Some nonlinearity in the dependence $g(\eta)$ concerned with a non-negligible term $g(\eta) \propto \eta^3$ has been detected in the recent work [12]. However, this term can hardly contribute to $g(\eta)$ function in the region close to the PT temperature where the amplitude η is small enough.

As a result, Eq. (3) yields a linear relationship between the optical activity g measured in practice for our inhomogeneous optical medium and the mean squared order parameter fluctuation $\langle \eta^2(r) \rangle$ related, in its turn, to nonzero Fourier components $\eta_{\mathbf{K}}$:

$$g^2 = a^2 \langle \eta^2(r) \rangle \approx a^2 \sum_{\mathbf{K}=0}^{\mathbf{K}_{\max}} \langle \eta_{\mathbf{K}} \eta_{-\mathbf{K}} \rangle, \quad (4)$$

where $\eta(r) = \int \eta_{\mathbf{K}} \exp(i\mathbf{K}\mathbf{r}) d\mathbf{K}$ and the spectrum of Fourier-components $\eta_{\mathbf{K}}$ has been cut off at the reciprocal lattice vector \mathbf{K}_{\max} . Let us now neglect temperature dependence of the coefficients A , B and D and the corresponding temperature-induced reconstruction of \mathbf{K}_{\max} , which is quite justified for the region defined by Eq. (2). Employing the results [16] for the sum in the r. h. s. of Eq. (4), one can obtain

$$\begin{aligned} (g^2)^+ &= 2\lambda^+ \tau^{1/2} \quad (\tau > 0), \\ (g^2)^- &= a^2 AT_C \tau / B + 2\lambda^- |\tau|^{1/2} \quad (\tau < 0). \end{aligned} \quad (5)$$

The indices “+” and “-” in Eqs. (5) refer respectively to the regions above and below the PT point. In case of proper ferroelectric PTs the constants λ^\pm should be linked through $\lambda^- / \lambda^+ = 2\sqrt{2}$ [16]. Though it is often believed that the optical activity of the crystals under test obeys the law $g \propto |\tau|^{1/2}$ or, more generally, $g \propto |\tau|^\beta$ in all the ferroelectric phase, Eqs. (5) evidence that, strictly speaking, this is true only well outside the fluctuation region. In other words, finding the β index on the basis of experimental optical data makes sense only after the temperature region of notable fluctuations has

cal data makes sense only after the temperature region of notable fluctuations has been reliably determined.

There is another parameter closely associated with g^2 that carries a valuable practical information, its derivative $\zeta_g = d[g^2]/dT$. The point is that, within the plain Landau phenomenology (in fact, $\lambda^\pm \rightarrow 0$), the parameter ζ_g should have a step-like temperature dependence near T_C , similarly to the heat capacity. The corresponding ‘‘Landau step’’ is equal to $\zeta_L = a^2A/B$. Then any deviation of $\zeta_g(\tau)$ behaviour from the above classical results could be treated as a manifestation of critical fluctuations. With Eqs. (5) one gets

$$\begin{aligned}\zeta_g^+ &= \lambda^+ \tau^{-1/2} \quad (\tau > 0), \\ \zeta_g^- &= \zeta_L + \lambda^- |\tau|^{-1/2} \quad (\tau < 0),\end{aligned}\tag{6}$$

As seen from Eqs. (6), the fluctuations give rise to a critical divergence of the $\zeta_g(\tau)$ function right at T_C . By the way, this enables determining the temperature of second-order PTs with essentially high accuracy. Let us also stress that the temperature behaviour of the gyration or its derivative inside the region of strong fluctuations, which is in fact disregarded here, would be governed by the critical index α of the heat capacity rather than the index β related to the order parameter (for the case of small negative α we have $\zeta_g(\tau) \propto |\tau|^{|\alpha|}$ – see [16]).

The model has to involve consideration of effect of structural defects (see [17, 18]). If ‘‘local-temperature’’ (symmetry-preserving) defects are present, Eqs. (6) remain valid, though the ratio λ^-/λ^+ can change. The availability of ‘‘local-field’’ defects that break locally the symmetry of crystal would lead to violation of Eqs. (6), resulting in the dependence $\zeta_g(\tau) \propto |\tau|^{-3/2}$.

Practical utilization of the model for fitting experimental gyration data meets some difficulties associated first of all with the absence of a priori theoretical estimations of the Ginzburg parameter for many crystals (see Eq. (2)). Then the temperature region where Eqs. (6) are valid is not exactly known. On the other hand, one can roughly estimate G from the experiment itself, using the dependences $\zeta_g(\tau)$ (the details see in Ref. [16]).

Second, here we always deal with a multi-parametric fitting, which can generate additional errors. Nonetheless, the analysis of fluctuations after the optical activity possesses an evident advantage in this respect, when compare with the analysis based on the optical birefringence or thermal expansion data (see [16, 19–21]). Namely, the derivatives of the latter quantities include extra fitting parameters. These are ‘‘background’’ thermal coefficients ζ_B in the both ferroelectric and paraelectric phases, which have nothing to do with the influence of PT and, moreover, are very difficult to eliminate in practice, e.g., due to their possible temperature dependence.

3. Results and Discussion

3.1. Fluctuation phenomena

Optical activity of the solid solutions based on lead germanate has been repeatedly studied (see, e.g., [1, 3, 8–13, 22, 23]) with high-accuracy polarimetric techniques. In order to ascertain the critical behaviour of those crystals, we have used the most detailed data reported for $\text{Pb}_5(\text{Ge}_{1-x}\text{Si}_x)_3\text{O}_{11}$ [9, 12], $(\text{Pb}_{1-x}\text{Ba}_x)_5\text{Ge}_3\text{O}_{11}$ [12, 22], and $(\text{Pb}_{1-x}\text{Bi}_x)_5\text{Ge}_3\text{O}_{11}$ [23]. It is necessary to note that a direct observable accessible in the experiment is specific optical rotation $\rho = 180^\circ g / (\lambda \bar{n})$, where $g = g_{33}$ is the gyration tensor component relevant for the light propagation along the optic axis, λ the light wavelength and \bar{n} the mean refractive index. When compare with g , the ρ parameter includes additionally the refractive index \bar{n} that dependent also on the temperature and so on the order parameter (cf. with Eqs. (5) and (6)). However, the analysis shows that the relative temperature changes $\bar{n}(T)$ in the overall temperature range under interest are small enough (less than 1%), thus going into typical experimental errors for the specific rotation. This is particularly true for the much narrower fluctuation region. As a consequence, Eqs. (6) should approximately describe the temperature dependences of $\zeta_\rho = d[\rho^2]/dT$, too.

In Fig. 1 we show, as examples, the temperature dependences of derivatives of the gyration calculated with numerical differentiation of the data obtained for

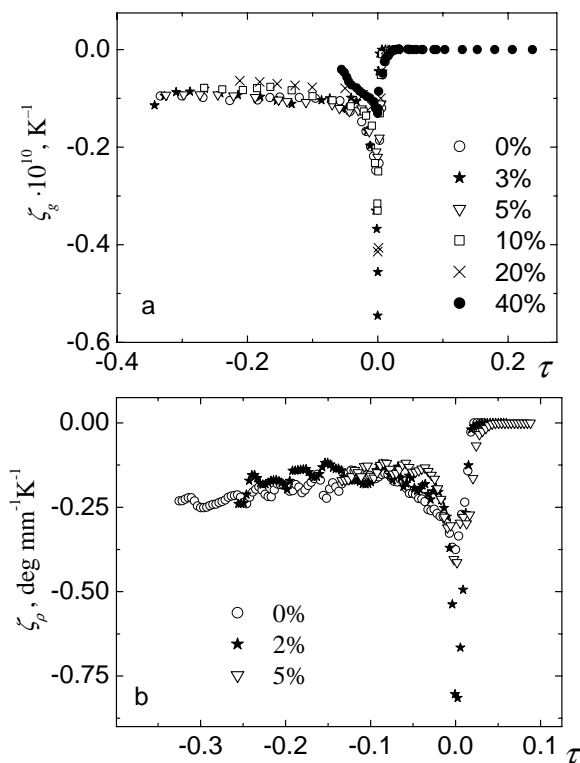


Fig. 1. Dependences of temperature derivatives ζ_g and ζ_ρ of the optical activity on relative temperature τ for the crystals of solid solutions $\text{Pb}_5(\text{Ge}_{1-x}\text{Si}_x)_3\text{O}_{11}$ (a) and $(\text{Pb}_{1-x}\text{Ba}_x)_5\text{Ge}_3\text{O}_{11}$ (b).

$\text{Pb}_5(\text{Ge}_{1-x}\text{Si}_x)_3\text{O}_{11}$ [12] and $(\text{Pb}_{1-x}\text{Ba}_x)_5\text{Ge}_3\text{O}_{11}$ [22]. Here the figures denote the concentrations of dopants in per cents. The results for the $(\text{Pb}_{1-x}\text{Bi}_x)_5\text{Ge}_3\text{O}_{11}$ system are not displayed in Fig. 1. Their quantitative analysis is less accurate because of insufficient quantity of data point for the paraelectric phase (see also below). In all of the $\zeta(\tau)$ dependences one can easily see sharp divergences at the PT points that are to be associated with the fluctuation phenomena. Notice also that notable deviations from the step-like behaviour predicted by the Landau start as far as 10 K from T_C . This correlates with nonlinearities seen by the authors [12] in the dependences of g vs. $(T_C - T)^{1/2}$ in the vicinity of up to 5 K wide below the PT point ($|\tau| \sim 10^{-2}$ – see Eqs. (5)).

Using the data presented in Fig. 1, we have found the PT temperatures gathered in Table 1. Our T_C 's differ slightly from the earlier results obtained with less accurate methods and, moreover, there are also clear discrepancies among the latter. This is quite natural since it is difficult to locate the PT point in case of a continuous PT close to second-order transformation, especially a diffused one. Note that the concentration dependence of the PT temperature for the most extensively investigated $\text{Pb}_5(\text{Ge}_{1-x}\text{Si}_x)_3\text{O}_{11}$ system is practically linear, with the slope equal to $dT_C/dx \approx -347.2$ K (see Fig. 2, insert) and the mean-square deviation being of the order of magnitude not larger than the discrepancies mentioned above (3.5 K).

Following the technique adopted in [16] and using the data represented in Fig 1, one can estimate the Ginzburg number G (see Table 1). Although we do not observe indisputable concentration dependences $G(x)$, substitution of Pb with Ba and Bi obviously gives rise to larger G , thus leading to decreasing thermodynamic coefficient D . It is known that the latter is linked with the correlation length Λ of fluctuations via the relation $D \propto \Lambda^2 T_C$ [15]. Therefore we have a shorter correlation length in the solid solutions $(\text{Pb}_{1-x}\text{Ba}_x)_5\text{Ge}_3\text{O}_{11}$ and $(\text{Pb}_{1-x}\text{Bi}_x)_5\text{Ge}_3\text{O}_{11}$, when compare with the pure lead germanate.

Table 1. Parameters of critical behaviour of optical activity for the solid solutions based on lead germanate.

Substitution (concentration x)	PT temperature, K	Ginzburg number G	Ratio $\lambda^-/(2\sqrt{2}\lambda^+)$
–	447.0	0.010	2.9
Si (0.03)	438.7	0.003	1.1
Si (0.05)	429.4	0.007	0.6
Si (0.10)	410.5	0.004	1.7
Si (0.20)	371.0	0.005	1.0
Si (0.40)	310.3	0.006	4.7
Ba (0.02)	403	0.02	1.8
Ba (0.05)	341	0.02	3.4
Bi (0.08)	392	0.02	0.4

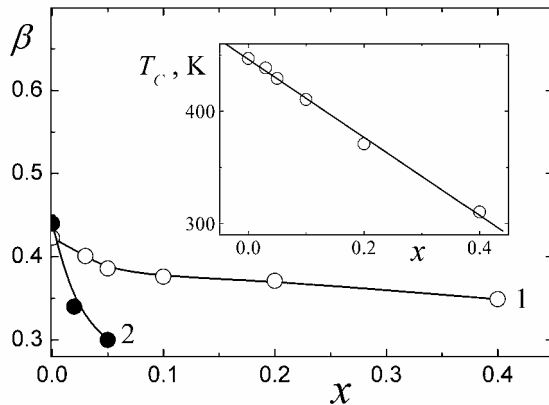


Fig. 2. Concentration dependences of critical index β of the order parameter for the solid solutions $\text{Pb}_5(\text{Ge}_{1-x}\text{Si}_x)_3\text{O}_{11}$ (1) and $(\text{Pb}_{1-x}\text{Ba}_x)_5\text{Ge}_3\text{O}_{11}$ (2) as calculated from the optical activity data [12, 22]. The insert shows concentration dependence $T_C(x)$ for $\text{Pb}_5(\text{Ge}_{1-x}\text{Si}_x)_3\text{O}_{11}$.

nate. This means broadening of the temperature region of fluctuations and, according to the Ginzburg-Levanyuk criterion given by Eq. (2), narrowing of the region where the first fluctuation correction approach is applicable.

On the contrary, in case of the substitution of Ge with Si, one can pay attention to a tendency to decreasing G , with the opposite conclusions. However, to make our consideration more universal, let us stress that the Ginzburg number would define, in the strict sense, only intrinsic (thermal) fluctuations but not extrinsic ones caused by structural defects. Those two fluctuation types are hardly distinguishable in any practical experiments and so our “experimental” G ’s involve additionally the effect of defects. That is why less G for Si-containing compounds and larger G for Ba- and Bi-containing ones may also imply less or larger amounts of structural defects in the solid solutions. This correlates well with the known fact that the PT in $(\text{Pb}_{1-x}\text{Ba}_x)_5\text{Ge}_3\text{O}_{11}$ and $(\text{Pb}_{1-x}\text{Bi}_x)_5\text{Ge}_3\text{O}_{11}$ is more essentially smeared than that in $\text{Pb}_5(\text{Ge}_{1-x}\text{Si}_x)_3\text{O}_{11}$ (see, e.g., [23]).

On the basis of G values and Eq. (2) we have estimated the limits of temperature regions of validity of the first fluctuation correction and fitted the $\zeta(\tau)$ functions using the theoretical relations (6). Unlike the method adopted in [16, 19] though similar to that used in the studies of critical fluctuations for deuterated triglycine sulphate [20, 21], we have put the fitting parameters λ^+ and λ^- to be free and introduced no a priori relations among them. The main results concerned with the ratio $\lambda^-/(2\sqrt{2}\lambda^+)$ are also displayed in Table 1.

It is seen that the above ratio is close to the unit value predicted theoretically, while the accuracy of the fitting is even higher than that characterising a simple order-of-magnitude correspondence. One of the possible reasons for deviation of $\lambda^-/(2\sqrt{2}\lambda^+)$ from the unity may be worse calculation accuracy for the paraelectric phase, the number of data points for which is mainly too small, though the fluctuation region in that phase can be wide enough [21]. On the other hand, the deviation could be induced by the influence of defects of the “random local PT temperature” type. The relative errors found for

the fitting parameters, which are not presented in Table 1, are equal to 10–50 per cent and do not differ too much for different solid solutions or ionic concentration, being mainly determined by the experimental errors and inaccuracies of the data processing. On the whole, we can state that the first fluctuation correction model suggested by the authors [16] is valid, at least qualitatively, for all of the solid solutions based on the lead germanate.

In addition to the optical activity, we have also processed temperature dependences of the spontaneous polarization, which represents the order parameter of proper ferroelectric PTs in the lead germanate family, in order to compare them with our purely optical data. Below we will focus only upon a single example, spontaneous polarization of $(\text{Pb}_{1-x}\text{Ba}_x)_5\text{Ge}_3\text{O}_{11}$ crystals [4, 22]. As with the gyration, the derivative $\zeta_p = d[P_s^2]/dT$ has been calculated as a function of temperature and fitted with Eqs. (6). The Ginzburg number for all the concentrations $x=0, 0.02$ and 0.05 is $G \approx 2 \times 10^{-2}$, the ratio $\lambda^-/(2\sqrt{2}\lambda^+)$ is equal respectively to 12, 3 and 6, while the relative error for the fitting parameters is high enough ($\sim 50\text{--}300\%$). Most probably, these results are not so accurate because of the fact that the standard Sawyer-Tower method or the related techniques cannot compete in relative precision with the modern polarimetric techniques. Besides, external electric fields necessary for measuring spontaneous polarization additionally smear the PT and so distort a true thermodynamic behaviour peculiar for zero biasing field (see, e.g., [10]).

3.2. Critical indices of the order parameter

Let us finally concentrate upon the problem of critical index of the order parameter. In order to work in terms of the Landau theory, we should not overstep the limits of its applicability and so exclude from our further analysis the temperature regions where the fluctuation phenomena are notable. Let us use trivial relations $g \propto \eta \propto (T_c - T)^\beta$ for the gyration parameter and the same for the optical rotatory power ρ . Plotting the temperature dependences of those parameters on log-log scale (see Fig. 3), we can derive the critical indices as the slopes. As already mentioned, we have not taken into account the data points too close to the PT temperature (see the points to the right in Fig. 3), which would have essentially decreased the calculated slopes. The results related to the β parameter are shown in Fig. 2 (for the cases of $\text{Pb}_5(\text{Ge}_{1-x}\text{Si}_x)_3\text{O}_{11}$ and $(\text{Pb}_{1-x}\text{Ba}_x)_5\text{Ge}_3\text{O}_{11}$) and Table 2. The cumulative errors associated with data processing are typically not larger than 0.01–0.02. In spite of easily predicted lower-quality results derived on the basis of spontaneous polarization (see the above discussion), we have also calculated the corresponding indices β , when disregarding the fluctuation regions in the analysis (see Fig. 3c and Table 2). These results correlate fairly well with the data derived from the optical data, though their accuracy is indeed lower.

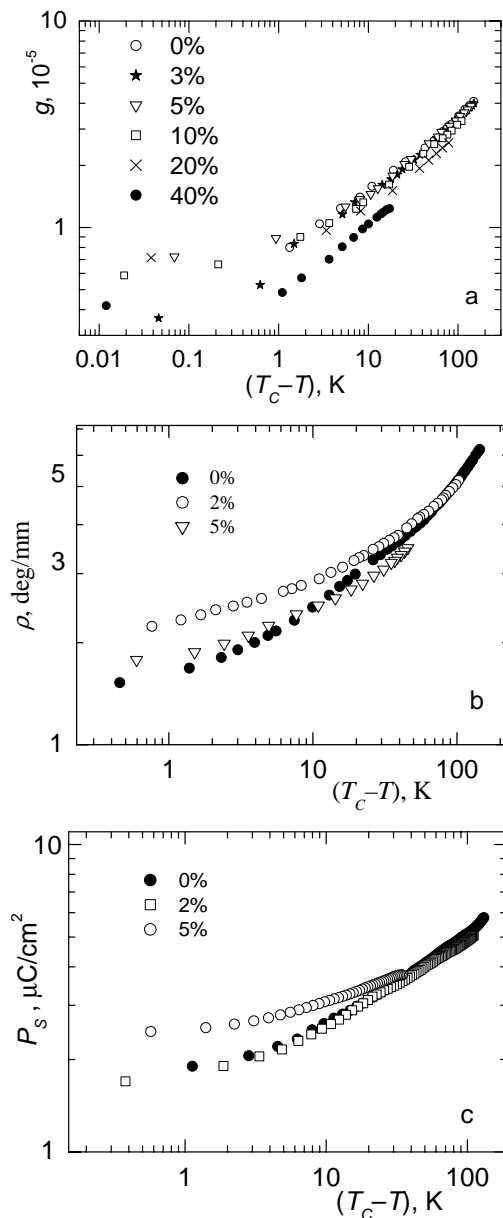


Fig. 3. Temperature dependences of optical activity (a, b) and spontaneous polarization (c) represented on the log-log scale for the solid solutions $\text{Pb}_5(\text{Ge}_{1-x}\text{Si}_x)_3\text{O}_{11}$ (a) and $(\text{Pb}_{1-x}\text{Ba}_x)_5\text{Ge}_3\text{O}_{11}$ (b, c).

(i) The results by the authors [12] can in no case be regarded as decisive enough, since they have observed decrease in the both thermodynamic coefficients A and B with increasing concentration rather than a decrease of B itself.

* It seems unlikely that a small amount of Cr^{3+} dopant can essentially change thermodynamic behaviour of the crystal, in comparison with the pure $\text{Pb}_5\text{Ge}_3\text{O}_{11}$.

It follows from Table 2 that the critical index for the pure lead germanate is not far from the mean-field result, contrary to the data by Konak et al. [7]. Notice also that our findings agree with the recent results obtained by Adamenko et al. [11] for $\text{Pb}_5\text{Ge}_3\text{O}_{11}:\text{Cr}^{3+}$ crystals*. On the other hand, our average value $\beta \approx 0.43$ deduced consistently on the basis of different experimental data should mean that a detectable deviation from the Landau theory does occur for the lead germanate. All the ionic substitutions cause decreasing β value. In particular, the effect is weak enough for the $\text{Pb}_5(\text{Ge}_{1-x}\text{Si}_x)_3\text{O}_{11}$ system and far more pronounced for $(\text{Pb}_{1-x}\text{Ba}_x)_5\text{Ge}_3\text{O}_{11}$ and $(\text{Pb}_{1-x}\text{Bi}_x)_5\text{Ge}_3\text{O}_{11}$. As follows from Fig. 2, some nonlinearity is observed in the $\beta(x)$ dependences for the first two solid solutions.

The most interesting result concerns the $(\text{Pb}_{1-x}\text{Ba}_x)_5\text{Ge}_3\text{O}_{11}$ crystals. Really, if the tendency towards lowering critical index would keep for higher Ba concentrations, it is not unlikely that a tricritical point can exist on the x, T -diagram, which separates the lines of second-order and first-order PTs (see the conclusions [12]). Here we should discuss the problem in a more detail:

Table 2. Critical indices β of order parameter for the PTs in the solid solutions based on lead germanate as determined from the optical activity and spontaneous polarization data.

Substitution (concentration x)	Critical index β		
	Optical activity data [12]	Optical activity data [9, 22, 23]	Spontaneous polarization data [4, 22]
–	0.42	0.44	0.45
Si (0.03)	0.40	0.39	–
Si (0.05)	0.39	–	–
Si (0.10)	0.38	0.37	–
Si (0.20)	0.37	0.32	–
Si (0.40)	0.35	–	–
Ba (0.02)	–	0.34	0.37
Ba (0.05)	–	0.30	0.23
Bi (0.08)	–	0.30	–

(ii) When extrapolating the dependence $\beta(x)$ presented in Fig. 2 towards higher Ba concentrations, one can roughly obtain that $\beta \rightarrow 1/4$ for the critical concentration $x_c \sim 0.10 - 0.15$, and so the evaluation $x > 0.05$ [12] seems to be vague.

(iii) A possibility for appearance of tricritical point in $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ and $(\text{Pb}_{1-x}\text{Ba}_x)_5\text{Ge}_3\text{O}_{11}$ crystals has earlier been suggested in the works [24, 25]. Since the effect of hydrostatic or uniaxial pressures on the Curie point is the same as that of increasing dopant concentration, it is believed that the pressure could help in achieving the critical conditions. Nonetheless, the authors [25] have not been able to find experimentally the tricritical point for the crystals with $x = 0.05$ subjected to pressure. They have predicted that the critical pressure can be about 2.4 kbar for the pure $\text{Pb}_5\text{Ge}_3\text{O}_{11}$.

(iv) It is also known [26] that in case of polycrystalline ceramics $(\text{Pb}_{1-x}\text{Ba}_x)_5\text{Ge}_3\text{O}_{11}$ the value $x \approx 0.06$ can turn out to be limiting, since at higher concentrations the compound $\text{BaPb}_8(\text{Ge}_2\text{O}_7)_3$ is formed, instead of lead-barium germanate. Therefore the tricritical point could prove to be merely hypothetical.

4. Conclusions

In the present work an approach is developed for investigating order parameter fluctuations in the vicinity of second-order PTs, which follows from the first fluctuation correction to the Landau theory known from the literature. The fluctuation phenomena appearing in the optical activity are quantitatively studied for the Si-, Ba- and Bi-containing solid solutions based on the lead germanate. The optical activity proves to be promising enough property for solving the related problems and, in particular, it allows making the

PT points more exact. Different experimental results are shown to fit fairly well into the model. In particular, the crucial ratio $\lambda^- / (2\sqrt{2}\lambda^+)$ has turned out to be not far from its theoretical unit value.

It is revealed that the substitution of Ge with Si tends to decrease the Ginzburg number. This reduces the temperature region of fluctuations and makes the long-range interactions more important (i.e., increases the correlation length), contrary to the ionic substitutions with Ba and Bi. Quite possible, this could also imply weakening of the influence of structural defects on the critical behaviour of Si-containing compounds. It is likely that these defects might prove to be of the “local temperature” type, which do not break local symmetry of the crystals.

We have demonstrated a need in excluding the fluctuation region from the analysis, when finding consistent values of critical indices of the order parameter. The β values determined by us are close to their classical limit $1/2$ for the pure lead germanate, though surely do not reach this exact value. Furthermore, the critical indices deviate notably from $\beta = 1/2$ for all of the solid solutions under test. As evident from our concentration dependences $\beta(x)$, the effect is the most drastic for the $(\text{Pb}_{1-x}\text{Ba}_x)_5\text{Ge}_3\text{O}_{11}$ system, which can, in principle, manifest the tricritical point somewhere in the region of $x \sim 0.10-0.15$. Some aspects of this phenomenon are critically discussed.

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