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# Optical activity and the critical exponent of order parameter in lead germanate crystals.

## 2. Electrogyration and dielectric properties of $\text{Pb}_5\text{Ge}_3\text{O}_{11}:\text{Cu}^{2+}$

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### Abstract

The work is devoted to studies of electrogyration effect and temperature behaviour of dielectric permittivity in  $\text{Pb}_5\text{Ge}_3\text{O}_{11}:\text{Cu}^{2+}$  crystals in the course of diffused phase transition. The concentration–temperature phase diagram for the lead germanate doped with different concentrations of Cu ions is obtained.

**Keywords:** electrogyration, lead germanate, dielectric permittivity

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### Introduction

In the first part [1] of the present studies we have shown that the temperature dependence of optical activity in solid solutions based on lead germanate crystals is well described by the model of diffused phase transition caused by some scalar inhomogeneity, e.g. scalar defects, which do not change the symmetry of crystalline matrix though impose distribution of Curie temperature over a sample. The approach has allowed us to determine correctly the critical exponent of the order parameter and a number of other parameters, such as the temperature range of phase transition diffusing. The present paper is devoted to measurements and analysis for temperature dependences of dielectric permittivity and electrogyration coefficients in  $\text{Pb}_5\text{Ge}_3\text{O}_{11}:\text{Cu}^{2+}$  crystals with different concentrations of Cu ions. We remind that the pure  $\text{Pb}_5\text{Ge}_3\text{O}_{11}$  crystal undergoes a proper second-order ferroelectric phase transition at  $T_c \approx 450$  K, with the change of point symmetry group  $\bar{6} \leftrightarrow 3$  [2–5].

### Experimental

Under the action of electric field the change in the gyration tensor components  $\Delta g_{kl}$  due to a linear electrogyration effect is described by the relation

$$\Delta g_{kl} = g_{kl} - g_{kl}^0 = \gamma_{klm} E_m, \quad (1)$$

where  $g_{kl}$  and  $g_{kl}^0$  are the axial second-rank tensors (gyration tensors) respectively at  $E_m \neq 0$  and  $E_m = 0$ ,  $E_m$  denotes the electric field vector component and  $\gamma_{klm}$  the axial third-rank tensor describing the linear electrogyration effects. In terms of measurable optical rotatory power we have

$$\rho = \frac{\pi}{\lambda n_o} G = \frac{\pi}{\lambda n_o} \Delta g_{kl} l_k l_l, \quad (2)$$

with  $G$  being the scalar gyration parameter,  $l_k$  and  $l_l$  the components of the unit wave vector in the spherical coordinate system,  $\lambda$  the light wavelength, and  $n_o$  the ordinary refractive index.

In case of the lead germanate crystals in their paraelectric or ferroelectric phases and under the experimental geometry  $E \parallel k \parallel Z$  (with  $k$  being the wave vector), the electrically induced optical rotation is defined by the relation

$$\rho = \frac{\pi}{\lambda n_o} \gamma_{333} E_3. \quad (3)$$

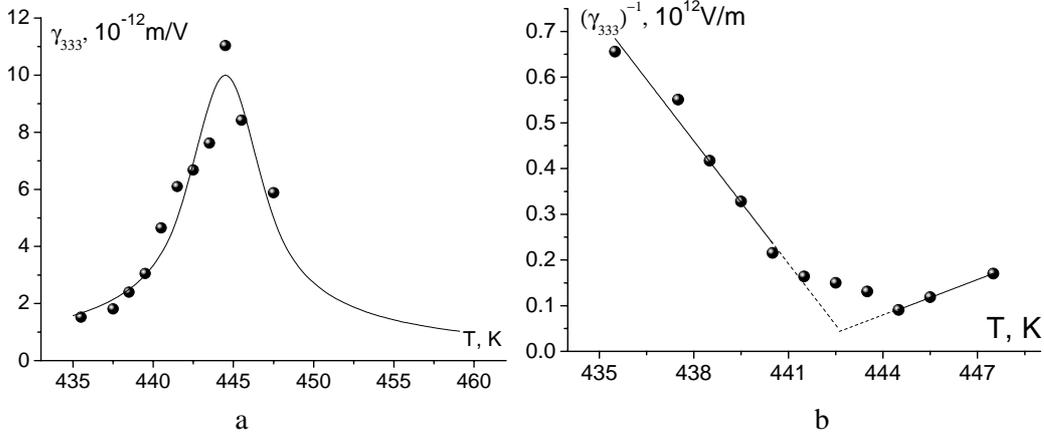
We have studied the electrogyration effect in  $\text{Pb}_5\text{Ge}_3\text{O}_{11}:\text{Cu}^{2+}$  for the light propagation along the optic axis and application of external electric field along the same direction, using the polarimetric set-up described in our recent papers [6, 7]. For varying the sample temperature we have employed a stage permitting temperature stabilisation with the accuracy not less than 0.01 K. The plate of  $\text{Pb}_5\text{Ge}_3\text{O}_{11}:\text{Cu}^{2+}$  crystal with its faces perpendicular to the optic axis and the thickness of 5.5 mm has been placed between transparent electrodes (glass plates covered by conductive tin oxide films), to which high voltages have been applied. The crystals used in our electrogyration experiments have been doped with 0.14 weight % of Cu. The dielectric permittivity  $\epsilon_{33}$  of  $\text{Pb}_5\text{Ge}_3\text{O}_{11}:\text{Cu}^{2+}$  crystals (0, 0.1, 0.2 and 0.5 weight % of Cu) has been studied at the frequency 1 kHz of electric field, using a common capacity-bridge method.

## Results and Discussion

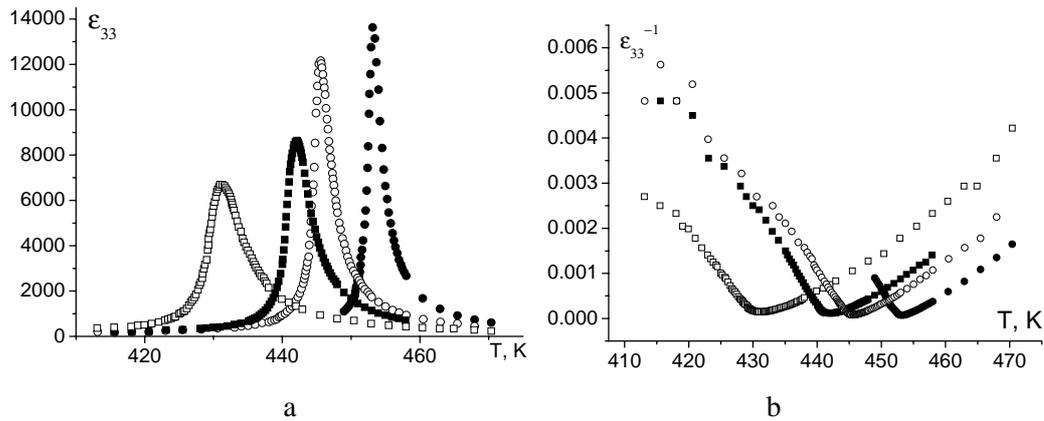
The hysteretic-like dependence of optical rotatory power on the electric field for different temperatures in the vicinity of phase transition has been presented in the work [1]. The electrogyration coefficient  $\gamma_{333}$  has been calculated from these data and Eq. (3). The refractive index has been assumed to be the same as for the pure lead germanate (i.e.,  $n_o = 2.12$  [8]). As one can see from Fig. 1a, this coefficient reaches its maximum  $\gamma_{333} = 1.1 \times 10^{-11}$  m/V at  $T = 444.5$  K.

Temperature dependences of the dielectric permittivity for the lead germanate crystals doped with different Cu ion concentrations, which have been measured along the principal z axis, are presented in Fig. 2. It is seen that the maximum of dielectric permittivity is shifted towards lower temperatures and becomes wider when the concentration of

Cu ions increases. Thus, one concludes that increasing Cu concentration leads to diffusing of the phase transition in lead germanate crystals and decreasing phase transition temperature (Fig. 3).



**Fig. 1.** Temperature dependences of electrogyration coefficient  $\gamma_{333}$  for  $\text{Pb}_5\text{Ge}_3\text{O}_{11}:\text{Cu}^{2+}$  at  $\lambda = 632.8 \text{ nm}$  (a) and its reciprocal (b). Solid curve in Figure a is a result of simulation with Eq. (8) (see text).



**Fig. 2.** Temperature dependences of dielectric permittivity component  $\epsilon_{33}$  (a) and its reciprocal (b): full circles – pure lead germanate, open circles –  $\text{Pb}_5\text{Ge}_3\text{O}_{11}:0.1\%\text{Cu}^{2+}$ , full squares –  $\text{Pb}_5\text{Ge}_3\text{O}_{11}:0.2\%\text{Cu}^{2+}$ , and open squares –  $\text{Pb}_5\text{Ge}_3\text{O}_{11}:0.5\%\text{Cu}^{2+}$ .

Let us now consider a thermodynamic potential for the proper second-order ferroelectric phase transitions:

$$F = F_0 + F_2(T - T_c)^{(s)}P^2 + \frac{1}{2}F_4^{(s)}P^4 + \frac{1}{3}F_6^{(s)}P^6 + \dots, \quad (4)$$

where  $F_2, F_4, F_6, \dots$  are the coefficients of thermodynamic potential, which do not depend on neither  $^{(s)}P$  nor  $T$ . Basing on Eq. (4) and accounting for the additional term

( $-PE$ ) and the condition  $\varepsilon = \partial D / \partial E$ , one easily finds the known relation for the dielectric permittivity:

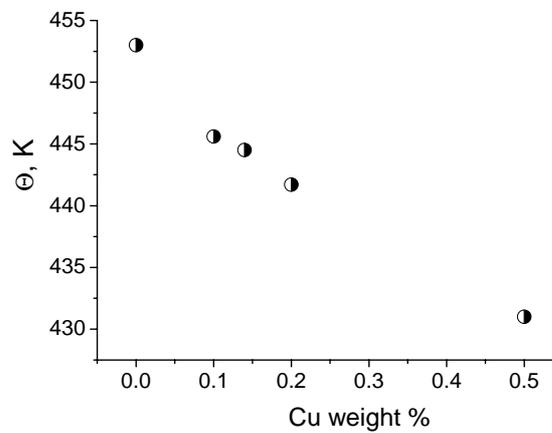
$$\varepsilon = \frac{C}{2(T_c - T)} \text{ for } T < T_c, \quad \varepsilon = \frac{C}{T - T_c} \text{ for } T > T_c, \quad (5)$$

where  $C = (2F_2)^{-1}$  means the Curie-Weiss constant. Taking into account standard relations  $\gamma_{333} = \tilde{\gamma}_{333} \varepsilon_0 (\varepsilon_{33} - 1) \approx \tilde{\gamma}_{333} \varepsilon_0 \varepsilon_{33}$  (with  $\varepsilon_0 = 8.854 \times 10^{-12}$  F/m being the free-space dielectric permittivity), one can obtain

$$\gamma_{333} = \frac{C \varepsilon_0 \tilde{\gamma}_{333}}{2(T_c - T)} \text{ for } T < T_c, \quad \gamma_{333} = \frac{C \varepsilon_0 \tilde{\gamma}_{333}}{T - T_c} \text{ for } T > T_c \quad (6)$$

for the electrogyration coefficients and, finally, derive some general relationships:

$$\frac{(\gamma_{333}^{-1})_{T < T_c}}{(\gamma_{333}^{-1})_{T > T_c}} = 2, \quad \frac{(\varepsilon_{33}^{-1})_{T < T_c}}{(\varepsilon_{33}^{-1})_{T > T_c}} = 2. \quad (7)$$



**Fig. 3.** Concentration-temperature phase diagram for the  $\text{Pb}_5\text{Ge}_3\text{O}_{11}:\text{Cu}^{2+}$  system.

For the  $\text{Pb}_5\text{Ge}_3\text{O}_{11}:0.14\%\text{Cu}^{2+}$  crystals, the ratio of electrogyration reciprocals for the ferroelectric and paraelectric phases is equal to  $(\gamma_{333}^{-1})_{T < T_c} / (\gamma_{333}^{-1})_{T > T_c} = 2.3$  (see Fig. 1b). The corresponding ratio for the dielectric permittivity reciprocals defined by Eq. (7) is equal to 2.8 for  $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ , 2.5 for  $\text{Pb}_5\text{Ge}_3\text{O}_{11}:0.1\%\text{Cu}^{2+}$ , 1.92 for  $\text{Pb}_5\text{Ge}_3\text{O}_{11}:0.2\%\text{Cu}^{2+}$  and 1.8 for  $\text{Pb}_5\text{Ge}_3\text{O}_{11}:0.1\%\text{Cu}^{2+}$  crystals. Probably, some disagreement of the values mentioned with those predicted by Eq. (7) is caused by diffusing of the phase transition in  $\text{Pb}_5\text{Ge}_3\text{O}_{11}:\text{Cu}^{2+}$ .

In the work [1] we have considered diffused phase transitions as those caused by some scalar inhomogeneity, e.g. due to scalar defects, which does not alter the symmetry of crystal but results in some variations of the Curie point over a sample. In this case the phase transition temperature should be distributed from one to the other point of crystal-line sample within some temperature range  $\Delta T = T_{cN} - T_{c1}$ , where  $T_{c1}$  and  $T_{cN}$  are the lowest and the highest Curie temperatures, respectively. The sample has been divided in

$N$  homogeneous elementary cells (in our simulation we have taken  $N$  to be  $N = 10^6$ ), the Curie point of each of which (the  $i$ th cell) is determined as  $T_{ci} = T_{cN} - i \times \Delta T / N$ . The temperature that characterises the condition when half a sample undergoes the phase transition is defined by the relation  $\Theta = T_{cN} - \Delta T / 2$ . Then the temperature dependence of the electrogyration coefficient and dielectric permittivity may be described by the relations

$$\gamma_{333} = \frac{C \varepsilon_0 \tilde{\gamma}_{333}}{2 \frac{A}{N} \sum_{i=1}^N (T_{cN} - i \times \Delta T / N - T)} \quad \text{for } T < T_c,$$

$$\gamma_{333} = \frac{C \varepsilon_0 \tilde{\gamma}_{333}}{\frac{A}{N} \sum_{i=1}^N (T - T_{cN} + i \times \Delta T / N)} \quad \text{for } T > T_c$$
(8)

and

$$\varepsilon_{33} = \frac{C}{2 \frac{A}{N} \sum_{i=1}^N (T_{cN} - i \times \Delta T / N - T)} \quad \text{for } T < T_c,$$

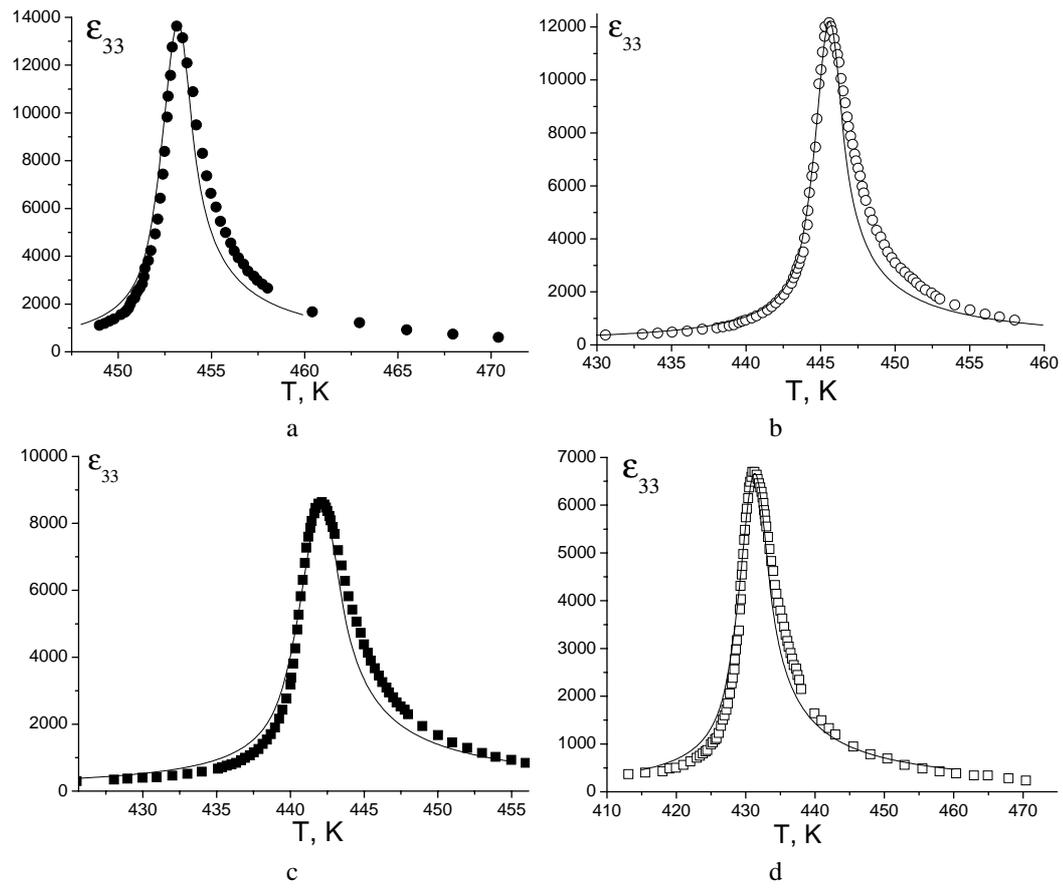
$$\varepsilon_{33} = \frac{C}{\frac{A}{N} \sum_{i=1}^N (T - T_{cN} + i \times \Delta T / N)} \quad \text{for } T > T_c$$
(9)

where  $A$  is a proportionality coefficient which remains the same for all the elementary cells. However, contrary to the relations like Eqs. (8) and (9) employed for simulation of temperature dependences of the order parameter, the parameter  $\Delta T$  does not play a part of actual range of phase transition diffusing if we consider temperature dependences of the dielectric permittivity or electrogyration coefficient. This fact is associated with dispersion of dielectric permittivity. As a result, we will use some effective value  $\Delta T^{ef}$ , instead of  $\Delta T$  appearing in Eqs. (8) and (9). The results of simulation of temperature dependences of the dielectric permittivity and the electrogyration coefficient using respectively Eq. (9) and Eq. (8) are presented in Fig. 1b and Fig. 4. The fitting parameters are gathered in Table 1.

Table 1. Parameters of temperature dependences of the dielectric permittivity and the electrogyration coefficient fitted with Eqs. (8) and (9).

Crystal	$\Theta$ , K	$\Delta T^{ef}$ , K	$A$	$R^2$
$\text{Pb}_5\text{Ge}_3\text{O}_{11}$	453	2.4	11000	0.968
$\text{Pb}_5\text{Ge}_3\text{O}_{11}:0.1\% \text{Cu}^{2+}$	445.4	2.7	11000	0.985
$\text{Pb}_5\text{Ge}_3\text{O}_{11}:0.14\% \text{Cu}^{2+}$	444.5	8.5	25	0.983
$\text{Pb}_5\text{Ge}_3\text{O}_{11}:0.2\% \text{Cu}^{2+}$	441.8	4.2	12000	0.985
$\text{Pb}_5\text{Ge}_3\text{O}_{11}:0.5\% \text{Cu}^{2+}$	430.5	6.3	14000	0.983

As seen from Fig. 1a and Fig. 4, we have obtained quite good coincidence between the experimental data and the simulation results. The temperature  $\Theta$  obtained from the



**Fig. 4.** Temperature dependences of dielectric permittivity  $\epsilon_{33}$ : (a)  $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ , (b)  $\text{Pb}_5\text{Ge}_3\text{O}_{11}:0.1\%\text{Cu}^{2+}$ , (c)  $\text{Pb}_5\text{Ge}_3\text{O}_{11}:0.2\%\text{Cu}^{2+}$ , and (d)  $\text{Pb}_5\text{Ge}_3\text{O}_{11}:0.5\%\text{Cu}^{2+}$ . Solid curves give the results of simulations with Eq. (9).

simulation of temperature dependence of the optical activity in  $\text{Pb}_5\text{Ge}_3\text{O}_{11}:0.14\%\text{Cu}^{2+}$  [1] is equal to 445 K, while that obtained from the electrogyration coefficient (444.5 K) is almost the same. However, the interval  $\Delta T = 30\text{ K}$  obtained from the optical activity differs essentially from that derived from the electrogyration data ( $\Delta T^{ef} = 8.5\text{ K}$ ). It is worthwhile that, if we compare the corresponding data for the pure lead germanate, we have the same results: the  $\Delta T$  parameter differs much from the  $\Delta T^{ef}$  value.

## Conclusions

The dielectric and electrogyration parameters of Cu-doped lead germanate crystals are studied in the course of diffused ferroelectric phase transition. It follows from the concentration-temperature phase diagram obtained by us that increased concentration of Cu ions leads to decreasing phase transition temperature and widening of the temperature range where the phase transition is diffused. We propose the approach for describing anomalous dielectric and electrogyration behaviours at the diffused phase transitions. It is also shown that the Curie-Weiss law is almost satisfied for all the compounds under study.

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*Анотація.* Дана стаття присвячена вивченню температурної поведінки електрогіраційного ефекту та діелектричної проникливості в кристалах  $Pb_5Ge_3O_{11}:Cu^{2+}$  при розмитому фазовому переході. Отримано концентраційно-температурну фазову діаграму для кристалів германату свинцю з різною концентрацією іонів Cu.