Dielectric properties of $Pb_5Ge_3O_{11}$: Cu^{2+} crystals

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Abstract

The peculiarities of dielectric behavior caused by off-center Cu^{2+} ions relaxation dynamics in $Pb_5Ge_3O_{11}$ crystals are presented. The relaxation frequency ($\tau_0^{-1} \approx 10^{12}$ sec^{-1}) and activation energy (ΔW = 0.24 eV) of Cu^{2+} thermal hopping between off-center positions are coincided with results of ESR experiment. Observed additional dielectric loss peaks may be attributed to OH^- groups located in structural tunnels along polar axis.

Key words: dielectric relaxation, off-center impurity ion, structural tunnels, hydroxyl group

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Introduction

The results of Cu^{2+} ESR spectra studies in $Pb_5Ge_3O_{11}$ (PGO) crystals were reported earlier [1, 2]. The measurements of the orientation and temperature dependencies of ESR spectra show that Cu^{2+} centers replace Pb^{2+} ions in positions with trigonal symmetry [3]. The anisotropy and motional averaging of ESR spectra are interpreted as the result of the off-center localization and thermally activated dynamics of Cu^{2+} centers [4, 5]. Shifting of Cu^{2+} in (**ab**) plane, perpendicular to polar **c** axis, should obviously lead to appearance of the local dipole moments. In this case the dielectric properties of PGO:Cu^{2+} would demonstrate the characteristic peculiarities of the temperature and frequency behavior [6, 7].

In this paper the results of the temperature-frequency studies of dielectric permittivity ε and tangent of dielectric losses tgδ in PGO:Cu^{2+} (0.5% wt.) are reported.

Experimental results

The PGO:Cu^{2+} crystals were grown by Czochralski method. Samples of **a**- and **c**- cuts with Pt electrodes were used. The measurements were carried out by bridge method in the temperature interval 80÷300 K at the fixed frequencies 1, 4, 15 kHz.

The results obtained along **a** direction are shown in figure 1. As can be seen the temperature dependencies clearly show two peaks of tgδ(T) and correspondent step-like changes of ε(T) (insert), which shift to high temperatures when the frequency increases. Temperature dependencies of dielectric parameters measured along polar **c** direction are presented in figure 2. Those show two peaks of tgδ(T) and anomalies of ε, shifted to high temperatures with increase of frequency.

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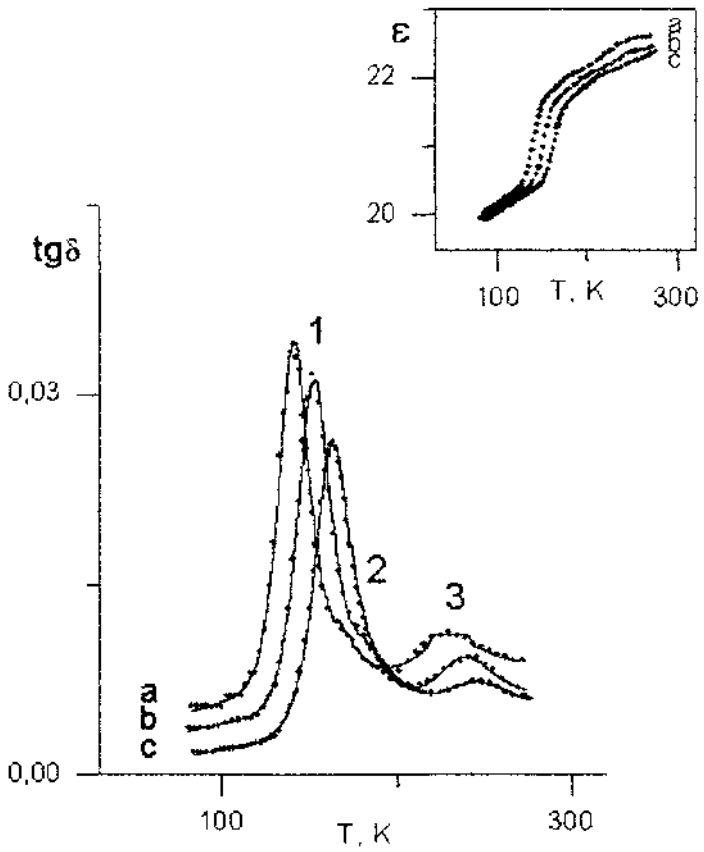

Fig.1. Temperature dependencies of tgδ and ε (insert) for **E** || **a** and frequencies 1 kHz (a), 4 kHz (b), 15 kHz (c). Circles - experiment, solid lines are calculated with the help of (l).

Discussion

Analysis of the data presented in figures 1, 2 leads to the conclusion that in PGO:Cu^{2+} crystals three different relaxation processes (shown as 1, 2, 3) are presented. The low temperature maximum of tgδ(T) in figure 1 corresponds to relaxation process 1 observed only in the directions perpendicular to polar axis. The tgδ(T) maximum in figure 2, when correspond to the processes denoted as 2 and 3, are due to relaxation motions oriented mainly along **c** direction. The residual contributions of 2, 3 processes to the dielectric parameters in **a** direction (figure 1) may be related to the structural anisotropy or/and experimental error.

It should be noted that observed temperature-frequency behaviour for all three processes is typical for Debye-like model and may be described by the following relation [8, 9]

$$\varepsilon^* = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)/(1 - i\omega\tau). \qquad (1)$$

In the expression (1) the relaxation time τ demonstrate Arrenius like behavior $\tau = \tau_0 \exp(\Delta W/k_B T)$ whereas static permittivity ε_0 changes in accordance with Curie law $\varepsilon_0 = \varepsilon_\infty(T)+C/T$. Frequency – temperature dependencies allow to determine the activation energies ΔW and "attempt" frequencies τ_0^{-1} of relaxing species for all three processes. Using the following parameters:

1 process:	$\tau_0^{(1)} = 3\cdot10^{-12}$ sec,	$\Delta W^{(1)} = 0.24 \pm 0.01$eV,	$C^{(1)} = 170$ K^{-1};
2 process:	$\tau_0^{(2)} = 8\cdot10^{-15}$ sec,	$\Delta W^{(2)} = 0.38 \pm 0.01$eV,	$C^{(2)} = 850$ K^{-1}; (2)
3 process:	$\tau_0^{(3)} \approx 10^{-20}$ sec,	$\Delta W^{(3)} = 0.77 \pm 0.01$eV,	$C^{(3)} = 950$ K^{-1};

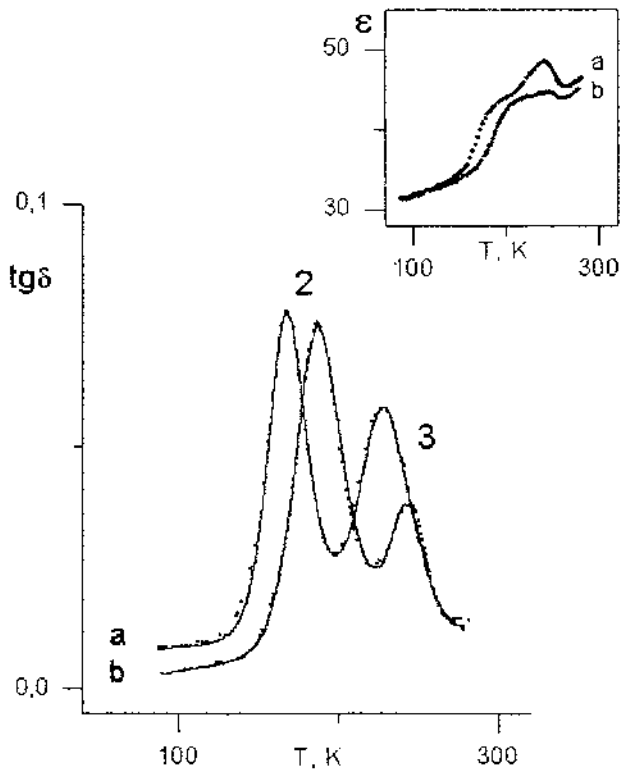

Fig.2. Temperature dependencies tgδ(T) and ε(T) for **E** || **c**. Measured frequencies - 1 kHz (a), 15 kHz (b). Circles - experiment, solid lines - theory (1).

and assuming linear dependence $\varepsilon_\infty(T)$, according to the relationship (1). The experimental data were fitted. The results are shown by solid lines in figures 1, 2. It should be noted that for process 3 it was impossible to describe the experimental dependencies at different frequencies using the same value of parameter $C^{(3)}$.

When analyzing the obtained data one has to take into account that according to ESR results Cu^{2+} ions equiprobably occupy one of the three off-center positions, displaced from the trigonal lattice points in (ab) crystallographic plane [2]. The dielectric experiment directly shows that process 1 corresponds to relaxation dynamics in (ab) plane. It has to be noted that the relaxation dynamics parameters $\tau_0^{(1)}$ and $\Delta W^{(1)}$, derived from ESR [2] and dielectric measurements, exhibit exact coincidence. Thus one can conclude that dielectric relaxation related to the process 1 (figure 1) can be attributed to hopping of Cu^{2+} centers between three off-center positions.

We suppose that relaxation process 3 is due to reorientation of OH^- dipoles, which penetrate in empty structural tunnels along polar c-axis. The possibilities of incorporation of these species in crystalline lattice of PGO were reported earlier [11]. The high value of the thermal vibration amplitude of OH^- groups in c-direction reported for the hydroxyl apatite [12] may be also observed in PGO crystals, which posses apatite-like structure. Note that process 3 cannot be described exactly by Debye model. There are two main evidences for this. The first one is connected with extremely high value for "attempt" frequency $(\tau_0^{(3)})^{-1} \approx 10^{20}$ Hz. The second one is concerned with classical Debye-Langeven response which requires that the logarithm of loss peak amplitude should decrease linearly with the logarithm of the loss peak frequency. Last fact means that Curie constant is to be of the same value in all temperature- frequency "window", where this process is detected. Nevertheless it has been mentioned above that Curie constant $C^{(3)}$

decreases with increase of measured frequency. Classical Debye theory deals with polar non-interacting molecules freely floating in dielectrically inert non-polar fluid. There are at least three reasons which may cause discussed discrepancies

i) the polar species in our case are additionally charged particles, i.e. OH^- ions may contribute to polarization due to hopping charge carriers;

ii) in the case of high concentration of OH^- species in tunnels it is very important to take into consideration their mutual interaction which, as supposed in [13], is the main mechanism of OH^- dipole rotation in hydroxyl apatite inside structural tunnels;

iii) surrounding media is not non-polar but due to ferroelectric nature is strongly polarized, which may influence through spontaneous polarization field on ordering and/or freezing of permanent dipoles.

The experimental study of physical nature of discussed process 3 is now in progress and results will be reported soon.

Also it should be emphasized that the relaxation process II is strongly c-directed and may be related to OH^- ions incorporated in structural tunnels. We suppose that this may be caused by proton transferred between two neighboring OH^- dipoles.

Conclusions

The investigations of PGO:Cu^{2+} dielectric properties, performed here, deals with relaxation phenomena, caused by thermally activated dynamics of Cu^{2+} centers. The data obtained give evidence that Cu^{2+} in PGO structure induce local dipole moments, oriented perpendicular to the polar ferroelectric axis. The results presented here confirm the assumption about off-center copper ions localization reported earlier in [1, 2].

Two other relaxation processes detected in polar direction may be attributed to the OH^- groups, incorporated in structural tunnels.

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References

1. Vazhenin V.A.. Gorlov A.D., Krotkij A.I. Off-center Cu^{2+} ions in lead germanate crystals // In: Radiospectroscopy of impurity centers in crystals with phase transitions (Kiev, IPM AN USSR), 1989, chapt.3, p.5-7. (in Russian).
2. Trubitsyn M.P., Ermakov A.S., Linnik V.G., Zabara Yu. V. Local Dynamics of Cu^{2+} Centers in Lead Germanate Ctystals // In: Abstract Book of IV Ukrainian-Polish Meeting on Phase Transition and Ferroelectric Physics (Dniepropetrovsk, Ukraine, June 15-19), 1998, p. 104. Trubitsyn M.P., Volnianskii M.D., Ermakov A.S. Motional averaging of Cu^{2+} ESR spectra in lead germanate crystals // Visnyk DDU, 1999, in print. (in Russian).
3. Kay M.I., Newnham R.E., Wolfe R.W. The crystal structure of the ferroelectric phase of $Pb_5Ge_3O_{11}$ // Ferroelectrics, 1975, vol. 9, p. 1-6.
4. Bersuker I.B. Structure and properties of coordination compounds // Khimia Leningrad, 1971, 312 p. (in Russian).
5. Abraham A., Bleney B. Electron paramagnetic resonance of transition ions // Mir, Moscow, 1972, vol. 1, 651 p. (in Russian).
6. Deigen M.F., Glinchuk M.D. Paraelectric resonance of non central ions // Uspekhi Fiz. Nauk, 1974, vol. 114, No. 2, p. 185-211 (in Russian).
7. Sochava L.S. Non central 3d-ions in crystals // In: Spestroscopy of crystals (Nauka, Leningrad), 1978, p. 166-175 (in Russian).

8. Poplavko YU..M. Physics of dielectrics // Vyscha Schkola, Kiev, 1980, 398 p. (in Russian).
9. Mashkovich M.D. Electrical properties of inorganic dielectrics in microwave range // Sov.radio, Moscow, 1969, 240 p. (in Russian).
10. Bush A.A., Venevtsev YU.N. Monocrystals with ferroelectric and related properties in Pb-O-GeO_2 system and probable applications // NIITEKHIM, Moscow, 1981, 71 p. (in Russian).
11. Duda V.M., Baranov A.I., Slade R.S.T. Proton insertion and conductivity in PGO single crystals // In: Abstract Book of IV Ukrainian-Polish Meeting on Phase Transition and Ferroelectric Physics (Dniepropetrovsk, Ukraine, June 15-19), 1998, p. 35.
12. Kay M.I., Young R.A. and Posher A.S. Crystal structure of hydroxy apatite // Nature, 1964, vol. 204, p. 1050.
13. Arends Y., Royce B.S.H., Siegel Y. and Smoluchowski R. Dielectric relaxation in hydroxy apatite // Phys. Let., 1968, vol. 27A, No. 10, p. 720-721.