Effect of lanthanum dopant on dielectric dispersion of Lead Germanate (Pb$_5$Ge$_3$O$_{11}$) single crystals.

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Abstract: Dielectric dispersion and loss dispersion for pure and lanthanum doped lead germanate (Pb$_5$Ge$_3$O$_{11}$) single crystals were studied in the frequency region 100 Hz to 100 KHz. The measurements were taken at room temperature, 100 °C and 200 °C. The observed dielectric and loss dispersion is discussed.

Keywords: Dielectric dispersion, doping effect

1 Introduction

Dispersion is expressed as a variation of dielectric parameters with frequency. The mechanism responsible for these variations can be characterized as a relaxation. The electronic, ionic, dipolar, and space charge related polarization are the four significant modes of relaxation observed in dielectric and ferroelectric materials.

Ferroelectric lead germanate (Pb$_5$Ge$_3$O$_{11}$) has attracted a number of investigators due to its applications for devices. These crystals show the reversibility of spontaneous polarization and nonlinear optical properties. They are uniaxial ferroelectric which undergoes a second-order phase transition at 177°C, at which crystal symmetry changes from hexagonal, $P6$ to trigonal, $P3$ [1-5]. The precise amount of additives can influence appreciably the growth and dielectric properties of Pb$_5$Ge$_3$O$_{11}$ [6-8].

The study of dielectric dispersion in lead germanate material has been attempted by various investigators. L.E.Cross et al[9] have linked the observed dielectric spectra of pure lead germanate single crystal over frequency range 10KHz to 1MHz with Maxwell Wagner mechanism. The authors believe that the relaxation may be linked with the wall motion and rearrangement of trapped charges associated with the wall, for high and intermediate frequency. V.V. Dem’yaneve et al [10] suggested that the low frequency dispersion in lead germanate crystals is caused by interaction among the dynamic polarization and conduction band electrons in the frequency range $10^2$ to $10^6$ Hz. The second dispersion between $10^6$Hz-$10^9$Hz was possibly due to the motion of the domain wall while the third dispersion between $10^9$Hz-$10^{11}$Hz was of relaxation type. However, M. Polamska et al [11] recommended that the same may be due to the presence of lattice defects contributing to the polarization of the crystals. J.H. Kim et al[12] reported the presence of two dispersion mechanisms in lead germanate, one is caused by the hopping process associated with polaron, and the other is concerned with the intrinsic polarization of the ferroelectric material. The thickness dependence dielectric constant at frequencies 1,10 and 100KHz was also reported by A. Mansingh et al [13]. The author explained observed results by considering homogeneous surface layer formation due to a potential barrier at the metal-insulator junction.

Y Goto et al[14] measured the complex dielectric constant of single crystals of ferroelectric Pb$_5$Ge$_3$O$_{11}$ as a function of temperature in a frequency range below KHz order. He observed the dependence of dielectric dispersion on sample thickness and non-formation of circular arc by the conventional coelecle plot. The author attributed this to the Maxwell-Wagner relaxation. The capacitance $C(\omega)$ and
conductance $G(\omega)$ at the angular frequency $\omega$ for the Maxwell-Wagner model, which assumes a dielectric consisting of two layers with capacitances $C_1, C_2$ and conductance $G_1, G_2$ respectively, are given by

$$C(\omega) = C(\infty) + \frac{C(0) - C(\infty)}{1 + (\omega \tau)^2}$$

$$G(\omega) = G(\infty) + \frac{G(0) - G(\infty)}{1 + (\omega \tau)^2}$$

Where,

$$C(0) = \frac{G_2^2 C_2 + G_1^2 C_1}{(G_1 + G_2)^2}, \quad C(\infty) = \frac{G_1 \cdot C_2}{(C_1 + C_2)}, \quad G(0) = \frac{G_1 \cdot G_2}{(G_1 + G_2)},$$

$$G(\infty) = \frac{G_1 C_2^2 + G_2 C_1^2}{(C_1 + C_2)^2}$$

and $\tau = \frac{(C_1 + C_2)}{(G_1 + G_2)}$. 

$C(0)$, $G(0)$ are the C and G values at $\omega \to 0$, and $C(\infty)$, $G(\infty)$ are the C and G values at $\omega \to \infty$. C.G. Koops et al [15] has shown that $C(\omega)$ and $G(\omega)$ depend upon the ratio of the thickness of one layer to another layer, hence can be changed by varying the sample thickness.

The paper presents a study of dielectric dispersion in pure (LG), 0.5wt% (LG1), and 1wt% (LG2) lanthanum doped lead germanate single crystals.

2 Experimental

Single Crystals of pure lead germinate (LG) were prepared by controlled cooling of the melt using high grade reagents of PbO (99.9%, Aldrich USA) and GeO$_2$ (99.999%, Reachim USSR) in 5:3 molar composition. The initial material was prepared by mixing the weighed PbO and GeO$_2$ in agate pestle mortar for about three hours. The thoroughly mixed material was divided into three parts. The first part was used to grow LG crystals. La$_2$O$_3$ (99.9%, Indian Rare Earths) was added as a dopant in 0.5wt% and 1wt% in the other two parts of starting material, to grow LG1 and LG2 crystals respectively. The powders were thoroughly mixed and converted into tablets by applying a pressure of 1 ton per square inch with the help of a hydraulic press. The calcination was done at 600 °C in a platinum crucible for about six hours in a closed furnace in the air. Tablets of LG, LG1, and LG2 were re-crushed to fine powder and crystals were grown using platinum crucible. The melting points, as confirmed by DTA, are 730.2 °C, 733.1 °C and 733.3 °C for LG, LG1 and LG2 respectively. X-ray diffraction was carried for grown compositions at R.T. ranging from $\theta = 5^\circ$ – $95^\circ$ with target Cu K $\alpha$ and wavelength 1.54184Å. The estimated values of lattice parameters are ($a_0 = 10.232$ Å, $c_0 = 10.679$ Å), ($a_0 = 10.2274$ Å, $c_0 = 10.685$ Å) and ($a_0 = 10.2271$ Å, $c_0 = 10.674$ Å) for LG, LG1 and LG2 respectively.

Samples of LG, LG1, and LG2 crystals used for measurements were cleaned, polished and a thin layer of air-drying silver paste is used for electroding the surfaces. The crystal holder consisting of highly insulating alumina blocks for separating two electrodes was designed for the measurements. Dielectric dispersion and loss dispersion for LG, LG1, and LG2 crystals were studied in the region of frequencies 100 Hz to 100 KHz. The measurements were taken at Room Temperature, 100 °C and 200 °C. The precision LCR Hi Tester (HIOKI 3520) of Hioki E.E. Corporation of Japan was used to measure frequency dispersion of dielectric constant and loss factor between 100Hz to 100 KHz.
3. Results and Discussion:

Figure 1 shows the dependence of dielectric constant with frequency at room temperature, 100 °C and 200 °C for LG, LG1, and LG2 single crystals. The similarities in the dielectric dispersion curves are

- All three compositions show a peak at 4 KHz at room temperature.
- These compositions show an increase in dielectric constant with temperature.
- They show an exponential reduction of dielectric constant with increasing frequency and absence of peaks, at higher temperatures.

However, the dopant affected the dispersion curves in the following aspects.

- At room temperature, an additional peak is existing at 40 KHz in both doped compositions LG1 and LG2.
- The peak values of dielectric constant are increasing with concentration of dopant i.e. in LG2 crystals.
Overall the dielectric constant is reduced in doped crystals as compared to pure crystals except at room temperature in frequency ranges 400 Hz to 3 KHz and 20 KHz to 100 KHz where it is increasing with doping concentration.

![Variation of Dielectric Loss with Frequency](image)

**Figure 2. Variation of Dielectric Loss with Frequency at R.T., 100 °C and 200 °C.**

The loss dispersion curves for LG, LG1, and LG2 single crystals at room temperature, 100 °C and 200 °C are shown in figure 2. The similarities in loss dispersion behavior of these compositions are:

- All three compositions are showing loss peaks at the frequencies corresponds to dielectric dispersion maxima at room temperature.
- Both pure and doped compositions show peaks at higher temperatures for loss dispersion which are absent in dielectric dispersion.
- They show a peak at 400Hz at 100 °C and disappearance room temperature peaks at a higher temperature.
- The loss factor increases with increasing temperature in all three compositions.

However, the lanthanum doping influenced loss dispersion as follows.

- The doped crystals show additional peaks at room temperature, 100 °C and 200 °C compared to pure crystals in the frequency range 100Hz to 1KHz.
- The room temperature peak value is increased with increasing lanthanum concentration.
Overall loss factor decreases with lanthanum doping as compared to pure crystals except at room temperature in frequency ranges 400Hz to 3KHz and 20KHz to 100KHz where it is increasing with doping concentration.

The observed low-frequency dispersion in lead germanate crystals can be discussed as follows. At room temperature, LG crystals show significant low-frequency dispersion. However, doped LG1 and LG2 show comparatively enhanced dispersion in this region. This low-frequency dispersion can be understood using the Maxwell Wagner model suggested by Y. Goto et al [14]. This model assumes a dielectric consisting of two layers with capacitances $C_1$, $C_2$, and conductance $G_1$, $G_2$ respectively. Our grown crystals can be looked upon as a bulk sandwiched between two surface charge layers as shown in Figure 3. The effective capacitance is decided by the surface charge density of the space charge. The observed variation in low-frequency dielectric dispersion can be attributed to the variation of surface charge density.

Thus the capacitance $C(\omega)$ and conductance $G(\omega)$ at angular frequency $\omega$ of such sandwiched crystal will be given by Eqns. (1) & (2) respectively as mentioned in Maxwell–Wagner model.

Contrary to observations of Goto and Polanska no room temperature dielectric dispersion is observed below 1 KHz in LG by us. At higher temperatures, the observed dielectric and loss dispersion may be attributed to defects, activated space charge, and its interaction with conduction band electrons as suggested by V.V. Dem’yanove et al [10]. A.A. Bush et al [16] also suggested that dielectric characteristics of lead germanate depend on degree of polarization, the kind and concentration of defects in the crystals.

In the present work, a lanthanum dopant can replace either Pb$^{2+}$ ion or Ge$^{4+}$ ion depending upon the valance and ionic radii of dopant and host atom. It will have a higher probability of replacing lead substitutionally, due to their similar ionic radii and valence compensation [7]. It becomes a case of heterovalent or non-isovalent impurity due to electroneutrality, as three Pb$^{2+}$ ions are equivalent to two La$^{3+}$ ions. It leads to the vacancy formation at the Pb site. This introduces the non-homogeneous distribution of defect states in LG1 and LG2 lattice in the form oflead ion vacancies. These defect states may change internal field configuration in LG1 and LG2 which further influence dipolar orientation, charge layer formation, and its density. The concentration of doping will significantly affect the formation of surface charge density. It may affect degree of polarization and concentration of defects in the crystals. The reduction in dielectric constant in doped LG1 and LG2 at temperatures other than room temperature can be linked to the defects, change of polarization and the structural changes in the crystals.
Consistent maxima in dielectric and loss dispersion observed for both pure and doped crystals at 4KHz and at 40KHz only for doped LG1 and LG2. The additional dielectric and loss peaks may also be attributed to these defect states.

An electron trapped at one of the molecular sites produces a local static polarization which results in polarons. In our grown LG compositions, there is a possibility of the creation of vacancies because of the loss of lead and oxygen during growth despite several precautions. The electron trapped at different lead sits may form polarons. Thus, hopping of polarons may also contribute towards dielectric relaxation in the present case as suggested by J.H. Kim et al [12].

4. Conclusion:

The present study leads to the conclusions as follows.

1. The observed low-frequency dispersion in LG, LG1, and LG2 crystals is discussed in light of the Maxwell Wagner model suggested by Y. Goto
2. Both dielectric and loss dispersion in pure and doped crystals can be attributed to the variation of defect states and surface charge density.
3. Hopping of polarons may also contribute towards dielectric relaxation.

5. References:

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