Effect of Nd^{+3} and K^{+} Substitutions on Phase Transition of Ferroelectric lead Germanate Single Crystals

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ABSTRACT

Double doped (Nd^{+3} + K^{+}) ferroelectric lead germanate single crystals were grown by controlled cooling of melt. Greenish tinge crystals of 5 x 4 x 3 mm^3 were found embedded in the solid. Pure lead germanate was grown by cz technique for comparative analysis. Dielectric constant and loss tangent of pure crystals showed a sharp dielectric peak at 179°C while dielectric constant of doped crystals showed temperature dependence with diffuse dielectric maxima at 350°C. Results suggest a significant positive shift of ferroelectric transition temperature by 171°C. Mechanisms for the shift in transition temperature and diffuse nature of dielectric maxima are discussed.

1. INTRODUCTION

Ferroelectrics, because of their high dielectric constant, non-linear behaviour, polarization reversal and domain structure have become potentially useful sensor materials, particularly in temperature ranges where semiconducting materials fail. It has been further established that dopants tremendously change the physical behaviour of the material. With the choice of appropriate dopants, ferroelectric materials can be tailored to suit in device applications. It was these two aspects that provided us a motivation to study the impact of double doping in ferroelectric materials.   The objective was to observe the change in physical behaviour and to understand the change in terms of changes in microscopic parameters like bond length, bond strength, atomic radii of the substituents, defect states etc. Single doping incorporates defect states resulting in change in losses. As device materials, ferroelectric materials cannot afford to tolerate increase in losses due to doping.   The present work of double doping of lead germanate with Nd^{+3} and K^{+} was undertaken keeping this objective in mind.

Because of large spontaneous polarization, its reversibility and non-linear optical properties, ferroelectric lead germanate (LG) has become an attractive material for device application. Extensive work has been reported regarding tailoring of ferroelectric behaviour through doping. This paper reports the effect of double doping of monovalent K^{+} and trivalent rare earth Nd^{+3} on dielectric behaviour of lead germanate single crystals.

Ferroelectric lead germanate undergoes a second order phase transition at 177°C from a ferroelectric phase with a trigonal space group (P3) to a paraelectric phase with a hexagonal space group (P6) [1-10]. It is probably the only material whose Curie constant lies between the Curie constant of displacive (~10^5) and order-disorder (~10^3) types of phase transition [10]. V. N. Gavrilov et al [11] predicted that at T = T$_c$ only the atoms located in the Ge$_2$O$_7$ tetrahedra assume new positions in the ferroelectric phase. This causes the P6-P3 change in symmetry throughout the cell and generates a spontaneous polarization,

which is entirely due to displacement in Ge$_2$O$_7$. Based on Raman Scattering and Brillouin scattering various authors [5,12-15] have predicted the origin and attenuation of the soft mode as a characteristic feature of the ferroelectric phase transition in LG crystals. J. J. Lockwoods and K. B. Lyons investigations of Raman [16-17] and submillimetre spectra [18] reveal the softening of the low frequency optic phonon and give evidence in favour of a displacive character of ferroelectric phase transition in LG crystals. According to M. P. Trubitsyn [19] on approaching the transition point from the ferrophase (above ~100°C), the soft phonon becomes overdamped, critical dynamics slow down and gain pronounced relaxation features peculiar to an order-disorder scheme of a structural phase transition. Studies of soft mode in LG by neutron and Raman scattering by R. A. Cowley [13] showed that Raman scattering did not give soft mode parameters near T$_c$. It is well known that impurities and defects exert strong influence on the ferroelectric phase transitions in LG crystals [20-22]. H. H. Otto et al [23] reported that the substitutions of Cs or Bi at Pb^{2+} sites in LG reduces ε and T$_c$. They have suggested that the cooperative effect between the lone pair electrons of neighboring Pb^{2+} ions can be easily disrupted by substituting other ions for Pb^{2+} and T$_c$ decreases nonlinearly with the concentration of the dopants. Moiseenko et al [14] have reported the influence of Bi or La doping on soft mode frequency in lead germanate. They observed that the change in structure caused by the phase transition in lead germanate involves displacement of Pb atoms, the vibration of which dominates the soft mode. Jae Hyung Kim et al [7] reported a diffuse phase transition with of Tc with increasing Sr concentration in LG. According to them the diffuse phase transition of Sr^{+2} doped LG single crystal was caused by local polarization due to a positional disorder. M. L. Nanda Goswami et al [24] have reported that the ionic radii of the dopant ions have direct bearing on the transition temperature of the modified lead germanate compounds. With the decrease in the ionic radii of the dopant ion, the transition temperature decreases and ε-T peak becomes more diffused. Trubitsyn [25] investigated the EPR and dielectric properties of copper ion doped LG crystals. They showed that Cu^{2+} ions replace Pb^{2+} in trigonal symmetry positions and occupy three off-center positions displaced from a crystal lattice site in a plane perpendicular to the polar axis c. The temperature variation of EPR spectra and dielectric properties indicates the presence of thermally activated jumps of Cu^{2+} ions between off-center positions. Their experiments with various directions of the measuring field proved that the additional peaks of tan δ(T) correspond to residual contributions of relaxation processes that are observed mainly along the polar axis c. Trubitsyn et al [26] further reports the effect of Cu^{2+} ions on the phase transition in lead germanate in terms of the copper center model. They inferred that the introduction of a copper impurity leads to a shift of the transition point towards lower

temperatures and to a broadening of the ε anomaly. According to them the concentration induced lowering of T_c indicated that the copper ions were 'rigid' defects, which stabilize their symmetric environment when cooled below the transition temperature of the ideal structure [22]. According to them the broadening of the thermodynamic anomalies upon the introduction of different impurities was a fairly general phenomenon, which could be associated with a non-uniform distribution of defects over the crystal matrix [27]. They have attributed this behavior on the method of ceramic preparation. R. N. P. Choudhary et al [10] have observed a diffuse phase transition in barium doped polycrystalline LG. According to them the width of the Curie temperature region depends both on the range of compositional fluctuations and on the sensitivity of the Curie temperature to such compositional changes. The observed increase in the dielectric constant above T_c may be explained by space-charge type polarization in the compounds, arising from the defect impurities present in the bulk or at the surface of the material.

2. EXPERIMENTAL

High purity starting materials PbO (Johnson Matthey, 99.99 %), GeO_2 (Koch-Light Lab, 99.999 %) were used to grow Nd^{+3} + K^+ double doped lead germanate (DDLG) by the method of controlled cooling of the melt. The materials were taken in 5:3 molar ratio and growth was initiated in a platinum crucible. Nd_2O_3 (Indian Rare Earths, 99.99 %) and K_2CO_3 (Aldrich Chemical Co., 99.99 %) were added as dopants in 0.2 mole % each. . The powders were mixed thoroughly for 12 hr in an agate pestle mortar. Tablets were made on a hydraulic press by applying pressure of 5 tons per square inch. The calcination was done at 550° C for 12 hr in a closed furnace. Tablets were recrushed to fine powder. The melting point was detected at 765°C. In the growth procedure first the melt was maintained at a thermal equilibrium of 8 hr at 770° C. An initial cooling rate of 1°C/hr was maintained uptil 760°C. Following cooling rates of 2°, 5° and 10° C/hour successively the melt was cooled down to room temperature. Greenish tinge single crystals of dimension 5 mm X 4 mm X 3 mm were found embedded in the solid. LG was grown by Czrochalski's technique. The XRD analysis of DDLG reported earlier [28] suggests that 1) DDLG crystals are trigonal with lattice parameters a=10.23723 A° and c=10.6124 A° and 2) that doping has decreased the lattice parameters. The crystals were made ready by cutting on Crystal Cutting Unit (South Bay Technology, USA), polishing with fine emery paper, and electroding by air-drying silver paste. A specially designed spring-loaded crystal holder with highly insulating alumina tubes and silver electrodes was used for mounting of the crystals. Temperature dependence of dielectric constant and loss tangent were studied using a HIOKI 3520 LCR HI TESTER bridge (Japan) in the temperature range of 40°C to 400°C for doped samples and from 40°C to 250°C for pure samples. The test frequency applied was 1 kHz. Readings were taken in an interval of 10°C while in the vicinity of respective transition temperatures readings were recorded at an interval of 2°C. The test probes of HIOKI LCR HI TESTER bridge were highly silvered. A specially designed spring loaded crystal holder, to ensure better ohmic contact throughout the measurement range was used. Highly insulating alumina tubes, along with silver electrodes were used to better the quality of the crystal holder.

3. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of dielectric constant and tan δ up to 250°C for pure samples and up to 400°C for doped samples. Both the dielectric constant and tan

δ show a marginal increase in their room temperature values as a result of doping. The temperature dependence of dielectric constant of LG shows a sharp maximum at 179°C corresponding to its ferroelectric transition temperature. The dielectric constant of DDLG increases with temperature initially and then shows a rapid rise at 350°C. The sharp rise at 350°C corresponds to the ferroelectric transition temperature of DDLG. After a small decrease after the transition temperature, the dielectric constant increases with temperature in DDLG. As is evident from Figure 1, LG shows a sharp peak while DDLG exhibits a diffuse phase transition.

The temperature dependence of tan δ for LG shows a peak at 179°C. Above 230°C it goes on increasing with temperature. The temperature dependence of tan δ for DDLG shows increase of tan δ up to 150°C and large temperature dependence beyond 150°C. The 1/epsilon –T curve (Figure 2) shows that LG obeys Curie-Weiss law while DDLG significantly deviates from Curie-Weiss law.

Three significant behaviors of DDLG namely, increase in ferroelectric transition temperature, diffuse phase transition and an increase in dielectric constant in paraelectric phase with temperature along with deviation from Curie-Weiss law have to be correctly understood in terms of prevailing theories as a consequence of double doping.

According to Newnham et al [29], the structure of lead germanate is reported to be hexagonal containing 3 formula units. Each formula unit consists of one GeO_4 tetrahedron and a double tetrahedron Ge_2O_7 linked through one of the oxygen atoms and which are disposed alternately along c-direction making a layer like structure in the remaining lead frame as shown in figure (Fig 3A). The O (3) atom is one of the component oxygen of GeO_4 tetrahedron and just lying on the mirror plane and O (7) atom belongs to Ge_2O_7 group. O (3) is elongated along c direction while O (7) is elongated along the plane perpendicular to c direction (Fig 3B). Iwata [3] has reported the following facts from neutron diffraction data at high temperature. In pure lead germanate when the temperature is lowered towards the transition temperature, the reorientation of the GeO_4 and Ge_2O_7 germanate groups occur. The oxygen atom O (3) which is oscillating with very large amplitude in the paraelectric phase takes a stable position in the ferroelectric phase. The Pb (1) atom undergoes a large displacement and is most effective for phase transition. This leads to inclination of GeO_4 tetrahedra and twisting of Ge_2O_7 tetrahedra at the same time. Through strong interaction between Oxygen and Lead the neighboring lead atoms get displaced and the crystal takes a polar structure. The soft mode frequency related to PbO decreases to a limiting value at the phase transition. Thus the existence of unstable or largely agitated oxygen atom in the paraelectric phase suggests that the phase transition is of displacive type. The observed polarization is due to the displacement of Pb (1) and twisting and translation of Ge_2O_7 in which Oxygen in GeO_4 acts as a trigger for a phase transition.

A dopant can go either to Pb^{2+} site or to Ge^{4+} site, its distribution on the two sites being a function of the valence and ionic radius of the dopant and host atom. Following Kaminskii et al [30] the dopant Nd^{+3} enters one or more of Pb^{2+} sites in lead germanate because of similar ionic radii of Lead (1.75 A°) and Neodynium (1.82 A°) in DDLG. For the reason of electro-neutrality, 2 Nd^{+3} ions are equivalent to 3 Pb^{2+} ions. Therefore there is a possibility of the formation of vacancies at lead positions. This introduces defect states on the lead germanate lattice in the form of Pb ion vacancies. In order to compensate for the defect states, generated because of Nd^{+3} at Pb^{2+} site,

Potassium (K^+) has been introduced which will occupy the vacancies created at Pb^{2+} sites. This leads to a local polarization due to positional disorder. Thus addition of Nd^{+3} and K^+ leads to microscopic compositional fluctuations and localized disorder. The dopants disturb homogeneity in the crystal lattice. This also changes the bond strength, the bond length, internal field configuration and nature of bonding as suggested by S. Sugihara et al [31]. The dopants entering the Pb (1) site will affect the bond length between Pb-O and will result in the change in magnitude of displacement of Pb (1), degree of rotation of GeO_4 and twisting and translation of Ge_2O_7 tetrahedra. This may result in the shift in the transition temperature by 171°C (179°C to 350°C) as observed by us. The shift of transition temperature towards higher temperature side suggests that in the doped crystals Pb-O bonds gets stronger due to double substitutions and consequently bond strength, bond length, internal field configuration and the nature of bonds are not subject to change till 350°C.

M. P. Trubitsyn et al [26] suggests a similar influence of copper doping in lead germanate where he finds that the effect of substitution of Cu^{2+} at Pb^{2+} site influences tetrahedral and double tetrahedral orientation, rotation and twisting which may result in the shift of phase transition.

Increase of the dielectric constant beyond the transition temperature in DDLG is unlike normal ferroelectric behaviour. Similar increasing trend has also been reported by M. P. Trubitsyn et al [27] and R.N.P Choudhary et al [10] in LG. Choudhary et al attributes it to space charge created because of the defect states in the crystal. Trubitsyn et al attribute the increase to off-center substitution. In DDLG there is every chance that some of these substitutions may be off-center as suggested by M. P. Trubitsyn. Presence of defect states in DDLG also envisages space charge formation. The observed increase in dielectric constant in DDLG in paraelectric phase is attributed to the presence of off-center effects and space-charge effects.

Deviation from Curie-Weiss behaviour is attributed to presence of defect states and reflects the extent of change in the bond strength due to presence of defects.

The small broadening observed in the dielectric peak in DDLG is probably arising from of the asymmetric and inhomogeneous distribution of dopants. The uniformity of distribution of K^+ and Nd^{+3} in the symmetry of the probable Pb^{2+} substitution sites cannot be guaranteed because of minor fluctuations in temperature during the thermal processes of preparation and growth of DDLG. Thus the relaxor behavior in DDLG is arising because of double doping.

Overall increase in tan δ at higher temperatures can be attributed to the increase in dc conductivity of the crystals observed by us [32]

Doping distorts the internal field and influences the polarization. Sook [33] suggests that presence of cation vacancies makes domain motion easier and increases room temperature dielectric constant in $Pb(Zr,Ti)O_3$. According to D. Zhang [34] the dopants Bi^{3+}, K^+ in double doped $BaTiO_3$, increases ε through charge compensation mechanism. Both valency compensation conditions and the resulting generation of defect states, as suggested by In Sook et al [33] and Zhang [34], are present in DDLG. There is a high probability of non-uniform distribution of dopants as well as off-center distribution of Nd^{+3} and K^+ double dopants in DDLG. This also generates non-uniform distribution of internal field and enhances the ease of domain motion. The marginally enhanced

dielectric constant due to double doping in DDLG can be attributed to presence of non-uniform and off-center double dopants, distribution of generated vacancies and internal field.

4. CONCLUSION

The temperature dependence of dielectric constant and loss tangent have been studied in pure lead germanate and Nd^{+3} + K^+ doped lead germanate. Phase transition mechanism is discussed in lead germanate. The shift in T_c observed in DDLG is attributed to the changes in the crystal lattice due to incorporation of double dopants Nd^{+3} and K^+. The increase in the dielectric constant in the paraelectric phase after the peak behavior is attributed to the presence of off-center effects and space charge effects because of the presence of double dopants in the crystal lattice.
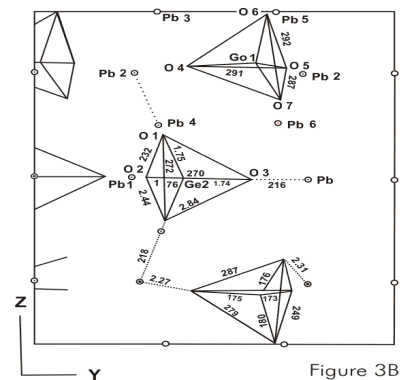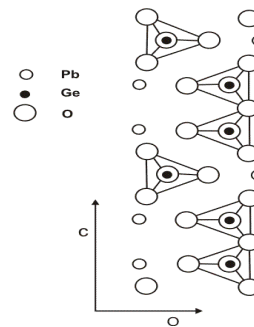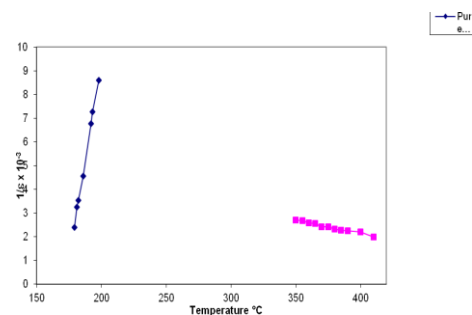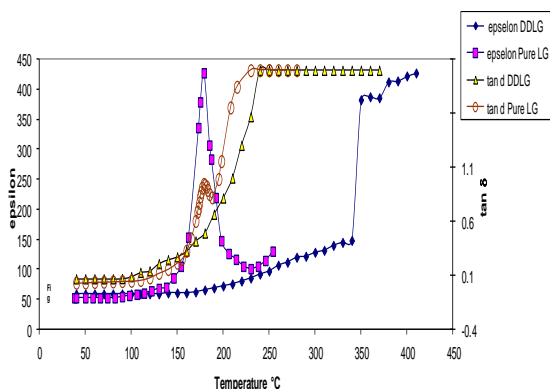

Figure 3B

Figure 3A

Figure 2 : Variation of 1/ε with temperature for LG and DDLG

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