

X - Ray Diffraction and Raman Scattering Study of Pure and Neodimium Doped Lead Germanate Single Crystal

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Abstract: *Pure Lead Germanate (LG) and Neodimium doped Lead Germanate single crystal have been grown from melt by controlled cooling method. The X ray diffraction study for pure and doped Lead Germanate was carried out. The comparative study of three different diffractograms suggest that the doping influences the relative peak intensity, number of peaks and changes the a_0 and c_0 parameters significantly in lead germinate. Substitution of Nd^{+3} leads to microscopic compositional fluctuations which leads to disturbance in homogeneity in crystal lattice. The marginal change in lattice parameter and unit cell volume in doped compositions suggest the possibility of reduction in bond strength with doping. Room temperature Raman scattering spectra for pure and doped compositions are obtained. Comparison of the data, suggest that doping changes the bond length and bond strength which influenced the vibrational spectrum and phonon interaction process.*

Keywords: *Lead germinates, Raman spectra, Neodimium doping*

1. INTRODUCTION

Lead Germanate have attracted considerable interest because of its ferroelectric, non linear optical behavior and pyroelectric characteristic. It is extensively studied and tailored to get modified properties with different doping element. Its crystal structure consists of layers arranged alternately along the c - axis within a Pb frame. These layers consist of germanate groups: GeO_4 tetrahedra and Ge_2O_7 double tetrahedra [1, 2, 3]. It is ferroelectric below Curie temperature $450^\circ K$ with space group P3 (trigonal). At T_c it undergoes a second order phase transition with hexagonal symmetry P6, however the value of T_c depends upon the crystal growth conditions and sample preparation i.e. thermal history, defect content or strains [4-7].

The elastic behavior of LG was studied by [8]. The decrease in Curie temperature with uniaxial pressure was reported by [9] and with doping of Si and Ba by [10, 11]. The nonstoichiometry and conductivity anisotropy of LG single crystal was reported by [12]. Polaron type conductivity of doped and undoped Lead Germinate with different activation energy was reported by [13]. The chemical induced phase transition in the metallic electrode attached to LG was reported by [14]. [15] Reported XPS electronic structure measurement of Ba doped lead germanate single crystals along the principle directions revealed a deviation of stoichiometry, which was the reason for the structural disorder and broadening of core level lines. Thermal properties such as thermal conductivity, thermal diffusivity was studied by [16, 17]. La^{+3} doping modify the growth habit of LG [18], and the shift in T_c with addition of Nd^{+3} and K^+ and the increase in dielectric constant is attributed to the presence of off centre and space charge effects because of the presence of double dopant in the crystal lattice[19] .

Raman scattering at structural phase transition has been extensively studied. The increase of the silicon impurity lowers the soft mode frequency, the effects on the line width are small [20]. The soft mode frequency seems to be mainly influenced by the change of the short range harmonic force due to the silicon doping is investigated by [21]. Now a day's Germanate based glasses have proved to be a host materials in the field of optoelectronics because of their excellent optical properties [22-27]. In this paper we are reporting the X ray diffraction and Raman scattering study in pure Lead Germanate and Nd^{+3} doped compositions.

2. METHODS

High purity starting material (PbO 99.99% Aldrich, GeO_2 99.999% and Nd_2O_3 99.999% Ritchem) were used to grow pure Lead Germanate (LG) and Neodmium doped Lead Germanate single crystal from melt by controlled cooling method. 0.1 wt % and 0.2 wt % Nd^{+3} was doped in LG.1Nd and LG.2Nd respectively. The molten charge was cooled slowly, at the rate of 1° per hour to few degrees below the melting point. Then subsequently with moderate rates the molten charge was cooled to room temperature. The X ray diffraction study for pure and doped Lead germanate was carried out using Phillips PW 1700 diffractometer, The diffraction pattern is obtained by using X rays at 35 kV, 20 mA rating , for Fe- $\text{K}\alpha$ radiation of wavelength $1.93735 \mu\text{m}$ and the scanning rate is maintained , $2\theta = 2.4^\circ/\text{min}$.

The atomic vibrations in a Raman scattering is a unique fingerprint for a given material at a given external condition. These vibrations are sensitive to changes of strain, temperature, pressure and external field. Room temperature Raman scattering spectra for pure and doped compositions are obtained at wavelength of 488 nm up to 1000 cm^{-1} .

3. RESULT AND DISCUSSION

3.1. X Ray Diffraction Study

The comparative study of three different diffractograms for pure and doped compositions suggest that the first three values of LG composition closely agree with the first three 'd' values reported by [28]. LG.1Nd and LG.2Nd reveal the marginal change in the d values as compared to LG. The doping influences the relative peak intensity and number of peaks. In LG, our calculated lattice parameters are closely agree with reported values within experimental error. A reasonably good agreement of calculated and observed d-values of all diffraction lines of pure and Nd^{+3} doped LG suggest that at room temperature there is no change in the crystal structure of lead germinate.

In LG.1Nd, the a_0 and c_0 have increased by 0.002 \AA and 0.035 \AA respectively. The unit cell volume is also increased by 10.66 cubic \AA . Similarly in LG.2Nd, the a_0 has decreased by 0.004 \AA and c_0 has enhanced by 0.034 \AA . However the unit cell volume has shown enhancement by 6.98 cubic \AA without changing hexagonal structure.

The prototype structure of Lead Germanate single crystal have been discussed by various workers [29, 30]. In doped compositions, the extent of impurity substitution depend upon the location of impurity. As per [1], the Pb-O bonds are comparatively weaker to break. Similarly the ionic radius of Neodymium is comparable to ionic radius of Pb ($\text{Pb}^{+2} = 1.18\text{\AA}$, $\text{O}_2 = 1.4\text{\AA}$, $\text{Ge}^{+4} = 0.53\text{\AA}$ and $\text{Nd}^{+3} = 0.995\text{\AA}$). Using the known data for bond length and bond strength as well as ionic radii of host and guest atoms we conclude the possibility of Neodymium going to Pb site is higher than that of going to Ge site. The structure of Lead Germanate provides multiple Pb sites and the change in ferroelectric behavior as indicated by shift in transition temperature can be brought by Pb(1) and Pb(2) sites only, suggesting that probability of substitution of Nd at these two sites is equally strong.

To decide which of the Pb site to be substituted by Neodymium we stretch Dergunova's [31] model to Lead Germanate. According to them the substitution induces local lattice distortion around the impurity atoms and change in overall lattice constant. In LG.1Nd the Nd^{+3} is about 0.066 % as confirmed by ICPA (Inductive coupled plasma analysis), the calculated value of

elastic energy is positive. Therefore Nd^{+3} may replace Ge^{+4} . However in LG.2Nd the impurity Nd^{+3} is about 0.133 atomic %. According to [31] for $X > 0.1$ atomic % this higher doping concentration leads to overlapping of local lattice distortion and to interaction between impurity atoms. Then the difference between unstrained bond length or corresponding ionic radii becomes energetically more favorable and hence impurity cation Nd^{+3} may replace Pb^{+2} .

To evaluate distribution of dopant between two sites of ABO_3 type ceramic relative to its ionic radius [32], as radius of Nd^{+3} is 0.995 \AA , the probability that it will occupy Pb site is 70 % (figure 1b). [21] reported the reduction in lattice parameter as a result of impurity doping may be due to increase in phonon frequency. In fact the frequency of external and librational modes except for soft mode increase with amount of impurity doping. Doping has change the a_0 and c_0 in both LG.1Nd and LG.2Nd. If Nd^{+3} is replacing any of the lead or germanium site, the substitution will create local lattice distortion and mechanical strain in the lattice and hence change the overall lattice parameters. If Nd replaces Pb (1), possibility of affecting c_0 parameter will be more as Pb (1) is attached with O (3), the oxygen component with strong Columbian force, which elongate along c- axis. If Nd replaces Pb(2), the possibility of affecting a_0 parameter will be more, as Pb(2) is lead bridge between GeO_4 and Ge_2O_7 which affect the relative displacement of oxygen component in Ge_2O_7 tetrahedra where O(7) is elongated along the direction perpendicular to c- axis.

It is observed that in both the doped compositions doping has significantly increased c_0 parameter. Hence there is probability that Nd has replaced some Pb (1) atoms in both the doped compositions. Similarly in LG.1Nd, a_0 parameter is increased by 0.002 \AA and in LG.2Nd it is decreased by 0.004 \AA , which suggest that Nd might have replaced some Pb(2) atoms also, resulting the change in lattice parameters and volume of unit cell. Thus the marginal changes in lattice parameter and unit cell volume suggest the possibility of reduction in bond strength with doping. The observed change in lattice parameters reveal that Neodymium has been incorporated in the structure of Lead Germanate. As suggested by [33] the doping also changes the bond strength, bond length, internal field configuration and nature of bonding in our case also. The similar influence of copper doping in lead germanate suggested [34] that substitution of Cu^{+2} at Pb^{+2} site influences tetrahedral and double tetrahedral orientation, rotation and twisting resulting shift in transition temperature.

3.2. Raman Scattering

Room temperature Raman scattering spectra for pure and doped compositions are obtained at wavelength of 488 nm up to 1000 cm^{-1} . Fig. 2 show the details of Raman spectrum obtained for LG, LG.1Nd and LG.2Nd. The graph reveals following facts.

- 1) Change in Raman shift is observed as a result of doping.
- 2) The intensity of peaks obtained is maximum for LG.1Nd and minimum for LG.
- 3) The peak observed at 200 cm^{-1} in LG has been suppressed for doped compositions.
- 4) In doped compositions the shift ' R_s ' is towards higher frequency side upto 600 cm^{-1} and it is towards lower frequency side beyond 600 cm^{-1} .

The peaks are observed due to molecular vibrational frequency of PbO , GeO_4 and Ge_2O_7 . The shift in peak as a result of doping reveals that Neodymium has incorporated in LG structure at Pb as well as Ge site. The observed change in frequency at peaks due to doping suggest that doping has influenced the vibrational spectrum as well as phonon interaction process. The change in Raman shift indicate the change in vibrational pattern, change in bond length and change in bond strength as a result of doping.

4. FIGURES

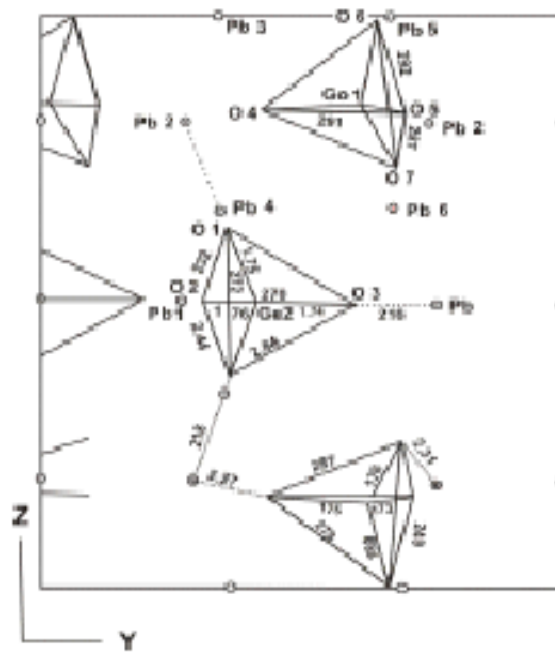


Fig. 1 a (Ref 1)

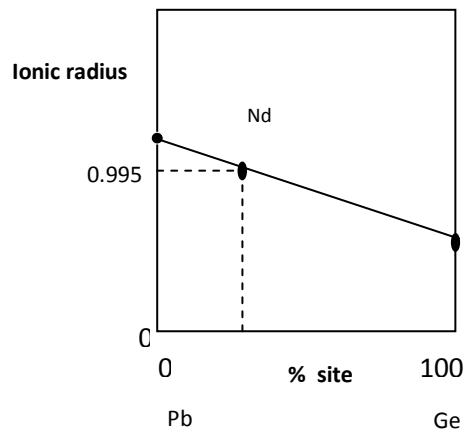


Figure 1b

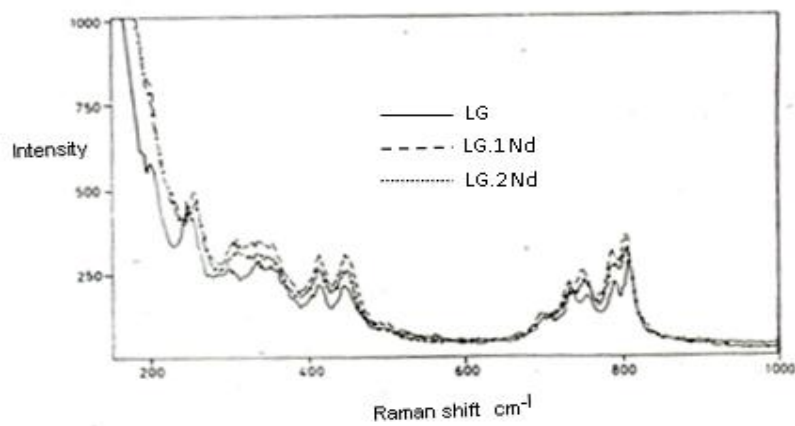


Fig 2. Comparison of Raman Spectra for LG, LG.1Nd and LG.2 Nd

5. CONCLUSION

Doping changes the a_0 and c_0 parameters significantly in lead germanate. Substitution of Nd^{+3} leads to microscopic compositional fluctuations which leads to disturbance in homogeneity in crystal lattice. Comparison of room temperature Raman spectra for pure and doped compositions suggest that doping changes the bond length and bond strength which influenced the vibrational spectrum and phonon interaction process.

ACKNOWLEDGEMENT

The authors are thankful to YCCE college authority for the encouragement and support.

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