

Optical and X-ray photoelectron spectroscopy of PbGeO_3 and $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ single crystals

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Abstract. $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ crystals are found to exhibit pale yellow colouration while PbGeO_3 are colourless. X-ray photoelectron spectroscopy (XPS) measurements show lead deficiency in both the crystals. The results also reveal a stronger ionic character for PbGeO_3 as compared to $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ crystal. The binding energy of Ge3d core level in the case of $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ crystal is found to be smaller than the binding energy of germanium oxide, thereby indicating the incomplete oxidation of Ge ions in the crystal lattice. On gamma ray irradiation, the transmission of both the crystals is observed to deteriorate uniformly over the entire wavelength range, which has been attributed to the oxidation of some of the lattice Pb ions. On gamma irradiation the changes observed in O1s core level energies for both the crystals are seen to be consistent with the changes noted in the $\text{Pb}4f_{7/2}$ and Ge3d spectra. Interestingly, the results reveal oxidation of surface Ge atoms with atmospheric oxygen under gamma irradiation.

Keywords. Czochralski technique; PbGeO_3 and $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ single crystals; optical absorption; XPS; gamma irradiation.

1. Introduction

There are in all five different compositions in the phase diagram of PbO and GeO_2 which solidify in crystalline phase (Iwasaki *et al* 1971). The compositions, PbGeO_3 (LGO-1) and $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ (LGO-2), both exhibit ferroelectric properties. Consequently, efforts were made during seventies to grow LGO-2 single crystals of high quality and characterize them for growth related defects and photorefractive, electro-optic and pyroelectric properties (Iwasaki *et al* 1971a, b; Bichard *et al* 1972; Houlton *et al* 1975; Goswami *et al* 1998; Yue *et al* 1998; Reyher *et al* 2001). Besides, several chemical substitutions for tetrahedral oxygen coordinated Ge^{4+} ion or in the large Pb polyhedral were also attempted to improve the pyroelectric sensitivity of LGO-2 (Iwasaki *et al* 1972; Watton *et al* 1976; Bush and Venevtsev 1979; Otto *et al* 1980; Landolt-Börnstein 1982; Talik *et al* 2006). Recently, the photoelectron spectroscopy of Ba-doped LGO-2 crystals was also performed to investigate the electronic structure of the crystal. While some attention has been given to LGO-2 crystal, the same has not been the case with LGO-1. A comparative study of the electronic properties of the two crystals is envisaged to be important from the point of view of both basic understanding and crystal application.

In this communication, we report on the optical properties and photoelectron spectroscopy of the two crystals. The LGO-2 crystals are found to have pale amber colouration, while LGO-1 crystals are colourless. The colouration is attributed to different electronic structures of the crystal and not to the presence of any impurity ion in the lattice. The effect of gamma exposure on crystal transmission has been investigated to obtain information about the crystal defect structure. The crystal transmission is uniformly decreased throughout the wavelength range investigated, which indicates the generation of free carriers in the lattice. The XPS technique has been used to examine the composition of the crystals and the chemical state of the constituent elements. The XPS results show that the ionic character of LGO-1 is stronger than LGO-2, implying the former crystal to be more insulating. The results of d.c. electrical resistivity measurements carried out are in conformity with this result.

2. Experimental

The crystals of 20 mm diameter and 50 mm length were grown by Czochralski technique, using an automatic diameter controlled crystal puller. For preparation of the starting charge, 4N pure PbO and GeO_2 constituent oxides mixed in stoichiometric proportion and taken in a 40 mm diameter platinum crucible, were rapidly raised to the melting temperature under normal ambient. Grown cry-

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stals were brought to room temperature at a uniform rate of $30^{\circ}\text{C h}^{-1}$. All the measurements reported in this paper were carried out on un-poled crystals.

For optical transmission measurements, crystal slices were cut from the crystal ingots and the broad opposite faces were optically polished. The optical transmission spectra of the polished samples were recorded over the wavelength range of 300–1100 nm by a Techcomp spectrophotometer, Model 8500. The XPS spectra were recorded using $\text{AlK}\alpha$ radiation (1486.6 eV) and an Omicron EA-125 photoelectron spectrometer at a base pressure better than 5×10^{-10} Torr. The overall energy resolution of the electron energy analyser was 0.8 eV with a pass energy of 50 eV. The source was operated at an emission current of 10 mA and an anode voltage of 10 kV. To correct the shifts in binding energies of core levels due to the charging effect, C 1s peak at 284.6 eV was used as an internal reference.

The samples were irradiated to gamma rays in a ^{60}Co gamma chamber. For d.c. electrical resistivity measurements crystal slices having a flat surface of $\sim 40 \text{ mm}^2$ were provided gold electrodes by evaporation to which thin silver wires were attached with silver paste. A stabilized d.c. high voltage supply and a Keithley picoammeter were used for the resistance measurement.

3. Results

The LGO-2 exhibited pale amber colouration while LGO-1 crystals were colourless. The optical transmission plots recorded before and after gamma irradiation for both the crystals are shown in figures 1 and 2. The transmission characteristics exhibited by LGO-1 crystals are clearly superior to those of the LGO-2 crystals. For LGO-1 the

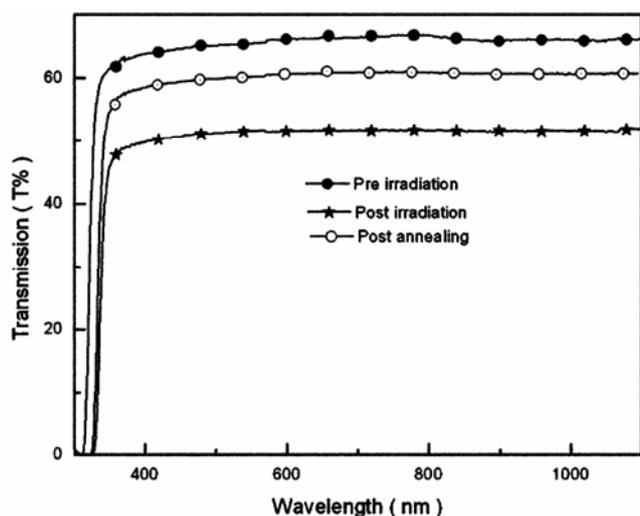


Figure 1. Optical transmission spectra of PbGeO_3 crystal before (\bullet), after gamma irradiation (\ast) and post irradiated and annealed at 150°C for 24 h (\circ). Exposure, 100 kGy.

lower wavelength cutoff is observed to be at 330 nm with a sharp edge as against that of the 420 nm for LGO-2. Further, for LGO-1 the transmission above the absorption edge is found to be quite flat over the entire wavelength range investigated. In contrast, the transmission of LGO-2 crystal decreases monotonically at lower wavelengths. The band gaps computed from the absorption edge data of LGO-1 and 2 are 3.76 eV and 2.95 eV, respectively. On gamma ray irradiation, transmission of both the crystals is found to uniformly decrease over the entire wavelength range. In case of LGO-1, the lower wavelength cut-off is also slightly shifted towards higher wavelength side, while no such effect is observed in LGO-2. In case of LGO-2, a small hump peaking around 460 nm is also observed in its absorption spectrum. In order to further investigate the changes occurring on gamma irradiation, the irradiated samples were subjected to thermal annealing at 150°C . A significant recovery in transmission is observed for both the crystals. The transmission plots obtained after 24 h of thermal annealing of the crystals have been shown along with their respective transmission plots recorded before and after irradiation in figures 1 and 2. The transmission can be fully recovered by extending the annealing period to ~ 60 h.

The XPS spectra of the two crystals recorded in the energy range of 0–1400 eV are shown in figure 3. Several peaks corresponding to Ge 3d, Pb 4f, C 1s, Pb 4d_{1/2}, Pb 4d_{3/2}, O 1s, Pb 4p_{3/2}, Pb 4p_{1/2}, Ge 2p_{3/2}, Ge 2p_{1/2} core levels and Ge LMN AUGER level are observed here, which confirm the chemical composition of the crystals. After taking the survey scans, narrow range scans for O1s, Pb 4f_{7/2} and Ge 3d core levels were also taken for peak analysis and the plots obtained are shown in figures 4–6 and the binding energy values of the core levels are

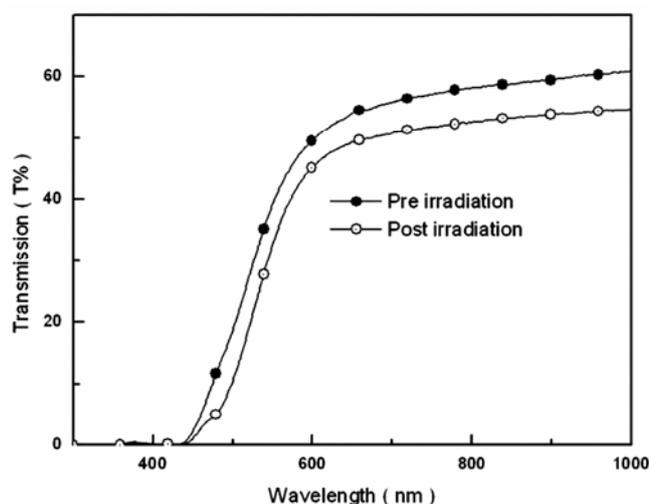


Figure 2. Optical transmission spectra of $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ crystal before (\bullet), after gamma irradiation (\circ). Exposure 100 kGy.

summarized in table 1. Also narrow scans of C 1s peaks show that the shifts due to charging effect in LGO-1 and LGO-2 are nearly the same, viz. 12.1 and 12.3, respectively. This shows the insulating nature of both the crystals. The relative concentrations of various constituents were determined using peak area of the suitable intense lines of the constituent atoms and standard atomic sensitivity factors (Moulder *et al* 1992). The XPS peak fitting program, XPSPEAK41 (www.phy.cuhk.edu.hk/~surface/XPSPEAK/) was used for background subtraction and Gaussian-Lorentzian peak fitting for different core levels. The XPS measurements were also carried out after irradiating the crystals with gamma rays. O 1s, Pb 4f and Ge 3d core level spectra of both the crystals are presented in

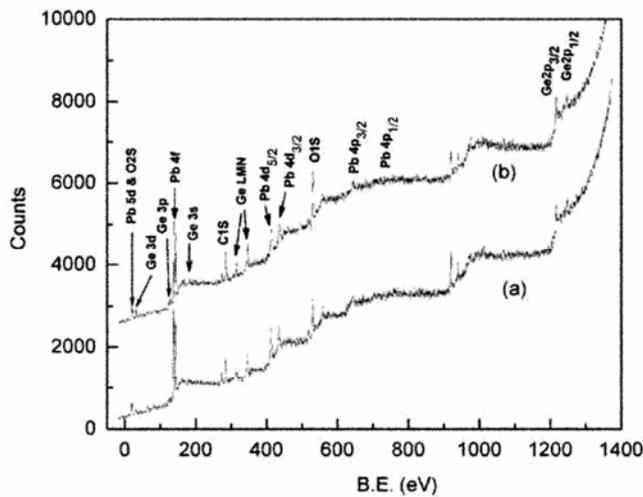


Figure 3. Survey scans for core level XPS spectra: (a) PbGeO_3 and (b) $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ crystals.

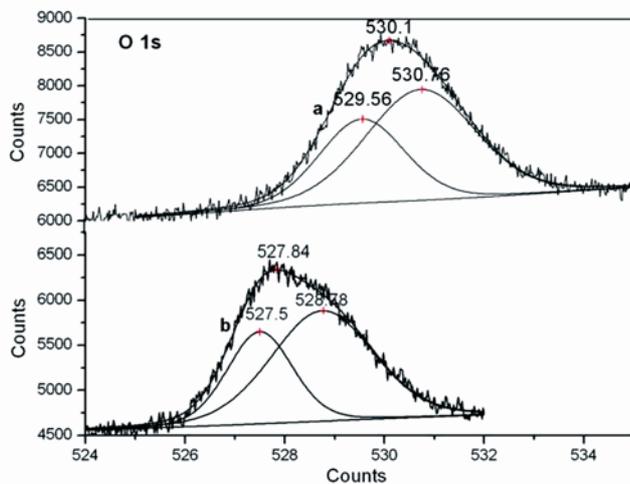


Figure 4. O 1s core level XPS spectra: (a) PbGeO_3 and (b) $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ crystals. In both the cases the spectra are asymmetric and resolved into two peaks with binding energies as given in table 1.

figures 7–9 and the binding energy values and other parameters of the core level peaks obtained are given in table 1.

The room temperature d.c. resistivity measured along the polar axis of an as grown LGO-2 crystal was found to be $\sim 4 \times 10^{11} \Omega\cdot\text{cm}$. In comparison, the LGO-1 crystal was found to have slightly higher resistivity of $8 \times 10^{12} \Omega\cdot\text{cm}$. In both the cases, the resistivity was found to remain unaffected on gamma irradiation.

4. Discussion

The optical transmission characteristics of LGO-2 shown in figure 2 are in agreement with those reported in literature (Yue *et al* 1998). The pale amber colouration in

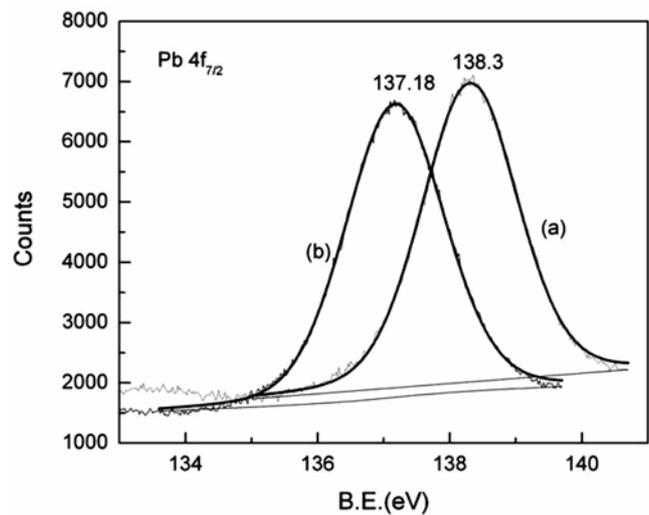


Figure 5. Pb 4f_{7/2} core level XPS spectra of (a) PbGeO_3 and (b) $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ crystals.

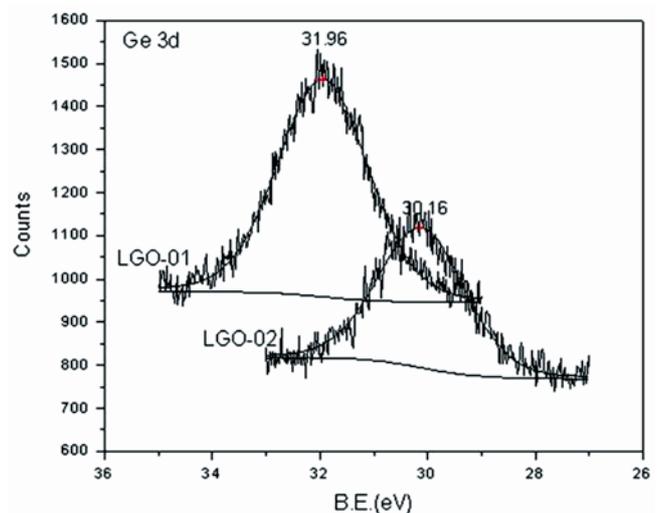
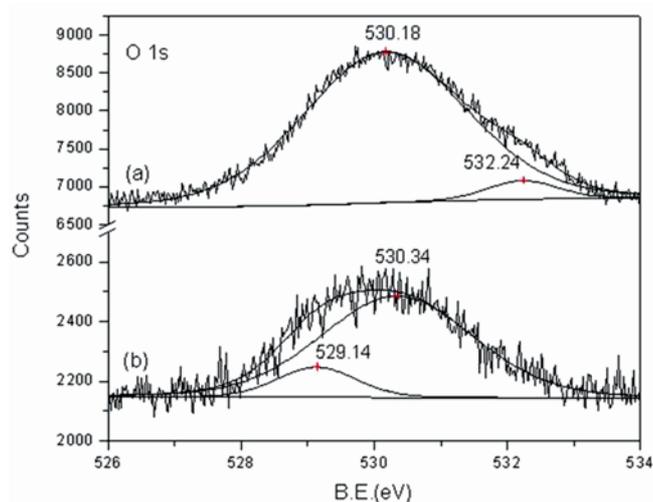
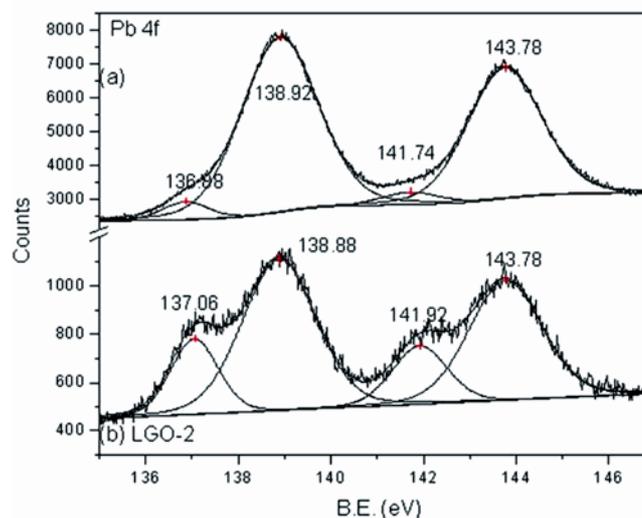


Figure 6. Ge 3d core level XPS spectra of (a) PbGeO_3 and (b) $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ crystals.

Table 1. Binding energy values for O1s, Pb4f_{7/2}, and Ge 3d core levels before and after exposure to gamma rays.

Crystal	Core level	Set	B.E. (eV)	
			Unirradiated	After γ -ray irradiation
PbGeO ₃	O 1s	Set 1	529.56	530.18
		Set 2	530.76	532.24
	Pb 4f _{7/2}	Set 1	138.3	136.88, 138.92
		Set 2		141.74, 143.78
	Ge 3d		31.96, 32.32	
Pb ₅ Ge ₃ O ₁₁	O 1s	Set 1	527.5	529.14
		Set 2	528.78	530.34
	Pb 4f _{7/2}	Set 1	137.18	137.06, 138.88
		Set 2		141.92, 143.78
	Ge 3d		30.16, 32.32	

**Figure 7.** O1s core level XPS spectra after gamma irradiation: (a) PbGeO₃ and (b) Pb₅Ge₃O₁₁ crystals.**Figure 8.** Pb 4f_{7/2} core level XPS spectra after gamma irradiation: (a) PbGeO₃ and (b) Pb₅Ge₃O₁₁ crystals. In both cases the spectra are asymmetric and resolved into two peaks with binding energies as given in table 1.

LGO-2 crystals observed has also been reported by other investigators (Houlton *et al* 1975; Iwata 1977). It may be mentioned that the starting charges used for crystal growth of LGO-1 and LGO-2 were prepared from the same lot of PbO and GeO₂ raw oxides. Since LGO-1 crystals did not exhibit any colouration and hence the observed pale amber colouration in LGO-2 crystals could not be due to the presence of impurity ion(s). The result of a uniform decrease in the optical transmission on gamma ray exposure over the entire wavelength range implies the existence of energy states above the valence band. The results of thermal annealing show that the damage caused to lattice by gamma rays is not permanent and can be annealed.

The results of figure 4 show asymmetry in the O1s core levels of both the samples and the spectra could be best fitted with two Gaussian–Lorentzian peaks. This result suggests the presence of two non-equivalent oxygen sites

in the system. For LGO-1, the two binding energies computed are 530.76 eV and 529.56 eV. Whereas, for LGO-2 the binding energies obtained are 528.78 eV and 527.5 eV. These observations are consistent with the fact that LGO-2 structure consists of GeO₄ tetrahedra and Ge₂O₇ double tetrahedral disposed alternately along the *c*-direction (Newnham *et al* 1973; Iwata 1977). The O1s spectrum of LGO-1 is found to be broader than in LGO-2, suggesting a comparatively higher degree of disorder in the former case.

The XPS core level spectra of Pb4f_{7/2} for both the crystals are shown in figure 5, which yielded different binding energies for the two crystals. The Pb4f_{7/2} core spectra could be best fitted with a single Gaussian–Lorentzian peak. The core levels in the two crystals were found to be separated by 1.12 eV, it being higher in LGO-1. The

same trend is also seen in $\text{Ge}3d$ spectra of the two crystals shown in figure 6. Binding energy value for $\text{Ge}3d$ in LGO-1 is higher than in LGO-2. All these results show a stronger ionic character of LGO-1 as compared to LGO-2 crystal. From the peak areas obtained from XPS spectra shown in figures 4–6, the atomic fractions obtained for LGO-1 and LGO-2 crystals were computed using the following sensitivity factors: 0.733 for $\text{O}1s$, 3.85 for $\text{Pb}4f_{7/2}$ and 0.38 for $\text{Ge}3d$. The atomic fractions computed for LGO-1 and LGO-2 were $\text{Pb}_{0.88}\text{Ge}_1\text{O}_4$ and $\text{Pb}_{4.2}\text{Ge}_3\text{O}_{12.8}$, respectively. Within the limits of experimental errors of $\pm 10\%$ the observed results show that LGO-2 is comparatively deficient in Pb. The results of an earlier investigation also showed that LGO-2 is slightly Ge rich (Talík *et al* 2006). The excess atomic fraction of oxygen is attributed to the surface contamination.

High resolution XPS has been used to analyse thin layers of germanium oxide grown on a chemically etched germanium under various conditions (Tabet *et al* 2003). The $\text{Ge}3d$ line recorded for the oxide layer is located at 32.4 eV, while a lower value of 28.9 is reported for non-oxidized Ge atoms. An assessment of the binding energy values reported in table 1 show oxide binding of Ge in LGO-1 in which case the binding energy of 31.96 eV obtained is close to that of germanium oxide. However, a lower binding energy of 30.16 eV for LGO-2 crystal shows incomplete oxidation of Ge atoms which is sort of expected as these crystals are found to be Ge rich.

Figure 7 shows the $\text{O}1s$ XPS spectra of LGO-1 and LGO-2 crystals after gamma irradiation. Deconvolution of these spectra resulted into two peaks. The peak around 530 eV, which is the stronger one, is common in both the crystals and the two other peaks in LGO-1 and LGO-2 appear at 532.2 eV and 529.1 eV, respectively. Comparing the data summarized in table 1, it is noted that in

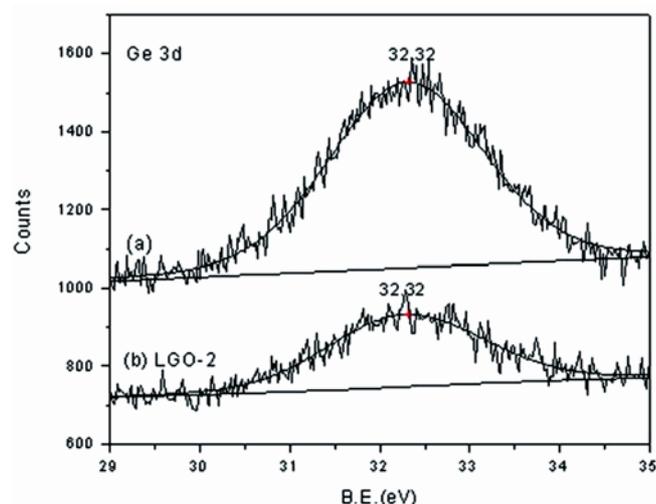


Figure 9. $\text{Ge}3d$ core level XPS spectra after gamma irradiation: (a) PbGeO_3 and (b) $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ crystals.

both the crystals the oxygen with lower binding energy is affected on gamma irradiation.

The results of figure 8 show the signatures of two sets of spin-orbit component of $\text{Pb}4f_{7/2}$ core level, which is further confirmed by deconvolution of the spectra. The binding energy determined for sets 1 and 2 are around 137 eV and 139 eV, which are different from that of pre-irradiated case. The intensity ratio of set 1–set 2 for $\text{Pb}4f_{7/2}$ is more in LGO-2 as compared to that of LGO-1, which indicates that environment of lead in LGO-1 is negligibly changed as compared to that of LGO-2 crystal after irradiation. The same trend is also observed from the analysis of $\text{Pb}5d$ core level spectra (not shown here). A higher binding energy value of $\text{Pb}4f_{7/2}$ for set 2 indicates that some of the Pb^{+2} ions are oxidized to higher oxidation state, the concentration of which is more in LGO-2. Indeed evidence of the formation of Pb^{3+} lattice ions in LGO-2 crystal under an illumination of 100 W Xe lamp has been reported in literature (Reyher *et al* 2001). Thus, $\text{Pb}4f_{7/2}$ core levels are the ones which are modified in both the crystals on irradiation. Also noted is the fact that gamma irradiation causes changes in the optical transmission of both the crystals. Thus, a relationship between the two observations is inferred from these results.

For both the crystals changes in the $\text{Ge}3d$ core levels are observed on gamma irradiation. In the case of LGO-1 crystal the binding energy is slightly increased from 31.91–32.32 eV. On the other hand, a much larger change from 30.1–32.32 eV is observed for LGO-2 crystals. These results show that gamma exposure promotes the reaction of atmospheric oxygen with crystal surface resulting in complete oxidation of Ge atoms.

The crystals of oxide materials are very often found to exhibit inherent deficiency in the cation sub-lattice, which depending upon the material and crystal preparation may extend up to a few percent (Morris 1990). The non-stoichiometry manifests in different ways by influencing the optical and other physical properties of the crystal or it may promote the incorporation of impurities during crystal growth (Sabharwal *et al* 1996, 2006; Sabharwal and Sangeeta 1999, 2008). The colouration of LGO-2 is related to Pb deficiency as borne out by the present measurements. The charge neutrality condition requires some of the lead ions in the lattice to stabilize in the trivalent state thus providing energy states above the valence band which are responsible for crystal absorption near band edge. The support to this model comes from the fact that doping the crystal with trivalent rare earth ions improves crystal transmission (Newnham *et al* 1973).

5. Conclusions

The single crystals of the two compositions viz. PbGeO_3 and $\text{Pb}_5\text{Ge}_3\text{O}_{11}$, in the phase diagram of PbO and GeO_2

have been grown by Czochralski technique under normal ambient. The optical transmission characteristics of the two crystals are found to be different, whereas the effect of the gamma exposure is observed to be same in both the crystals. The changes brought about by gamma irradiation are reversible under thermal annealing at moderately elevated temperatures. The X-ray photoelectron spectroscopy shows the presence of two non-equivalent sites of oxygen in both the crystals. $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ crystals are found to be germanium rich with $3d$ level having a binding energy of 30.1 eV which shows incomplete oxidation of Ge atoms. The results also show stronger ionic character of PbGeO_3 compared to $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ crystal. The d.c. resistivity of PbGeO_3 crystals is found to be an order of magnitude higher than that of $\text{Pb}_5\text{Ge}_3\text{O}_{11}$. There is no measurable effect of gamma irradiation on resistivity of both the crystals.

References

- Bichard V M, Davies P H, Hulme K F, Jones G R and Robertson D S 1972 *J. Phys. D: Appl. Phys.* **5** 2124
- Bush A A and Venetsev Yu N 1979 *Sov. Phys. Crystall.* **24** 602
- Goswami Nanda M L, Choudhary R N P and Mahapatra P K 1998 *J. Phys. Chem. Solids* **59** 1045
- Houlton M R, Jones G R and Robertson D S 1975 *J. Phys. D: Appl. Phys.* **8** 219
- Iwasaki H, Sugii K and Miyazawa S 1971a *Mater. Res. Bull.* **6** 503
- Iwasaki H, Sugii K, Yamada T and Nilzecki M 1971b *Appl. Phys. Lett.* **18** 444
- Iwasaki H, Miyazawa S, Koizumi H, Sugii K and Niizeki N 1972 *J. Appl. Phys.* **43** 4907
- Iwata Y 1977 *J. Phys. Soc. Jpn* **43** 961
- Landolt-Börnstein 1982 *Ferroelectrics and related substances: oxides* (Berlin: Springer-Verlag) **Vol. 16**
- Morris P A 1990 *J. Cryst. Growth* **106** 76
- Moulder J F, Stickle W F, Sobol P E and Bomben K D 1992 *Handbook of X-ray photoelectron spectroscopy* (Minnesota, USA: Perkin-Elmer Corp.)
- Newnham R E, Wolfe R W and Darlington C N W 1973 *J. Solid State Chem.* **6** 378
- Otto H H, Stock M and Gebhardt W 1980 *Ferroelectrics* **25** 543
- Reyher H J, Pape M and Hausfeld N 2001 *J. Phys.: Condens. Matter* **13** 3767
- Sabharwal S C and Sangeeta 1999 *J. Cryst. Growth* **200** 191
- Sabharwal S C, Sangeeta, Desai D G, Karandikar S C, Chauhan A K, Sangiri A K, Keshwani K S and Ahuja M N 1996 *J. Cryst. Growth* **169** 304
- Sabharwal S C, Sangeeta and Desai D G 2006 *Cryst. Growth & Des.* **6** 58
- Sangeeta and Sabharwal S C 2008 *J. Cryst. Growth* **310** 2899
- Tabet N, Faiz M, Hamdan N M and Hussain Z 2003 *Surf. Sci.* **523** 68
- Talik E, Adamiec M and Molak A 2006 *Mater. Sci.-Poland* **24** 714
- Watton R, Smith C and Jones G R 1976 *Ferroelectrics* **14** 719
- Yue X, Mendricks S, Hu Y, Hesse H and Kip D 1998 *J. Appl. Phys.* **83** 3473