EXAFS investigations on PbMoO₄ single crystals grown under different conditions

A K POSWAL, D BHATTACHARYYA*, S N JHA, SANGEETA[†] and S C SABHARWAL

Applied Spectroscopy Division, [†]Crystal Technology Laboratory, TPPED, Bhabha Atomic Research Centre, Mumbai 400 085, India

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Abstract. Extended X-ray absorption fine structure (EXAFS) measurements on PbMoO₄ (LMO) crystals have been performed at the recently-commissioned dispersive EXAFS beamline (BL-8) of INDUS-2 Synchrotron facility at Indore, India. The LMO samples were prepared under three different conditions viz. (i) grown from a stoichiometric starting charge in air ambient, (ii) grown from a stoichiometric starting charge in argon ambient and (iii) grown from PbO-rich starting charge in air ambient. The EXAFS data obtained at both Pb *L*₃ and Mo K edges of LMO have been analysed to determine Pb–O, Pb–Mo and Mo–O bond lengths in the crystals. The information thus obtained has been used to examine the microscopic defect structures in crystals grown under different conditions.

Keywords. Extended X-ray absorption fine structure; lead molybdate.

1. Introduction

The application of PbMoO₄ (lead molybdate/LMO) crystal as acoustic–optic modulators has been known for a long time. However, not much was reported in literature about its growth related defect structure till recently (Zeng 1997, 2006; Bochkova *et al* 2003; Sabharwal *et al* 2006; Sangeeta *et al* 2006). The single crystals of LMO grown by Czochralski technique are found to be prone to cracking and colouration (Zeng 1997; Sangeeta *et al* 2006). Recent investigations have shown that the colouration and cracking are associated with stoichiometric deviations in the crystal (Sangeeta *et al* 2006; Sangeeta and Sabharwal 2008; Tyagi *et al* 2008; Bhattacharyya *et al* 2009a). Recent studies have also established the profound influence of material synthesis and crystal growth conditions on other physical properties of the crystals (Sangeeta and Sabharwal 2008; Tyagi *et al* 2008). Some information pertaining to the presence of possible impurity phases in stoichiometry deficient crystals was also reported recently (Sangeeta *et al* 2006).

X-ray photoelectron spectroscopic (XPS) investigations carried out have revealed the presence of a single peak in photoelectron spectrum of Mo 3*d* for LMO crystals grown from stoichiometric precursors in air. The splitting of this peak into a doublet with energies corresponding to Mo⁵⁺ and Mo⁶⁺ states for crystals grown under argon atmosphere showed that the constituent atomic species in LMO can attain different valence states, depending on crystal stoichiometry (Sangeeta *et al* 2006). Preliminary X-ray absorption measurement results obtained for LMO samples (Bhattacharyya *et al* 2009b) were qualitatively explained in terms of Mo

vacancies occupied by a Pb ion stabilizing in +4 states or excess of Pb²⁺ ions present at interstitial sites. It may be mentioned that further understanding of defect structure arising due to stoichiometric deviations is required to develop model for structure property correlation. In this communication, we report on the EXAFS measurements made at both Pb *L*₃ edges and Mo K edges of LMO samples grown under different conditions. The results obtained have been analysed to determine Pb–O, Pb–Mo and Mo–O bond lengths and the local structure in different samples has been discussed.

2. Experimental

The X-ray absorption measurements on LMO samples were performed in the transmission mode at the recently commissioned BL-8 Dispersive EXAFS beamline at INDUS-2 Synchrotron Source at RRCAT, Indore (Bhattacharyya *et al* 2009c). The beamline uses a Si(111) single crystal which is elliptically bent using a mechanical bender in such a way that a band of radiation around a central energy (decided by the Bragg angle between the crystal and the beam) falls on the sample and the transmitted divergent beam is detected by a position-sensitive CCD detector. The whole absorption spectrum can thus be recorded simultaneously in a short duration of ~300 ms. The present measurements on LMO samples were carried out around Pb *L*₃ edge at 13.03 keV by appropriately setting the Bragg angle and the radius of curvature of the crystal bender. The absorption edges of 99.99% pure PbO and Bi₂O₃ samples were recorded at the same experimental setting to calibrate CCD channels in terms of energy. As can be seen from figure 1, the absorption edges of Pb and Bi in these samples were obtained at channel numbers of 560 and 990, respectively. From the known *L*₃ edge values of Pb

* Author for correspondence (dibyendu@barc.gov.in)

Figure 1. Absorption spectra of PbO and Bi₂O₃ powders taken in 13000 eV setting of crystal bender and goniometer.

and Bi at 13035 eV and 13419 eV (X-ray Data Booklet), the calibration factor of CCD in this energy regime was found to be 0.9 eV per pixel. The absorption spectra of LMO samples were subsequently taken at this setting and the CCD channels were calibrated in energy scale using the above calibration factor.

3. Results and discussion

The LMO samples discussed here were prepared from a mixture of PbO and MoO₃ powders following the process discussed elsewhere (Sabharwal *et al* 2006). The total absorption (μt , μ being the linear absorption coefficient and t being the thickness of the sample) vs photon energy (E) spectra for the three LMO samples grown under different conditions viz. (a) from a stoichiometric mixture of PbO and MoO₃ (LMO-1) under air ambient, (b) from stoichiometric charge composition (LMO-2) under argon ambient and (c) from a PbO-excess charge (LMO-3) under air ambient are shown in figures 2(a)–(c). To find out the exact neighbourhood coordination around the Pb atoms, the EXAFS spectra of the samples were analysed in detail. Since the oscillations in the absorption spectra are important, following the procedure explained by Konigsberger and Prince (1988), the experimentally obtained μ vs E data are first converted to $\chi(E)$ vs E and subsequently are plotted as $\chi(k)k^3$ vs k spectra for all the three samples as shown in figures 3(a)–(c),

Figure 2. $\mu t(E)$ vs E spectra of LMO crystals at Pb L3 edge: (a) LMO-1, (b) LMO-2 and (c) LMO-3.

Figure 3. $k^3\chi(k)$ vs k spectra of LMO crystals: (a) LMO-1, (b) LMO-2 and (c) LMO-3.

where $\chi(k)$ is weighed by k^3 to amplify the oscillations at high k . Here χ represents the oscillatory part of μ and k is the wavenumber. Finally, the $\chi(k)k^3$ vs k spectra were Fourier

transformed to generate the $\chi(r)$ vs r spectra in terms of real distances from the centre of the absorbing atom.

A set of EXAFS data analysis programme available within the IFEFFIT package was used to obtain $\chi(r)$ vs r spectra from the absorption spectra (Newville *et al* 1995). This includes data reduction and Fourier transform of the experimental data, generation of the theoretical EXAFS spectra starting from an assumed neighbourhood coordination of the absorbing species and finally fitting of the experimental data with the theoretical spectra using FEFF 6.0 code. Contributions of single and multiple scattering of photoelectrons from nearest neighbours and next nearest neighbours have been taken into consideration during generation of the theoretical spectra. The amplitude, distance, phase and degeneracy of the contributions corresponding to different interactions (nearest neighbour and further interactions) have been used as fitting parameters for fitting of the experimental data. The fittings have been carried out assuming a tetragonal crystal

structure for LMO with lattice parameters $a = 5.433$ Å, $c = 12.11$ Å and having $I4_1/a$ space group symmetry (Zhang *et al* 1995).

The $\chi(r)$ vs r spectra derived from the experimental data along with the best theoretical fit for the three LMO samples are shown in figures 4(a)–(c). It can be seen from figure 4(a) that the neighbourhood of 2–3 Å of the Pb atom is characterized by two overlapping peaks, which by fitting, are found to be due to the two Pb–O bonds around 2.6 Å, while the neighbourhood of 3–4 Å is characterized by the second shell Pb–O bond and the Pb–Mo bond. The best fit values for the shortest Pb–O bond lengths (average value) and Pb–Mo bond lengths derived from the theoretical fittings for the three LMO samples have been summarized in table 1.

The absorption spectra of LMO samples were also taken at the K-edge of Mo at 20 keV. To calibrate the CCD channels at this energy regime, absorption edges of 99.99% pure Mo and Nb foils (M/s Goodfellow) were recorded under the same setting of crystal bender and goniometer, and a calibration factor of ~ 2 eV per pixel was found in this energy band. The absorption spectra of LMO samples recorded under this setting were plotted in energy scale using the above calibration factor. The μ vs E data were reduced following the recipe described above and the $\chi(r)$ vs r spectra along with the best theoretical fit for the three LMO samples obtained are shown in figures 5(a)–(c). It can be seen from the figure that the Mo neighbourhood between 0.5–3.5 Å is characterized by the shortest Mo–O bond of MoO₄ tetrahedra having a bond length, ~ 1.7 Å and the second shell Mo–O bond and the Mo–Pb bond having bond lengths ~ 3.2 Å and 3.7 Å, respectively. The actual Mo–O (shortest) and Mo–Pb bond lengths as determined from the theoretical fittings are given in table 1. It is to be noted that the derived bond lengths agree reasonably well with the theoretical values derived from the crystal structure analysis of PbMoO₄ (Piwowarska *et al* 2008).

It is seen from table 1 that the average Mo–O, Pb–O and Pb–Mo distances are higher for the crystal grown in argon compared to those grown in air. It has been observed earlier that LMO crystals grown from stoichiometric charge generally develop Mo vacancies due to preferential loss of MoO₃ over PbO during sintering (Sabharwal *et al* 2006; Sangeeta *et al* 2006). In case of the crystals grown in air, Mo vacancies may be occupied by Pb ions stabilizing in +4 state because of closer matching of the ionic radii of Pb⁺⁴ (0.76 Å) and Mo⁺⁶

Figure 4. $\chi(r)$ vs r spectra of LMO crystals along with best-fit theoretical simulations: (a) LMO-1, (b) LMO-2 and (c) LMO-3 (ooooooo, Experimental data; —, theoretical fit).

Table 1. Bond distances (in Å) in PbMoO₄ crystals obtained from EXAFS analysis.

Crystal	LMO-1 (stoichiometric, air-grown)	LMO-2 (stoichiometric argon-grown)	LMO-3 (Pb-excess, air-grown)
Pb–O	2.61	2.65	2.51
Pb–Mo	3.68	3.72	3.51
Mo–O (shortest)	1.71	1.74	1.61
Mo–Pb	3.65	3.70	3.55

Figure 5. $\chi(r)$ vs r spectra of LMO crystals derived from $\mu t(E)$ vs E spectra taken at Mo K edge along with the best-fit theoretical simulations: (a) LMO-1, (b) LMO-2 and (c) LMO-3 (ooooooo, Experimental data; —, theoretical fit).

(0.65 Å). However, the oxidation of Pb^{+2} to Pb^{+4} states would be suppressed when the crystal growth is carried out in argon atmosphere. The Mo vacancies if present in the lattice could not be occupied by Pb^{+2} ions due to a large mismatch between the ionic radii of Pb^{+2} (1.20 Å) and Mo^{+6} (0.65 Å) ions. Here, the non-stoichiometry is promoted in the oxygen sub-lattice which necessitates stabilization of some of the Mo ions in lower valence state. This model is also supported by our XPS results which show the presence of both Mo^{+5} and Mo^{+6} ions in samples grown under argon ambient (Sangeeta *et al* 2006). The proposition of the presence of Mo vacancies in argon-grown crystal and their compensation in air-grown crystal is also corroborated by the fact that argon-grown samples exhibit light yellow colouration and lower absorption as compared to air-grown samples (Sangeeta *et al* 2006). It has been proposed by other workers (Bollmann *et al* 1980; Bochkova *et al* 2003) that the colouration in LMO crystal is due to the presence of acceptor vacancies and electronic conductivity of coloured LMO crystals is converted to ionic conductivity in colourless crystals due to the absence of Mo vacancies and presence of Pb^{4+} ions (Neiman *et al* 1984). The present observation of increase in Pb–O, Mo–O and Pb–Mo bond lengths when the growth is effected in argon atmosphere may be attributed to the presence of relatively larger Pb^{2+} and Mo^{5+} ions in the crystal lattice.

On comparing the results of table 1 for LMO samples grown from stoichiometric and Pb-excess charges in air, it is seen that both Pb–Mo and Pb–O bond lengths are significantly smaller in Pb-excess case implying the presence of excess Pb ions at the interstitial positions. This should

cause significant distortion in the Pb tetrahedra leading to deformation of the local structure. This explains our earlier observation as to why the crystals grown from Pb-excess charge are highly crack-prone (Bhattacharyya *et al* 2009).

4. Conclusions

Summarizing, the above measurements have examined the defect structure in LMO crystals at microscopic level which is consistent with some of their macroscopic properties. The present local structure analysis by EXAFS measurements supports the view (i) occupation of Mo defects by Pb^{4+} ions in samples grown from stoichiometric charge under air ambient, (ii) presence of Pb^{2+} and mixed $\text{Mo}^{5+}/\text{Mo}^{6+}$ states in samples grown from stoichiometric charge under argon ambient and (iii) presence of Pb interstitials in samples grown from a Pb-excess precursor.

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