Structural and dielectric properties of $\text{Pb}(\text{Li}_{1/4}\text{Sm}_{1/4}\text{Mo}_{1/2})\text{O}_3$ ceramics

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MS received 25 March 1996; revised 25 June 1996

Abstract. The ceramic samples of lithium–samarium modified lead molybdate, $\text{Pb}(\text{Li}_{1/4}\text{Sm}_{1/4}\text{Mo}_{1/2})\text{O}_3$ (PLSM)—a member of ABO_3 family were prepared by solid state reaction technique at ≈ 600 – 700°C . Preliminary X-ray analysis suggests the formation of single phase orthorhombic compound of PLSM. Studies of surface morphology, uniform particle/grain distribution, and presence of elements in the compound were completed using scanning electron microscope (SEM). Measurements of dielectric constant (ϵ), loss ($\tan \delta$) and conductivity (σ) at different frequencies and temperatures provided that the compound has a strong dielectric anomaly at 107°C .

Keywords. Synthesis; dielectric anomaly; electrical conductivity.

1. Introduction

Nowadays, a complex ferro-, pyro- and piezo-electric compounds of different structural families are widely used for different device applications (Damjanovic *et al* 1986; Deb 1988; Roy Chowdhury 1993). Many pure ferroelectric compounds of perovskite and tungsten-bronze families (i.e. ABO_3 and $\text{A}'\text{B}'_2\text{O}_6$ type) have been modified by suitable substitution at different atomic sites for computer memory, display devices, transducer, hydrophone devices, pyroelectric detector, electro optical modulators etc (Okuyama and Hamakawa 1991; Tandon *et al* 1992). Li–Sm modified lead molybdate $\text{Pb}(\text{Li}_{1/4}\text{Sm}_{1/4}\text{Mo}_{1/2})\text{O}_3$ (PLSM) is a complex compound of ABO_3 family (A = mono, B = tri-, tetra-, penta or hexavalent ions). Though dielectric anomaly relating to ferro-paraelectric phase transition of a few members of the lead tungstate has been reported earlier (Bera and Choudhary 1995a–d), but other members could not be studied because of their high dielectric loss and electrical conductivity at low frequency (10^2 – 10^4 Hz). To get better understanding of phase transition and electric conductivity in the family, we carried out extensive studies of structural, thermal and electrical properties of the complex compound, $\text{Pb}(\text{B}'_{1/4}\text{B}''_{1/4}\text{B}'''_{1/2})\text{O}_3$ (B' = alkali ions, B'' = rare-earth ions and B''' = W or Mo). It has been observed that $\text{Pb}(\text{Li}_{1/4}\text{Sm}_{1/4}\text{Mo}_{1/2})\text{O}_3$ (PLSM) which is chemically similar to PLSW has phase transition above room temperature with high dielectric loss and conductivity (Bera and Choudhary 1995e). In this paper, we report the structural property and the dielectric anomaly relating to phase transition of PLSM ceramics.

2. Experimental

The polycrystalline samples of PLSM were prepared by solid-state reaction technique using high purity (AR grade) component oxides and carbonate: PbO (M/s Aldrich Chemical Co., USA), MoO_3 (M/s BDH Chemical Ltd.), Sm_2O_3 (M/s Indian Rare-Earth Ltd.) and Li_2CO_3 (M/s S. D. Fine Chemicals Co.) in desired stoichiometry.

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The component oxides/carbonate were mixed thoroughly in an agate-mortar for about 2 h and calcined the mixed powder at 550°C in an alumina crucible in air atmosphere for 12 h. The process of mixing and calcination was repeated three times to get homogeneous and fine PLSM powder at 680°C. The powder was made into cylindrical pellets (dia 10 mm and thickness 1–2 mm) by an isostatic hydraulic press at 6×10^7 N/m² pressure, with polyvinyl alcohol (PVA) as binder. These pellets were sintered at 700°C again in an alumina crucible and air atmosphere for 6 h. The formation of the single phase PLSM compound was checked by X-ray diffraction technique.

Room temperature (20°C) X-ray diffraction (XRD) patterns of the compound were taken on calcined powder as well as sintered pellet samples using Philips X-ray powder diffractometer ($\lambda = 0.19370$ nm) in a wide range of Bragg angle 2θ ($15^\circ \leq 2\theta \leq 110^\circ$) with scanning rate of $2^\circ/\text{min}$. The surface morphology/grain size and distribution on this surface of the compound were studied with stereoscan S-180, scanning electron microscope (SEM). The flat surfaces of the samples were polished, lapped and electroded with high purity fine particle (400 mesh) silver paste for electrical measurements. Dielectric constant (ϵ) and dielectric loss ($\tan \delta$) of the PLSM samples were measured with a GR 1620 AP capacitance measuring assembly at different frequencies (100 Hz to 10 KHz) in a wide temperature range (liquid nitrogen to 180°C) using a 3-terminal sample holder fabricated in our laboratory. A chromel–alumel thermocouple and PID temperature controller were used in the measurements.

3. Results and discussion

The sharp and single reflection peaks of sintered pellet sample have been shown in figure 1, which suggest the formation of single phase compound because all these peaks

Figure 1. X-ray diffraction (XRD) pattern of PLSM sintered pellet at 700°C for 6 h.

are different in position and interspacing from those of the component oxides/carbonate. All the peaks of the sintered pellet were indexed and cell parameters were determined in various cell configurations using a standard computer program 'powder'. Finally, a particular unit cell was selected for which sum of difference in observed and calculated d values of all the reflections (i.e. $\Sigma\Delta d = \Sigma(d_{\text{obs}} - d_{\text{cal}})$) was found to be minimum. The cell parameters of the selected cell refined by least-squares method were: $a = 4.7264(10) \text{ \AA}$, $b = 5.0681(10) \text{ \AA}$, $c = 12.1284(10) \text{ \AA}$. This unit cell is smaller compared to that of PLSW (Bera and Choudhary 1995e). It was not possible to determine the space group of the compound with limited number of reflection in our powder diffraction work. The linear particle size of PLSM was determined using Scherrer's equation

$$P_{hkl} = \frac{K\lambda}{\beta_{1/2} \cos \Theta_{hkl}},$$

K , a constant $= 0.89$, $\beta_{1/2}$ = half peak width.

The average particle size was found to be $250 \text{ \AA}$, which is comparable and consistent with the size determined from particle size analyzer and SEM. The density of the pellet sample determined from Archimedes method was found to be about 95% of the theoretical value. This high density of the pellet was confirmed with uniform and closely distributed grain/particle and presence of a few island/voids in the SEM micrograph (figure 2). The elemental analysis of PLSM by the energy dispersive of X-ray (EDAX) with a computer-controlled system attached to SEM shows the presence of Pb, Mo and Sm atoms in a suitable proportion (figure 3). The low atomic number (Z) element, Li and O could not be detected as expected.

Variation of ϵ and $\tan \delta$ of PLSM with frequency has been shown in figure 4 which indicates the normal behaviour of a dielectric/ferroelectric. At low frequency, ϵ has higher value, indicating presence of all types of polarizations, viz. ionic, dipolar, interfacial etc. The value of ϵ decreases slowly with increase of frequency. The dielectric loss ($\tan \delta$) also behaves in a similar way.

In figure 5, we have shown the temperature dependence of dielectric constant (ϵ) and dielectric loss ($\tan \delta$) of PLSM at 10 KHz. It has been observed that ϵ and $\tan \delta$ of the compound in the low temperature region (liquid nitrogen to room temperature) are almost constant and then start increasing very fast up to 107°C (i.e. transition

Figure 2. SEM micrograph of PLSM at $3 \mu\text{m}$ magnification.

Figure 3. Energy dispersive X-ray spectrum of PLSM pellet sintered at 700°C.

Figure 4. Variation of dielectric constant (ϵ) and dielectric loss ($\tan \delta$) as a function of frequency at room temperature.

Figure 5. Variation of dielectric constant (ϵ) and dielectric loss ($\tan \delta$) as a function of temperature at frequency 10 KHz.

temperature) with a maximum value of 38, and then decreasing to 16 at 150°C. Like tungstate compounds of the family, dielectric loss of the PLSM has high value (0.6) at high temperature, but sharp dielectric anomalies were found both in ϵ and $\tan \delta$ almost at the same temperature (i.e. 107°C). By comparing the nature and value of dielectric peaks of PLSW and PLSM, it was found that the PLSW peak is broader than that of PLSM with higher value of dielectric constant.

The electrical conductivity, σ , and activation energy E_a in PLSM were calculated by using the standard formula

$$\sigma = \epsilon \epsilon_0 \omega \tan \delta,$$

and

$$\sigma = \sigma_0 \exp(-E_a/KT),$$

respectively where there is usual meaning for all the terms. The value of E_a , calculated from the slope of $\log \sigma$ vs inverse of absolute temperature plot figure 6, was found to be

Figure 6. Variation of a.c. conductivity ($\ln \sigma$) as a function of inverse absolute temperature ($1/T$) of PLSM at 10 KHz.

0.047 eV which is lower compared to that of PLSW. The possible explanations for the small value of E_a in the paraelectric region (higher temperature) may be given as follows: (i) typical ionic solids, in contrast, possess limited numbers of mobile ions which are hindered in their motion by virtue of being trapped in relatively stable potential wells. Due to rise in temperature the donor cations are taking a major part in conduction. The donors created a level (Band-Donor level) which is much nearer to the conduction band. Therefore to activate the donors a small amount of energy is required and (ii) a slight change in stoichiometry (i.e. the metal to oxygen ratio) in multi-metal complex oxides causes the creation of large number of donors or acceptors which may create donor or acceptor like states in the vicinity of conduction or valence band. These donors or acceptors may also be activated with less energy (Buchanan 1986).

However, a small conductivity anomaly was observed exactly at the transition temperature obtained from dielectric studies. As expected, no proper hysteresis loop

has been observed on our ceramic samples in the Sawyer–Tower circuit system. However, an attempt is being made to verify the ferroelectric transition from this circuit.

4. Conclusions

- (I) PLSM isomorphous to PLSW, has orthorhombic structure at room temperature.
- (II) PLSM has a dielectric anomaly relating to ferro-paraelectric phase transition at 107°C.

Acknowledgement

The authors thank Mr B Das and Mr S Mitra for their help in X-ray and SEM studies respectively.

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