PREPARATION AND STRUCTURAL PROPERTIES OF $PbMnO_3$ CERAMICS BY SOLID STATE SINTERING METHOD

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Abstract

Analar grade PbO and MnO_2 are weighted by the stoichiometric compositions, (1 - x) PbO + (x) MnO_2, where x = 0.10, 0.15, 0.20, 0.25 and 0.30 respectively. Two starting materials, PbO and MnO_2 are mixed and grinded by agate mortar for each 3 hrs. Then, the mixture are heat treated at 500°C for each 3 hrs. After that, the mixture are grinded again by agate mortar. Finally, the mixture are heat treated at 700°C for each 3 hrs. All heat treatment schedules are solid state sintering processes. XRD technique is used to examine the structural properties and phase formation of the ceramic samples. From the XRD analyses, the variations of dopant concentrations with the structural properties are studied. In addition, dielectric properties of the ceramics samples are also investigated.

Keywords: solid state sintering, XRD, lattice parameter, crystallite size, lattice micro strain, dielectric properties

Introduction

Perovskite oxides with ABO_3 structure, have important properties in ferroelectricty, piezoelectricity, dielectricity, ferromagnetism and multiferronics. Most of properties of perovskite oxides are related to the network of BO_6 octahydra and the state of A/B site cations or mixture with different cations or/and vacancies. Potenial applications of perovskite oxides are uses in sensors and catalyst electrodes, certain types of fuel cells, solar cells, laser, memory devices and spintronics applications [Kuzushita et al., 2003; Misono, 2005; Goodenough and Zhou 2015].

Recently, perovskite type $PbMnO_3$ material is studied for uses in gas sensors and photocatalytic applications [Borhade et al., 2018; Borhade et al., 2018]. $PbMnO_3$ has a Goldsmith tolerance " t " factor or the geometric perovskite tolerance factor " t " is greater than 1 and form a perovskite polytype. In this study, $PbMnO_3$ ceramics is obtained by using eco - friendly solid - state sintering method and solid state sintering process. Processing parameters ae systematically investigated and optimized. X - rays diffraction studies are used to examine the phase formation and structural properties of ceramic samples. Dielectric properties of the samples are determined by using LCR meter.

Experimental Procedure

Analar grade PbO and MnO_2 were used as starting materials. PbO and MnO_2 powder were weighted and mixed by the stoichiometric compositions, (1 - x) PbO + (x)MnO_2, where x = 0.10, 0.15, 0.20, 0.25, and 0.30 respectively. The mixture were grinded by agate mortar for each 3 hrs and sintered at 500°C for each 3 hrs. Then, the mixture were grinded again by using agate mortar and sintered at 700°C for each 3 hrs. All heat treatment schedules were solid state sintering processes. X - rays diffraction studies were used to examine the phase formation and structural properties of ceramic samples, by mean of Rigaku Multiflux using Cu K_α (λ = 1.5418 Å) monochromatic radiation, as seen in figure (1). The voltage and current were 50 kV and 40 mA respectively. Specimen were scanned from 0° to 80° with step size of 0.01°/ sec. X- rays spectra

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were recorded at room temperature From the XRD analyses, variations of molar ratios with structural properties were studied.

The mixture powder were uniaxially pressed into circular shape disc of 20 mm in diameter and 3.5 mm in thickness. Silver paste was coated onto both surfaces of the samples for electroding (area of electrode = 7.0695 mm^2). Dielectric properties of the samples were examined by using LCR meter (TH 2821). Flow diagram of experimental procedure for $PbMnO_3$ samples was depicted in figure (2).

Figure 1 Diagram of XRD Rigaku Multiflux.

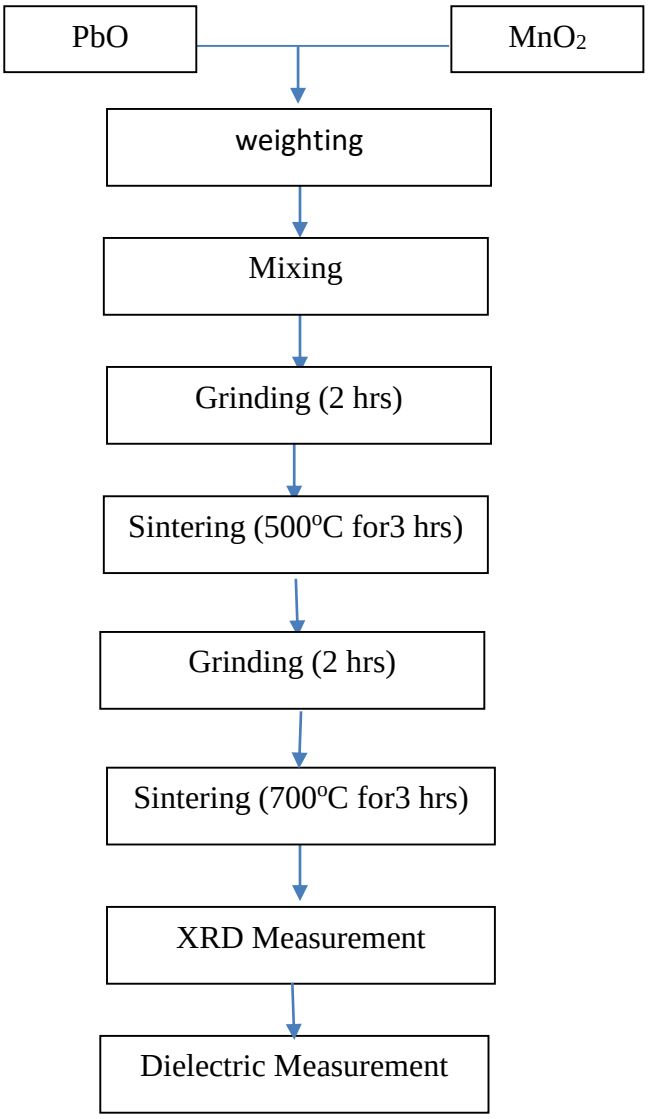

Figure 2 Flow diagram of experimental procedure for the $PbMnO_3$ ceramics.

Results and Discussion

Structural characterization of the prepared ceramic samples were examined by using XRD technique. The mixture of PbO, MnO_2 and $PbMnO_3$ structures were found in XRD patterns of Mn 10 mol % and Mn 15 mol %. In the XRD profiles of Mn 20 mol %, Mn 25 mol % and Mn 30 mol %, single phase, polycrystalline, and tetragonal $PbMnO_3$ structures were observed, as seen in figure (3).Lattice parameters are estimated by using the following equation (1):

$$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \qquad (1)$$

d = interplanar spacing

h, k, l = miller indices

a, c = lattice parameters

Cell volumes of the tetragonal $PbMnO_3$ specimens are studied by using the equation (2):

$$(\text{cell volume})V = a \times a \times c \quad (2)$$

Structural properties (lattice parameters, lattice distortion and cell volume) are estimated and listed in table (1). Crystallite size and micro strain are determined by using the Debye - Scherrer equations (3) and (4):

$$D = \frac{0.9\lambda}{\beta\cos\theta} \quad (3)$$

$$\varepsilon = \frac{\beta}{4\tan\theta} \quad (4)$$

In this equations, β is full width at half of the peak maximum (FWHM) and λ is the wavelength of the using X-ray and θ is the peak position which known as Bragg's angle. Structural properties such as lattice parameters, lattice distortion and cell volume are listed in table (1). Crystallite size and lattice micro strain are listed in table (2). Figure (4) shows the effect of Mn content on lattice parameters of $PbMnO_3$ ceramics. It is studied that lattice parameters increase with increasing Mn content. Figure (5) depicts the variation of Mn content with lattice distortion of $PbMnO_3$ ceramics. It is obvious that lattice distortion increases when Mn content is raised. It is due to increase of both lattice parameters a and c with increasing Mn content in $PbMnO_3$ ceramics. Influence of Mn content on unit cell volume of $PbMnO_3$ ceramics is depicted in figure (6). It is studied that unit cell volume increases with increasing Mn content. During the rapid thermal annealing, lattice micro strain, defect and dislocation appear in $PbMnO_3$ ceramics. Consequently, influence of Mn content on lattice parameter, lattice distortion and unit cell volume of the $PbMnO_3$ ceramics is observed, as seen in figures (4), (5) and (6) respectively. The results were nearly the same as others' reports. Structural optimization were done on tetragonal P4/mm (non - centrosymmetric) and P4/mm (centrosymmetric) structures [Subramanian S. S. 2014], using lattice parameters and results indicate that P4/mm structure is more stable than P4/mm structure. X - ray diffraction patterns cannot distinguish with the polar structure P4/mm versus the nonpolar structure P4/mm. Dielectric properties of ceramic samples were measured by using LCR meter (model TH 2821), and the results were listed in table (3). $PbMnO_3$ crystal structure is illustrated in figure 7 (a) and (b). Antiferromagnetic $PbMnO_3$ is a one of the potential candidates for spintronics.

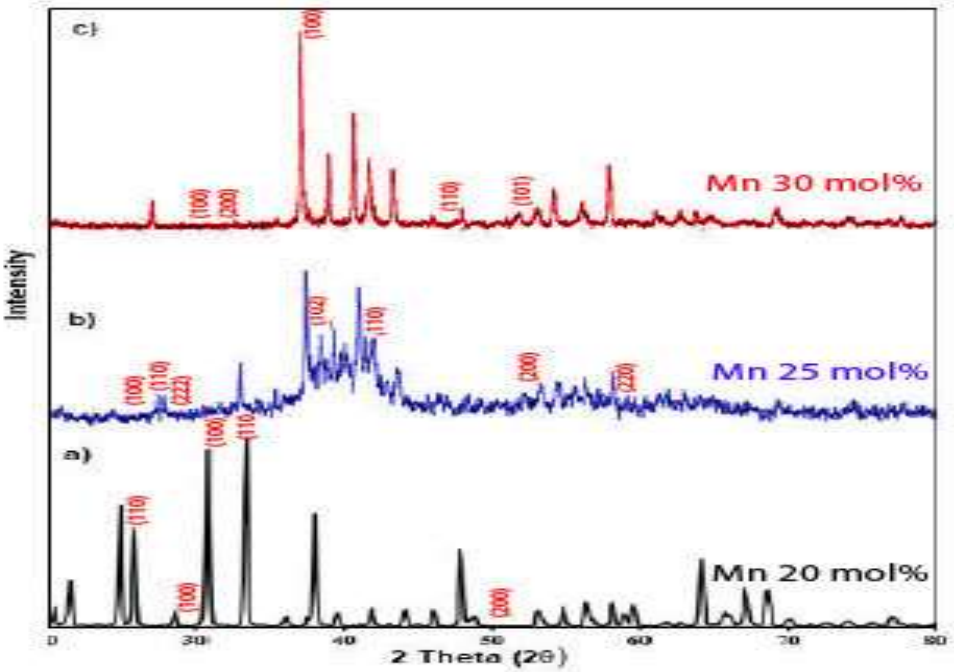

Figure 3 XRD profiles of $PbMnO_3$ ceramics with different Mn contents.

Table 1 Structural properties of $PbMnO_3$ ceramics with different Mn contents.

Molar concentration (mol %)	lattice parameter "a" (Å)	lattice parameter "c(Å)"	lattice distortion	Cell Volume $10^{-3}(m^3)$
Mn 20 mol%	3.8439	3.9114	1.0175	57.7931
Mn 25mol%	3.8481	3.9189	1.0184	58.0305
Mn 30mol%	3.8512	3.9251	1.0181	58.2160

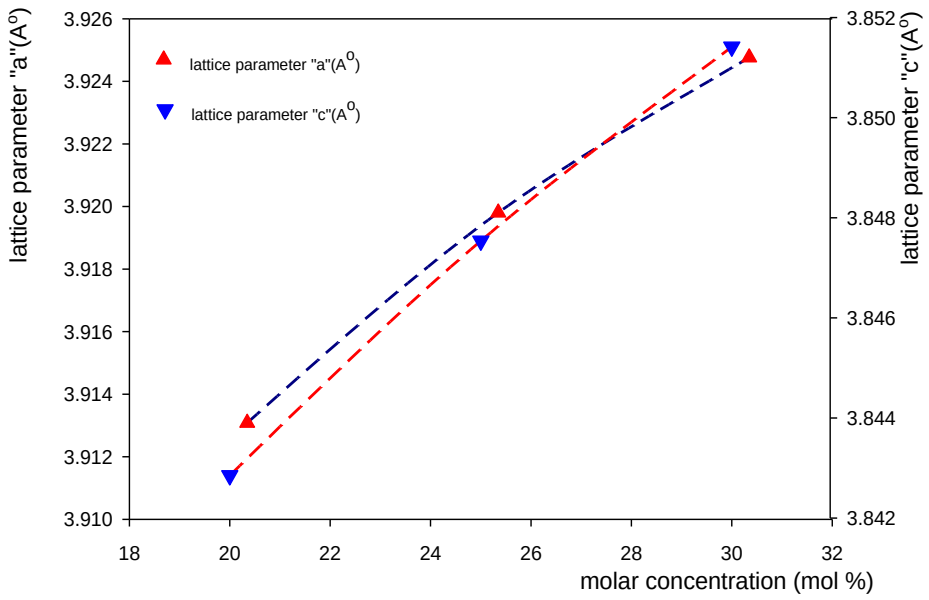

Figure 4 The effect of Mn content on the lattice parameters of the $PbMnO_3$ ceramics.

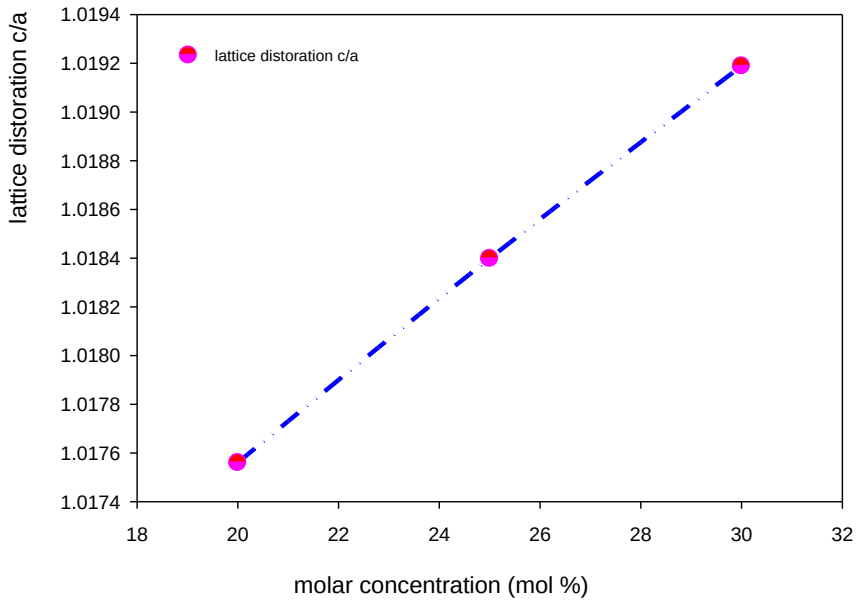

Figure 5 The variation of Mn content with lattice distortion of $PbMnO_3$ ceramics.

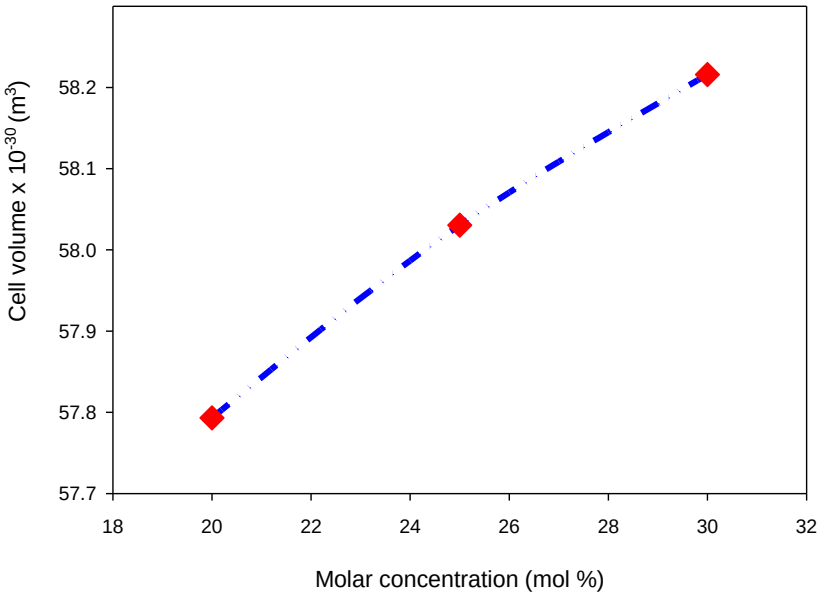

Figure 6 Influence of Mn content on unit cell volume of $PbMnO_3$ ceramics.

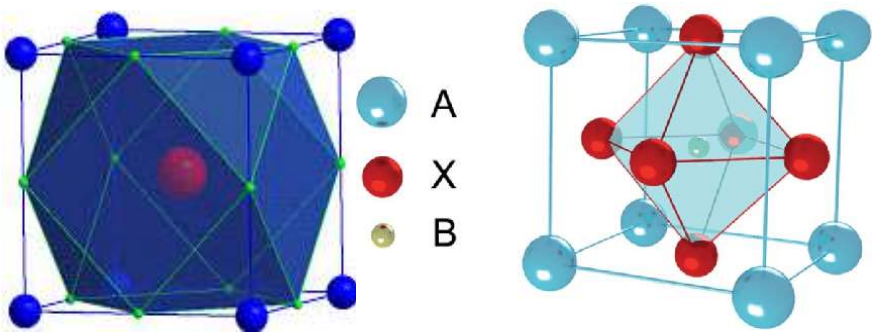

Figure 7 Crystal structure of $PbMnO_3$

Table 2 Crystallite size and lattice micro strain of $PbMnO_3$ ceramics at different Mn contents.

Molar concentration (mol %)	crystallize size (nm)	micro strain
Mn 20 mol%	31.297	4.468×10^{-3}
Mn 25 mol%	31.417	4.451×10^{-3}
Mn 30 mol%	36.941	3.778×10^{-3}

Dielectric properties of ceramic samples were measured by using LCR meter (model TH 2821), and the results were listed in table (3). The static dielectric constant is related to material's capacity of modifying electric flux density by phenomena such as polarization – a mere orientation of molecules or dissipation losses as heat,etc. One can consider as they remain approximately constant for a given temperature and frequency domain. The reported values of static dielectric constant is 37.5 ~ 41.85, and our results are agreed with reported value. [A V Borhade, et al. 2018].

Table 3 Dielectric properties of $PbMnO_3$ ceramics at different Mn contents.

Molar concentration (mol %)	Dielectric constant(ε_r) (measured at 1kHz)
Mn 20 mol%	38.91
Mn 25 mol%	38.95
Mn 30 mol%	39.46

Conclusion

$PbMnO_3$ ceramics were successfully prepared by using solid state sintering method. Processing parameters, such as sintering temperature, sintering time, grinding time and Mn concentration were optimized. Solid state reaction appears during the sintering process. It is eco - friendly, requires less times and easy to workup. The results obtained from XRD analyses are nearly the same as others ' reports. Antiferromagnetic material $PbMnO_3$ is a one of the potential candidates for gas sensor, photocatalytic and spintronic device applications. This paper provides the useful information's to the researchers, dealt with materials, chemical and electronic engineering.

Acknowledgement

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