Structural Formation And Dielectric Properties Of $Pb(Mn_{0.5}W_{0.5})O_3$ Ceramics With Guard Ring Electrode

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Abstract. Polycrystalline $Pb(Mn_{0.5}W_{0.5})O_3$, (PMW), a ferroelectric oxide, having perovskite structure was prepared by high temperature solid state reaction method. Structural and microstructural properties of PMW compound were studied by the X-ray diffraction (XRD) technique and scanning electron microscopy (SEM). In order to reduce the measurement error caused by edge capacitance, laboratory-made three-terminal guard ring electrode was constructed. Guard ring electrode was generally applied to electrode system of the material for the measurements of insulation resistance and dielectric constant. The frequency dependences of the capacitance (C), dielectric constant (ε_r), loss tangent (tan δ), volume resistivity (ρ_v) and surface resistivity (ρ_s) of PMW ceramics were investigated at different annealing temperatures. The PMW ceramics (300 °C) exhibited the smallest value of capacitance gap (the smallest error = 3.26 %) at 1 kHz while the maximum degree of capacitance gap was caused at PMW ceramics at 500 °C at 100 kHz. The smallest value of volume resistivity and surface resistivity were found to be 1.6×10^{-4} MΩ-cm and 0.0599 MΩ-cm respectively.

Keywords: XRD, SEM, Guard ring electrode; capacitance, dielectric constant, loss tangent, volume and surface resistivity
PACS:.81

INTRODUCTION

Ferroelectric effect is the ability of material to store an electric polarization in the absence of an applied electric field. Ferroelectric materials are widely used in various devices, such as transducers, acturators, optical integrated circuits, optical data storage and display devices, etc. [1].

The major use of ferroelectric materials continues to be in piezoelectric devices. Furthermore virtually all piezoelectric applications, with the exception of the very large business in quartz filters and oscillators, involve ferroelectric materials, mostly in ceramic form [2].

The applications for ferroelectric ceramics are manifold and pervasive, covering all areas of the workplaces, homes, and automobiles [3].

Lead-based materials, such as $Pb(Fe,W)O_3$, $Pb(Co,W)O_3$, $Pb(Fe,Nb)O_3$, $Pb(Mg,W)O_3$, have very interesting properties which are useful in devices. $Pb(Mn,W)O_3$ is one of the perovskite type ferroelectric compound. Ferroelectrics of the perovskite family having the general formula ABO_3 have been the subject of extensive research both because of their technological importance and because of the fundamental interesting in the physics of their phase transition [4].

A few perovskite compound exhibits simultaneous electric and magnetic ordering. In order to satisfy the necessary condition for the existence of magnetic and electric ordering simultaneously, ferroelectrically active as well as magnetic ions need to be introduced into octahedral position. Therefore, in the present case, Mn^{+2} and W^{+6} ions were introduced in B site while Pb^{+2} ions in A site [5].

In this paper we report structural, microstructural and dielectric properties of PMW ceramics. The magnitude of the dielectric properties of a material is a measure of the ability of a material to polarize in an electric field. Most polarization mechanisms are time dependant, so their dielectric properties are often frequency dependant [6].

EXPERIMENTAL PROCEDURE

Polycrystalline, $Pb(Mn_{0.5}W_{0.5})O_3$ was prepared by high temperature solid state reaction technique using oxides (PbO, MnO_2 and WO_3). Firstly, these oxide powders were weighed in desire molar proportion using digital balance. The three oxide powders were thoroughly mixed in agate mortar for 2 h to get homogeneous mixture. Secondly, the mixture was preheated at 1000˚C for 6 h followed by grinding. After that, the mixture powder was grinded with ball milling at constant speed for 10 h to get homogeneous mixture. Then, this sample was dispersed by the air-jet milling with constant pressure of 40 lb-in^{-2} to ensure good dispersion. The mixture PMW powders were mesh sieved to reduce the particle size and to get spherical shape uniformly particle. XRD investigation was carried out to examine the structural properties of PMW powder.

Then, microstructural properties of PMW powder were characterized by Scanning Electron Microscopy (SEM). And then, a three-state of heating treatment was carried out as follows. Each powder was annealed in electric furnace at 300°C, 400°C and 500°C during 1 h each. The calcined fine powder was cold pressed into cylindrical pellets of size 1.4 cm diameter and 0.3 cm thickness using a hydraulic press with a pressure of 5 tons. Saturated solution of polyvinyl alcohol (PVA) was used as a binder for pellets. These pellets were sintered at 600°C for 1 h. The binder was burnt out during the sintering of the sample. The flat surfaces of pellets were electroded with air-drying silver paste and dried at 200°C for 2 h before taking any electrical measurement.

The capacitance (C), capacitance (C), capacitance (C), dielectric constant ($\varepsilon_r^{'}$), loss tangent (tan δ), volume resistivity (ρ_v) and surface resistivity (ρ_s) of the compound were obtained as a function of frequency (1 kHz to 100 kHz) using Quad Tech 1730 LCR meter and laboratory-made three-terminal guard ring electrodes which compensated for any stray capacitance. The flowchart of preparation for PMW powder and ceramic was shown in FIGURE 1.

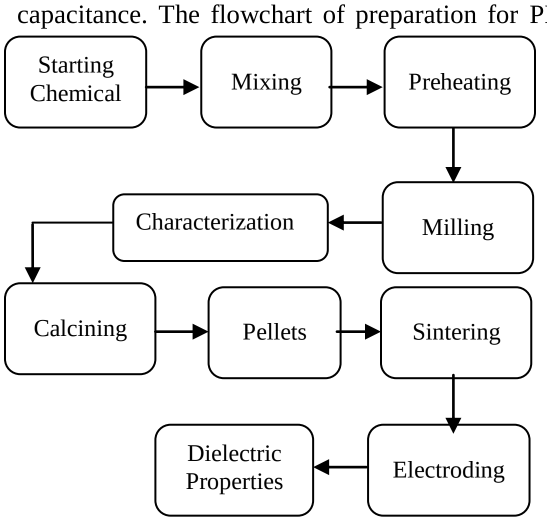

FIGURE.1. The flowchart of preparation for PMW powder and ceramics

Guard Ring Electrode

Guard ring electrodes are useful devices which enable accurate dielectric measurements to be made on small sample of insulting material. A three-terminal arrangement was used to prevent erroneous results caused by fringing effects. When simply measuring the dielectric material between two parallel plates electrode, stray capacitance or edge capacitance was formed on the edges of the electrodes and consequently the measured capacitance was larger than the capacitance of the dielectric material. The edge capacitance causes a measurement error, since the current flows through the dielectric material and edge capacitor as shown in FIGURE 2(a).

A solution to the measurement error caused by edge capacitance is to use the guard ring electrode as shown in FIGURE 2(b). The guard ring electrode absorbs the electric field at the edge and the capacitance that is measured between the electrodes is only composed of the current that flows through the dielectric material. Therefore accurate dielectric measurements are possible.

When the main electrode is used with a guard ring electrode, the main electrode is called the guarded electrode. The guarded electrode can reduce fringe effects because the sample size can be equal to or larger than the guard ring and can be any shape.
The other limitation when using guard-ring electrode was that the sample must contact only the electrodes and guard-ring, but no other part of the electrode. Then, the surface of the electrode must be flat and low compressibility to prevent an air gap between the sample and the electrodes.

A guard ring electrode eliminated parallel resistance paths that caused errors in materials resistance measurements. The another purpose of the guard ring electrode is to minimize errors due to surface conduction while volume resistivity measurements are being made and those due to volume conduction during measurements of surface resistivity.

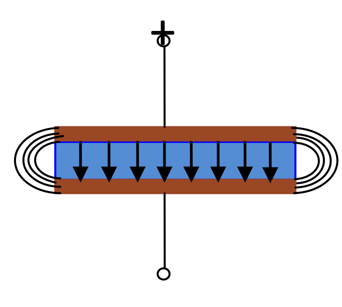

FIGURE 2(a). Two parallel plate electrode system

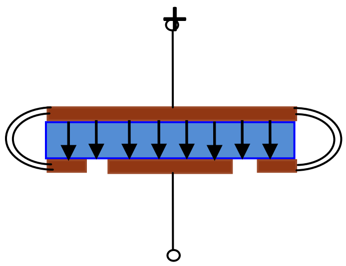

FIGURE 2(b). Effect of guard electrode

Results and Discussion

X-ray diffraction pattern (XRD) of fine calcined powder were taken with a Phillips X-ray powder diffractometer using monochromatic Cu-Kα radiation (λ = 1.54056 °A) in a wide range of Bragg angles, 2θ ($10^\circ \leq 2\theta \leq 70^\circ$) with a scanning rate of one degree per minute. According to the FIGURE 3, ten diffracted parts corresponding to (112), (004), (211), (200), (204), (220), (116), (132), (224) and (400) planes were produced. The lattice parameters of unit cell were refined using a least-squares method and were found to be: a = 7.9836 °A, b = 4.9698 °A and c = 11.9286 °A. From XRD measurement, it was obtained that the structure of PMW powder was orthorhombic structure. This fact revealed that the polycrystalline nature of fabricated powder.

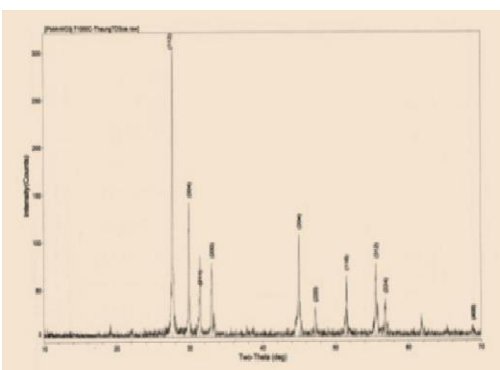

FIGURE 3. XRD pattern of PMW powder

FIGURE 4 showed the SEM images of PMW ceramic. As the detail analysis of SEM image, it was found that the surface of SEM image was flat, dense and crack-free. Agglomerations of grain were formed on SEM image. Ice-cracks like morphology were found and the particles on the SEM surface. The SEM surface was oriented toward right. The average grain size of compound is (0.38 ~ 075) μ m.

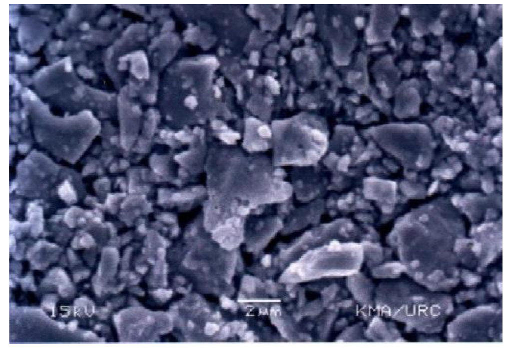

FIGURE 4. SEM image of PbMnWO3 compound

The PMW ceramic capacitor was obtained and examined its charge storage capacity. The dielectric constant and loss tangent are important practical parameter of ferroelectric materials so we need to get the accurate value of the capacitance of the material. To get the accurate value of the capacitance we should try to reduce the measurement error.

Therefore we measured the capacitance of the material by using guard-ring electrode instead of parallel plate electrode. The change in capacitance as a function of applied frequency for PMW ceramics at different annealing temperatures was shown in TABLE (1~3). From the table, it was found that the capacitance value was decreased with increasing the frequency.

TABLE 1. The value of capacitance for PMW ceramics at 300 °C

F (kHz)	C(pF) with parallel plate electrode	C(pF) with guard-ring electrode	Error (%)
1	4.361	4.233	3.26
10	4.220	4.058	3.99
20	4.163	3.992	4.28
50	4.070	3.892	4.57
100	4.022	3.845	4.60

TABLE 2. The value of capacitance for PMW ceramics at 400 °C

F (kHz)	C(pF) with parallel plate electrode	C(pF) with guard ring electrode	Error (%)
1	5.130	4.751	7.97
10	4.860	4.538	7.09
20	4.780	4.437	7.73
50	4.701	4.278	9.88
100	4.605	4.192	9.85

TABLE 3. The value of capacitance for PMW ceramics at500 °C

F (kHz)	C(pF) with parallel plate electrode	C(pF) with guard ring electrode	Error (%)
1	6.645	5.784	14.92
10	6.425	5.554	15.68
20	6.387	5.442	17.36
50	6.232	5.315	17.25
100	6.201	5.241	18.31

FIGURE 5(a-c) showed the frequency dependence of ε_r and tan δ of PMW at 300 °C, 400°C and 500°C. A decrease in dielectric constant was observed with increasing frequency because the compound exhibited different types of polarizations at lower frequencies (i.e., interfacial, dipolar, atomic, ionic, electronic, etc.). The tan δ increased with increase in frequency and became maximum at 50 kHz, because the active component of the current increased more rapidly than its reactive component.

At higher frequency (> 50 kHz) tan δ decreased with increasing frequency, because the active component of the current was practically independent of the frequency and the reactive component increased proportionally to the frequency. This type of variation was observed in some of the ferroelectric ceramics [7].

Volume and surface resistivity were evaluation parameters for insulating materials. The resistance of the insulating material was obtained by measuring current flow through the material. Volume resistivity was defined as the electrical resistance through a cube of insulating material. Surface resistivity was defined as the electrical resistance of the surface of insulating material. Since the surface length was fixed, the measurement was independent of the physical dimensions (i.e., thickness and diameter) of the sample. The value of volume and surface resistivity of PMW ceramics were calculated from the measurement resistance because the geometry of the current path is known. FIGURE 6(a-c) showed the frequency variation of the volume (ρ_v) and surface resistivity (ρ_s) of PMW at different annealing temperatures. When volume resistivity was measured the ring electrode acted as the guard electrode, and when surface resistivity was measured the upper electrode was the guard electrode.

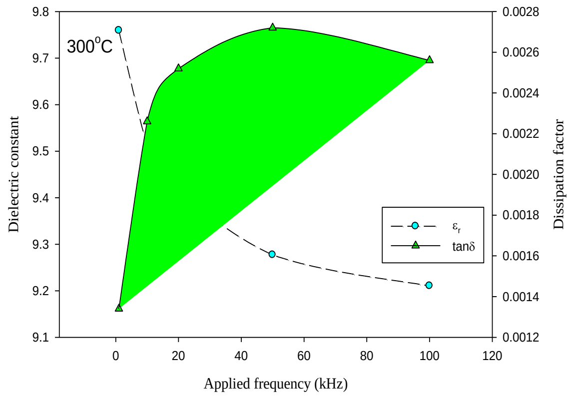

FIGURE 5(a) Frequency dependence of dielectric constant (ε_r) and loss tangent (tan δ) of PMW ceramics at 300°C

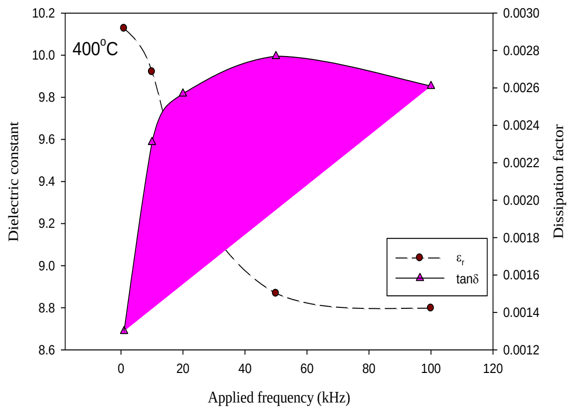

FIGURE 5(b) Frequency dependence of dielectric constant (ε_r) and loss tangent (tan δ) of PMW ceramics at 400°C

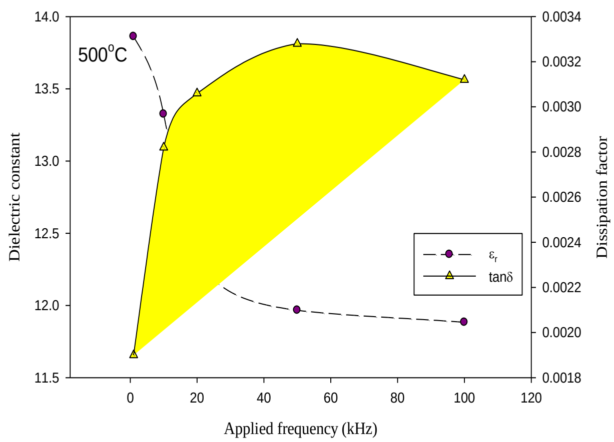

FIGURE 5(c) Frequency dependence of dielectric constant (ε_r) and loss tangent (tan δ) of PMW ceramics at 500°C

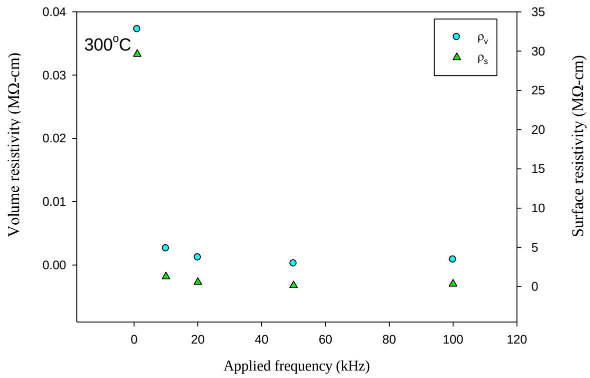

FIGURE 6(a) Frequency variation of the volume (ρ_v) and surface resistivity (ρ_s) of PMW ceramics at 300°C

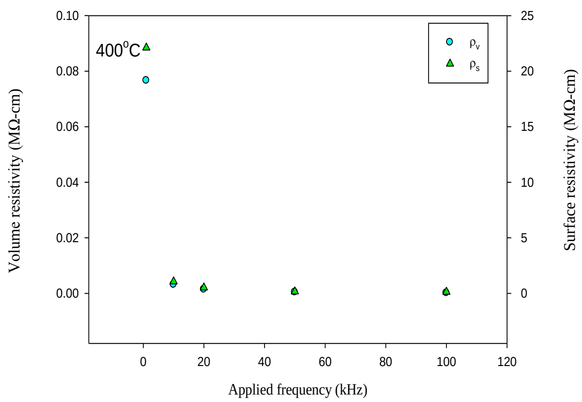

FIGURE 6(b) Frequency variation of the volume (ρ_v) and surface resistivity (ρ_s) of PMW ceramics at 400°C

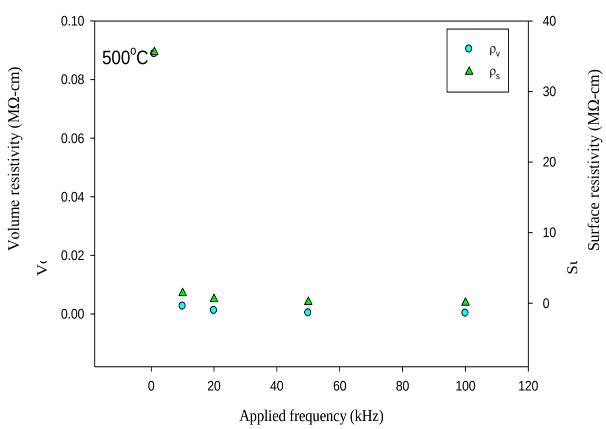

FIGURE 6(c) Frequency variation of the volume (ρ_v) and surface resistivity (ρ_s) of PMW ceramics at 500°C

Conclusion

Fabrication and microstructural of $Pb(Mn_{0.5}W_{0.5})O_3$ ceramic were successfully implemented. The sample was homogeneous single phase perovskite type with orthorhombic structure at room temperature. Ice-crack like morphology was observed on SEM images and agglomerations of grain were uniformly distributed. In order to eliminate the measurement error caused by edge capacitance, a three-terminal configuration (including a guard terminal) is employed. The guard electrode encompasses the guarded (or main) electrode and absorbs the electric field at the edge of the electrodes, making accurate dielectric measurement possible. The nature of the variation of ε_r-f and tan δ-f spectra showed the behavior of a dielectric for ceramics as expected. From the result obtained, it was a chance to get the ferroelectricity of PMW polycrystalline at the frequency corresponding to the highest dielectric constant. It satisfied the special requirements for development of memory device of low cost and Ecofriendly.

ACKNOWLEDGMENTS

This research was fully supported by Department of Physics, Yangon University, Myanmar (2012-2013).

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