Structural and Magnetic Properties of $SmFeO_3 - PbZrTiO_3$ Solid Solutions

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Abstract
Structural and Magnetic Properties of $SmFeO_3 - PbZrTiO_3$ with a general formula $(SmFeO_3)_x - (PbZr_{0.53}Ti_{0.47}O_3)_{1-x}$ (x = 0.2, 0.25, 0.3) have been prepared by solid state reaction route. X-Ray Diffraction studies of solid solutions revealed the formation of tetragonal phase. The SEM micrographs show surface morphology of the samples. EDAX confirmed the presence of elements in the samples. Raman spectroscopic studies were performed to reveal the chemical bonding in SF-PZT ceramics. VSM shows ferromagnetic like behavior of solid solutions.

Keywords
SF-PZT, Ceramics, SEM, Raman Spectroscopy, X-Ray Diffraction

I. Introduction

Multiferroic magnetoelectrics are materials that possess both ferroelectric and ferromagnetic order parameters in same phase. They have a spontaneous polarization that can be switched by an applied electric field and spontaneous magnetization that can be switched by an applied magnetic field. The coupling between ferroelectric and ferromagnetic in multiferroic material is known as magnetoelectric (ME) coupling.

Piezoelectric ceramics lead zirconate titanate (PZT) is a promising material for its wide applications in actuators, sensors, transducers and pyroelectric detectors [1,2]. Lead Zirconate Titanate has perovskite ABO_3 structure (A - mono or divalent and B – trihexavalent ions) [1,3]. It is solid - solution of antiferroelectric $PbZrO_3$ (T_c = 503K) and ferroelectric $PbTiO_3$ (T_c = 763K) [4]. PZT composition near the Morphotropic Phase Boundary (MPB) where Zr/Ti ratio ~53/47 possesses optimum piezoelectric properties [5]. MPB separates the two ferroelectric phases: A tetragonal phase and a rhombohedral phase [6].

The literature survey shows that very few studies have been done on PZT doped with samarium ferrites [7]. The present work aims to synthesize $SmFeO_3 - PbZrTiO_3$ (i.e SF-PZT) with Zr/Ti ratio ~53/47 and to study their structural and magnetic properties. This particular composition has been selected due to its proximity to MPB.

II. Experimental Procedure

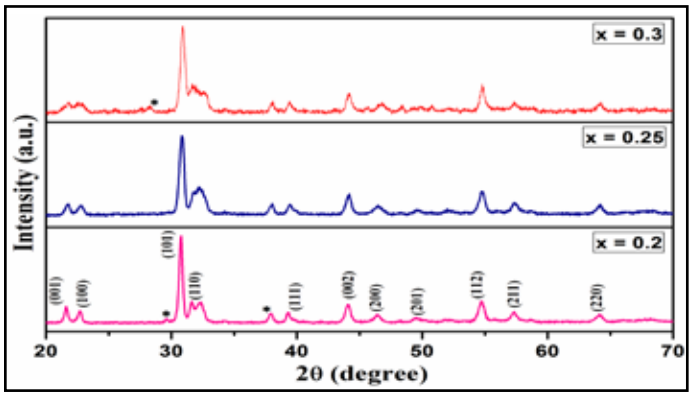
Solid solution of $(SmFeO_3)_x - (PbZr_{0.53}Ti_{0.47}O_3)_{1-x}$ (where x = 0.2, 0.25, 0.3) were prepared by solid state reaction route. The raw materials of 99.9% purity (Aldrich sigma) lead oxide (PbO), zirconium oxide (ZrO_2), titanium oxide (TiO_2), Iron oxide (Fe_2O_3) and samarium oxide (Sm_2O_3) (Molychem) were weighed in stiochiometric proportion and ball milled for 12 h in propanol medium at 300 rpm. Mixed powders were calcined at 950°C for 12 h for phase formation. 2wt% of Polyvinyl Alcohol (PVA) was mixed as binder to the calcined powder and pressed into pellets at a pressure of 10 MPa using hydraulic press. For proper grain growth and densification of samples sintering was carried out at 1200 °C for 2 h in lead environment (closed crucible arrangement) to reduce the weight loss due to lead volatility. The prepared bulk samples were then characterized by using various techniques. Structural characterization was carried out using X-Ray Diffraction (CuK_α radiation, SHIMADZU MAXima XRD - 7000) to determine the crystalline phase present in the sample. Scanning Electron Microscope (SEM) (Carl ZEISS Supra 55) was done to study surface morphology. The Raman Spectra was recorded by Renishaw inVia Raman microscope using 488 nm laser. Vibrating Sample Magnetometer (VSM) (MicroSense E29) was used to study the magnetic properties of the samples.

III. Results and Discussion

A. Structural Properties

1. Phase Analysis

Sintered powders were examined by X-Ray Diffraction to ensure phase purity and to identify the crystal structure. XRD pattern of $(SmFeO_3)_x - (PbZr_{0.53}Ti_{0.47}O_3)_{1-x}$ (SF-PZT) with x = 0.2, 0.25, 0.3 is shown in fig. 1 confirms the formation of single phase with tetragonal structure along with pyrochlore phase (marked with*) [3,8].

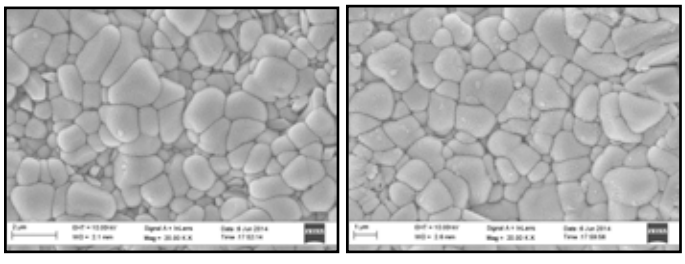


*Pyrochlore phase

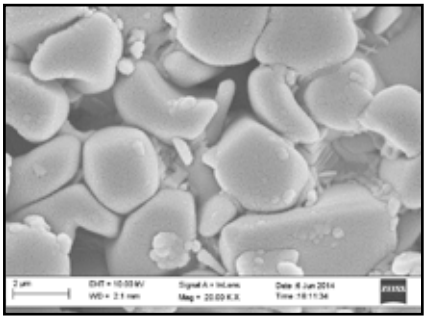
Fig. 1: XRD Patterns of Sintered Ceramics $(SmFeO_3)_x - (PbZr_{0.53}Ti_{0.47}O_3)_{1-x}$ for x = 0.2, 0.25 and 0.3.

2. Microstructure

Scanning electron micrographs of surface morphology of SF-PZT ceramics were taken at 20 kX as shown in fig. 2. All the sintered ceramics appear to be dense [9]. It is observed from Fig. 2 that the grain size is increased as SF content is increased from x = 0.2 to x = 0.3.



2(a) 2(b)



2(c)

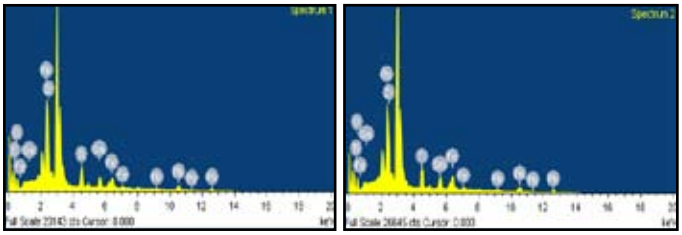
Fig. 2: SEM Micrographs of Sintered Ceramics $(SmFeO_3)_x$ – $(PbZr_{0.53}Ti_{0.47}O_3)_{1-x}$ (a) x = 0.2 (b) x = 0.25 (c) x = 0.3.

3. Composition

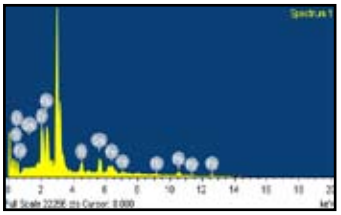
The Energy Dispersive X- Ray Spectra was taken to confirm the composition of elements Sm, Fe, Pb, Zr, Ti, O in all the samples as shown in fig. 3. The weight % of all samples are shown below in Table 1.

Table 1: Elemental Composition of Sintered Ceramics $(SmFeO_3)_x$ – $(PbZr_{0.53}Ti_{0.47}O_3)_{1-x}$ for x = 0.2, 0.25 and 0.3.

Sample	Weight %					
	Sm	Fe	Pb	Zr	Ti	O
x = 0.2	13.61	5.96	49.61	12.44	8.37	10.01
x =0.25	15.25	7.54	45.18	13.51	7.30	11.22
x = 0.3	22.68	4.46	33.18	21.96	4.33	13.39



3(a) 3(b)



3(c)

Fig. 3: EDAX Spectra of Sintered Ceramics $(SmFeO_3)_x$– $(PbZr_{0.53}Ti_{0.47}O_3)_{1-x}$ (a) x = 0.2 (b) x = 0.25 (c) x = 0.3.

B. Raman Spectroscopy

Raman spectra of SF-PZT ceramic samples recorded at room temperature is shown in fig. 3. The spectrum contains three peaks observed around 535 cm^{-1}, 693 cm^{-1} and 1376 cm^{-1}. These peaks shift due to increase in the content of SF [10].

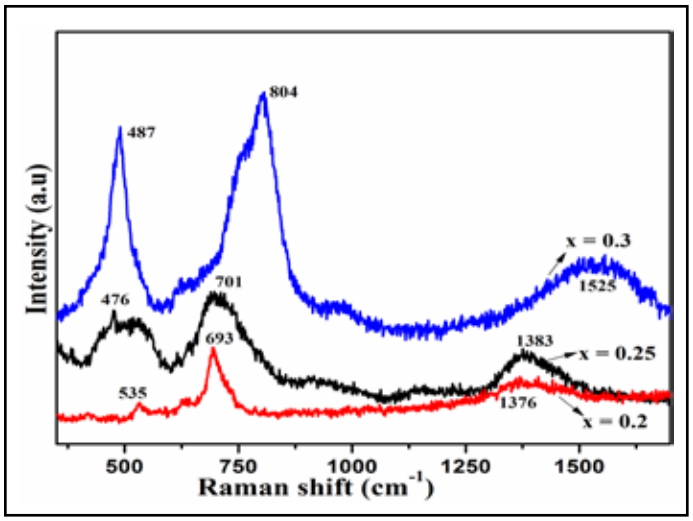
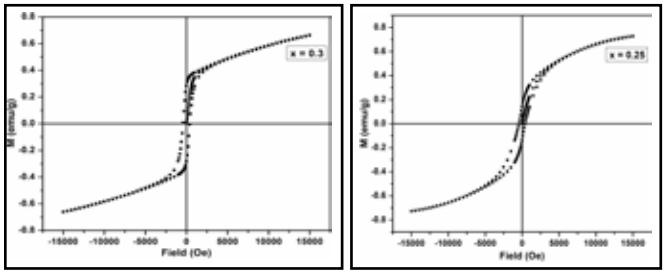


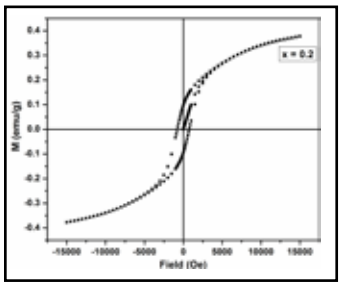
Fig. 4: Raman Spectra of Sintered Ceramics $(SmFeO_3)_x$ – $(PbZr_{0.53}Ti_{0.47}O_3)_{1-x}$ for x = 0.2, 0.25 and 0.3.

C. Magnetic Properties

Magnetization (M) versus Magnetic Field (H) hysteresis loops at room temperature for SF-PZT are shown in fig. 5.



5(a) 5(b)



5(c)

Fig. 5: Hysteresis Loops of Sintered Ceramics $(SmFeO_3)_x$ – $(PbZr_{0.53}Ti_{0.47}O_3)_{1-x}$ for x = 0.2, 0.25 and 0.3.

The values of remanent magnetization (M_r), saturation magnetization (M_s) and coercive field (H_c) are shown in Table 2. From which it is found that as the value of x increased, there is an increase in values of M_r, M_s whereas H_c decrease.

Table 2: Comparison of H_c, M_r, M_s of sintered ceramics $(SmFeO_3)_x$ – $(PbZr_{0.53}Ti_{0.47}O_3)_{1-x}$ for x = 0.2, 0.25 and 0.3.

Sample	Hc (Oe)	Mr (emu/g)	Ms (emu/g)
x = 0.2	769.848	0.091	0.377
x = 0.25	417.250	0.139	0.727
x = 0.3	203.941	0.307	0.662

IV. Conclusion

The SF-PZT ceramics exhibited a tetragonal phase prepared by solid state reaction route. The microstructure shows grains which tends to increase with increasing SF content. Raman

spectra shows shift of bonds in the samples. Results obtained from magnetic studies shows remanent magnetization (M_r), saturation magnetization (M_s) increases and coercive field (H_c) decreases as Sm, Fe content increases.

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