

## **INFLUENCE OF NANO-SIZED TiO<sub>2</sub> ON Pr<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> COMPOSITES: STRUCTURAL, MICROSTRUCTURAL AND MAGNETIC PROPERTIES**

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### **ABSTRACT**

Perovskite manganites have always been the research interest attributed to its intriguing colossal magnetoresistive (CMR) properties. Incorporation of an insulating secondary phase into the manganite composites has proven as an effective measure to enhance the low field magnetoresistance (LFMR). This paper reports the structural, microstructural and magnetic properties of Pr<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> (PSMO) composites synthesized by the solid-state reaction method. Different compositions of nano-sized TiO<sub>2</sub> (5 %, 10 %, 15 % and 20 %) were appended into the samples to study the effect on the physical properties. X-ray diffraction patterns show all samples exhibit polycrystalline PSMO as the major phase and strong orientation along (121) direction throughout the series. The microstructural parameter is presented by Rietveld refinement and indicates that TiO<sub>2</sub> only presents in 20 % samples. Nano-size TiO<sub>2</sub> has distorted the pure PSMO phase as there are other minor phases observed in the manganite composites. Crystallite size of PSMO composites is ranging from 37.7 – 63.2 nm with no direct relation to the TiO<sub>2</sub> content. Surface roughness and particle size show the increment along with increasing TiO<sub>2</sub> composition from the atomic force microscope (AFM) analysis. All samples possess the narrow hysteresis loop with weak ferromagnetic nature at room temperature. The PSMO: TiO<sub>2</sub> presented in this study is a promising manganite composite which could be utilized in the future spintronic applications with its interesting physical properties.

### **INTRODUCTION**

Colossal magnetoresistance (CMR) materials, namely perovskite manganites have been studied extensively since the discovery of ferromagnetic LaMnO<sub>3</sub> in 1950<sup>1</sup>. Intrinsic and extrinsic CMR have been recognised as the origin for this magnificent phenomenon<sup>2</sup>. The intrinsic CMR is explained by the double exchange (DE) mechanism which proposed by Zener<sup>3</sup>. It requires higher magnetic field (> 1 T) and only accentuates near the Curie temperature (T<sub>C</sub>). Whereas the extrinsic CMR is widely adapted to the research nowadays because of its lower requirement of magnetic field (< 0.3 T). Extrinsic CMR is also known as low field magnetoresistance (LFMR) and it can be achieved by the spin polarized tunnelling between the interfaces of grain boundaries in the manganite composite. The added oxide in manganite composite will act as pinning

centre in demagnetization by domain wall displacement. Hence, a small magnetic field is sufficient to align the neighbouring spin in order to create the CMR effect <sup>4</sup>.

PSMO system is one of a kind among the mixed-valence manganites and it always attracts the great study interest because of its charge-ordered (CO) and charge-delocalized (CD) states <sup>5</sup>. The aim of this work is to determine the influence of different ratios of TiO<sub>2</sub> on the PSMO composite. Structural, microstructural and magnetic properties of the composites are the focus of this study as they are essential physical properties of CMR materials other than magneto-transport properties.

### **EXPERIMENTAL DETAILS**

Praseodymium Strontium Manganese Oxide (1-x) PSMO: x TiO<sub>2</sub> (x= 0, 5, 10, 15 and 20 %) was prepared by the solid-state reaction method. Praseodymium (III, IV) Oxide (Pr<sub>6</sub>O<sub>11</sub>, 99.9 %), Strontium Carbonate (SrCO<sub>3</sub>, 99.9 %) and Manganese (IV) Oxide (MnO<sub>2</sub>, 99.9 %) were used as the starting materials. The stoichiometric ratio of starting powders was well mixed by ball-milling technique with analytical grade acetone for 24 hours prior to the drying process in the oven at 70 °C for 24 hours. The dried powders were then calcined at 900 °C and pre-sintered at 1200 °C. Finally, the PSMO powder was added with different ratios of Titanium Dioxide (TiO<sub>2</sub>, 98 %) nanopowder (40 nm) and pressed into pellet using the 13 mm pellet die before the sintering process at 1000 °C for 2 hours. The samples were then studied by X-ray diffractometer (Philips PW 3040/60 X'Pert PRO), atomic force microscope (Bruker Dimension Edge) and vibrating sample magnetometer (Lakeshore 7407).

### **RESULTS AND DISCUSSION**

The crystal structure of the samples was characterized by X-ray diffraction (XRD) method using CuK<sub>α</sub> radiation at room temperature in the 2 θ range of 20 ° to 80 °. All XRD results were analysed using HighScore Plus software. Figure 1 shows the XRD patterns of pure PSMO and PSMO composites with different ratios of TiO<sub>2</sub>. All samples exhibit Praseodymium Strontium Manganese Oxide (ICSD reference code: 98-006-8139) as the main phase and strong orientation along (121) direction. Minor phases start to show up on x = 10 % as depicted in Figure 1. Titanium Oxide, TiO<sub>2</sub> (ICSD reference code: 98-006-2552) peak has been observed in x = 20 % sample.

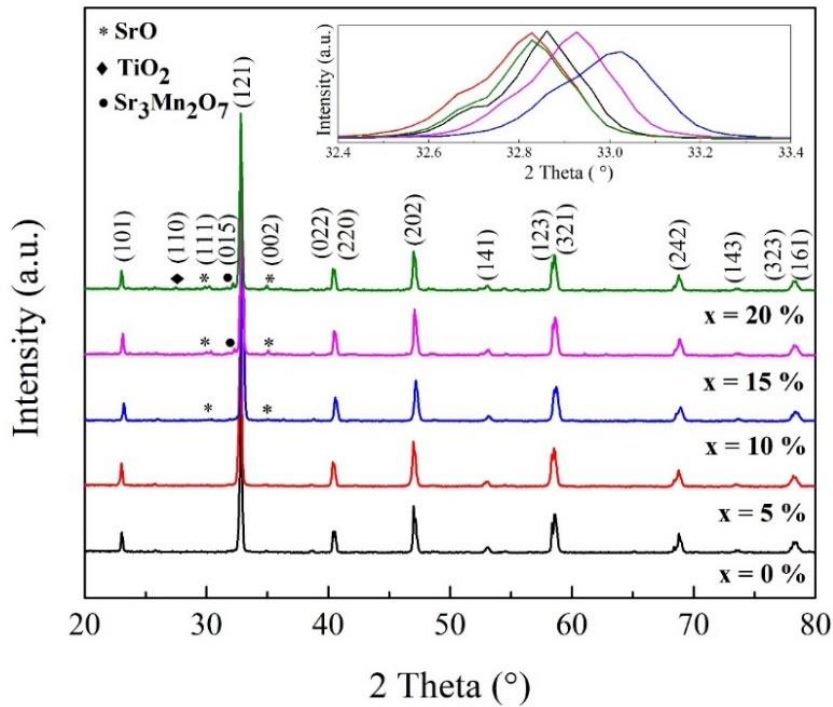


Figure 1: XRD patterns of (1-x) PSMO: x TiO<sub>2</sub> (x = 0, 5, 10, 15 and 20 %) manganite composites

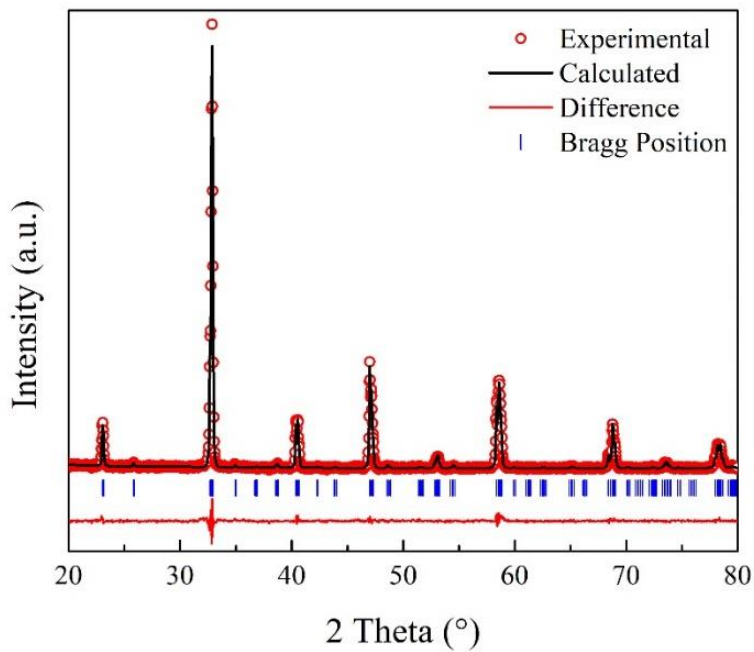


Figure 2: Rietveld refinement analysis of the pure PSMO sample

Table 1: Microstructural parameter of (1-x) PSMO: x TiO<sub>2</sub> (x= 0, 5, 10, 15 and 20 %)

Sample	Praseodymium Strontium Manganese Oxide				
Crystal Structure	Orthorhombic				
Space group	Pnma - 62				
TiO <sub>2</sub> Composition, x (%)	0	5	10	15	20
Lattice Parameter					
a (Å)	5.452	5.454	5.460	5.457	5.453
b (Å)	7.703	7.705	7.713	7.708	7.705
c (Å)	5.483	5.483	5.487	5.484	5.482
Bond Angle					
∠Mn-O <sub>1</sub> -Mn (°)	162.6	166.9	167.7	168.2	178.0
∠Mn-O <sub>2</sub> -Mn (°)	161.2	161.5	160.6	160.9	161.0
Bond Length					
Mn-O <sub>1</sub> (Å)	1.932	1.929	1.925	1.908	1.929
Mn-O <sub>1</sub> (Å)	1.979	1.964	1.968	1.981	1.938
Mn-O <sub>2</sub> (Å)	1.952	1.885	1.885	1.871	1.938
Mn-O <sub>2</sub> (Å)	1.952	2.019	2.027	2.037	1.968
R <sub>EXP</sub> (%)	3.996	3.813	3.907	3.828	3.982
R <sub>P</sub> (%)	3.739	3.694	3.861	4.171	4.838
R <sub>WP</sub> (%)	4.714	4.789	4.881	5.695	6.709
Goodness of Fit	1.391	1.578	1.561	2.213	2.839
Sample	Titanium Oxide (Rutile)				
Crystal Structure	Tetragonal				
Space group	P42/mnm - 136				
Lattice Parameter					
a (Å)	-	-	-	-	4.585
b (Å)	-	-	-	-	4.585
c (Å)	-	-	-	-	2.959

XRD data were further analysed using Rietveld refinement and Figure 2 illustrates the refinement analysis of the pure PSMO powder. The microstructural parameters of the PSMO composites are presented in Table 1. All data have a good fitting with the calculated data and with R<sub>WP</sub> that less than 7 %. The changes can be observed from the lattice parameter of pure PSMO with the composite samples. This is in agreement with the shifting of (121) peak as shown in Figure 1 inset.

Formation of Strontium Oxide (SrO) and Tristrontium Dimanganate (IV) (Sr<sub>3</sub>Mn<sub>2</sub>O<sub>7</sub>) in samples are the caused for the peak shifting when the addition of TiO<sub>2</sub> is increased. There is no peak corresponds to TiO<sub>2</sub> phase from 5 - 15 % samples. It is attributed to the evaporation or substitution of nano-sized TiO<sub>2</sub> with the parent compound during the high temperature (1000 °) sintering process. Quantification of minor phases from Rietveld refinement is presented in the Table 2. Percentage of SrO and Sr<sub>3</sub>Mn<sub>2</sub>O<sub>7</sub> increases as the TiO<sub>2</sub> composition increases. The formation of these two phases is

caused by the addition of TiO<sub>2</sub> and substitution might have occurred between TiO<sub>2</sub> and PSMO. Besides that, the average crystallite size has been calculated using Scherrer's equation. Crystallite size of PSMO composites is ranging from 37.7 – 63.2 nm with no direct relation to the TiO<sub>2</sub> content as shown in Table 2.

Table 2: Crystallite size, percentage of minor phases, coercivity and magnetization of PSMO composites

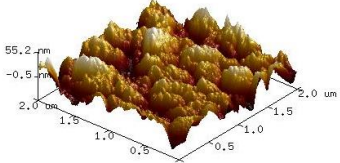
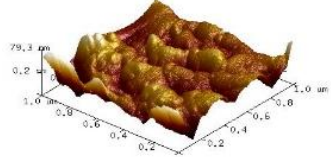
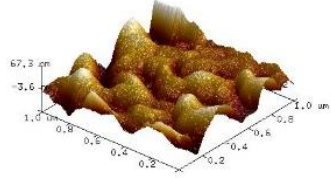
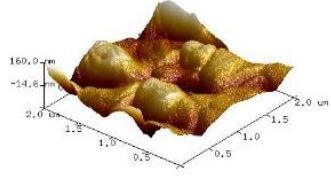
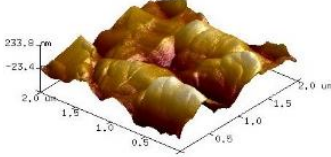
TiO <sub>2</sub> Composition / x (%)	Crystallite Size (nm)	Minor Phase (%)			Coersivity / Hc (Oe)	Magnetization / M (emu/g)
		SrO	Sr <sub>3</sub> Mn <sub>2</sub> O <sub>7</sub>	TiO <sub>2</sub>		
0	63.2	-	-	-	18.60	19.30
5	47.1	-	-	-	24.02	14.55
10	37.7	0.2	-	-	16.70	11.09
15	53.4	0.8	0.3	-	13.73	11.89
20	59.6	1.4	1.1	2.5	18.37	11.18

The topography of composites was studied from the 3D AFM micrographs which depicts the granular structures as shown in Table 3. Different particle size can be observed when the TiO<sub>2</sub> content was varied. The particle size increases as the percentage of TiO<sub>2</sub> in composite increases. Furthermore, same trend has also been observed from its surface roughness which implies that the surface topography can be well modified with the proper tuning of composition in composite.

Vibrating sample magnetometer (VSM) has been used to study the magnetic properties of the composites. Figure 3 shows the magnetization, M as a function of magnetic field, H for PSMO samples. Hysteresis loops clearly show the samples do not fully possess the paramagnetic behaviour. Previous work showed that PSMO manganite exhibit a broad Curie transition temperature, T<sub>C</sub> ranging from 255 K to 287 K<sup>6</sup>. Thus, all samples still have a slightly weak ferromagnetic alignment at room temperature (300 K) as depicted in Figure 3.

TiO<sub>2</sub> composition has weakened the overall magnetic properties and lowered the value of magnetization at 1 T as shown in Table 2. The pure PSMO sample shows the highest M<sub>s</sub> value following by the x= 5 % sample. From refinement quantification in Table 2, TiO<sub>2</sub> has already substituted in Mn site for x = 10, 15 and 20 % samples which results the formation of 2 other minor phases. The magnetic moment of PSMO is mainly contributed by 3d electron in Mn atom. Therefore, the magnetization is expected to be reduced and these three samples have shown a smaller value of magnetization compared to other samples.

Table 3: 3D Micrograph, surface roughness and particle size from AFM analysis

<b>TiO<sub>2</sub> Composition/ x (%)</b>	<b>3D Micrograph</b>	<b>Surface Roughness (μm)</b>	<b>Particle Size (nm)</b>
0		0.0166	114.01
5		0.0189	120.51
10		0.0198	125.88
15		0.0498	265.11
20		0.0681	279.53

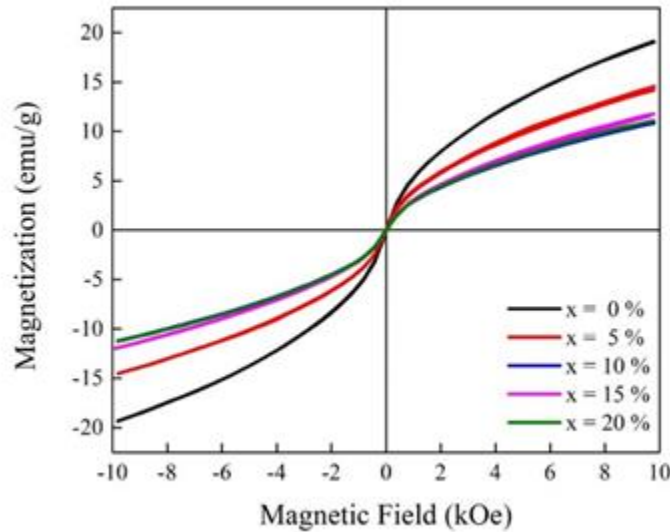


Figure 3: Magnetization, M against magnetic field, H of PSMO composites

## CONCLUSION

The structural, microstructural and magnetic properties of PSMO composites have been studied and the samples were successfully prepared via solid-state reaction method. The investigation of the structural properties by XRD analysis indicates that PSMO composites consist of two more other phases besides  $\text{TiO}_2$  as the secondary phase and it is possibly caused by the substitution of nano-sized  $\text{TiO}_2$  with the PSMO parent compound. In AFM analysis, the particle size and surface roughness increase as the ratio of  $\text{TiO}_2$  in composites increases. The magnetic properties measurement was carried out using VSM and the pure PSMO results the highest value of magnetization compared to the other samples at 1 T whereas the magnetization value decreases when Titanium Dioxide was added to the PSMO system. In conclusion, the PSMO:  $\text{TiO}_2$  presented in this study is a promising manganite composite with unique structural properties and huge possibilities which could be utilized in the future spintronic applications.

## ACKNOWLEDGMENTS

This research is funded and supported by UPM research grants, GP/2017/9567400 and GP-IPS/2018/9663900. The authors would like to thank to the supported staffs who helped in characterization measurements and facilities provided by Department of Physics, UPM.

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