IOP Conf. Series: Journal of Physics: Conf. Series **869** (2017) 012029 doi:10.1088/1742-6596/869/1/012029

The investigation of the mechanical properties of Mn doped $BaSnO_3$ nanoparticles

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Abstract. This study investigates the effect of Mn substitution on the structural and mechanical properties of nano $BaSnO_3$ using X-ray diffraction analysis (XRD), transmission electron microscopy (TEM), Scanning electron microscope (SEM) and Vickers microhardness. For this investigation, samples of type $BaSn_{1-x}Mn_xO_3$ with $0.04 \leq x \leq 0.4$ were prepared by co-precipitation method. XRD patterns indicate the formation of single phase cubic structure $BaSnO_3$ with space group (Pm3m) for $0 \leq x \leq 0.1$. $BaMnO_2$ hexagonal phase appears as impurity for $x > 0.1$. The crystallite size, increases as x increases. Vickers microhardness H_v was carried out at different applied loads varying between 0.98 N and 9.8 N at dwell time 40 seconds. The results show that H_v increases as the Mn-content increases, whereas it decreases as the applied load increase. The H_v results were analysed using Elastic Plastic Deformation and the Modified proportional specimen resistance models. The Vickers microhardness analysis indicates that Modified Proportional Specimen Resistance model is the most suitable one for describing the load independent microhardness region of the investigated samples.

1. Introduction

One of the interesting compounds, in materials science, for practical application as a sensor material for host gases [1,2], photocatalytic applications [3,4] and optical devices [5] is $BaSnO_3$. In the last few years, many preparation methods were reported to obtain nanoparticles of $BaSnO_3$ with cubic perovskite structure such as solid state reaction technique [6], sol gel method [7] and hydrothermal method [1,8]. One of the most suitable methods to prepare nanoparticles is the chemical co-precipitation method because of its simplicity and control of the crystalline size.

Balamurugan. et al reported the effect of transition elements such as Fe [9] and Mn [10] on the magnetic properties of $BaSnO_3$. They found that these samples exhibited a ferromagnetic behaviour at room temperature. Moreover, the mechanical properties of $BaSnO_3$ were studied by Maekawa et al. [11], where Vickers microhardness was found to be 5 Gpa. To our knowledge, there are no reports on the mechanical properties of $BaSnO_3$ doped by transition elements. Hence, the aim of this work is to study the effect of Mn doping on the mechanical properties of $BaSnO_3$ through Vickers microhardness investigation.

2. Experimental details

The nano-samples of nominal composition $BaSn_{1-x}Mn_xO_3$, with $0.04 \leq x \leq 0.4$, were prepared using co-precipitation method [12] where the starting materials were $BaCl_2.2H_2O$, $SnCl_4.5H_2O$ and

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$MnCl_2.4H_2O$. The nano-samples $BaSn_{1-x}Mn_xO_3$ were characterized by (XRD) analysis using Brucker D8 advanced power diffractometer with $20° < \theta < 80°$ range and Cu-Kα radiation ($\lambda = 1.54056$ Å). The surface morphology was examined using Jeol transmission electron microscope JEM 100CX and Scanning electron microscope (SEM) ASC-200, respectively. Vickers microhardness measurements were performed using a digital microhardness tester H_v MHVD-1000IS by using equation (1) [13]

$$H_v = 1854.4 \times \frac{F}{d^2} \quad , \tag{1}$$

where F is the applied load in Newton and d is the diagonal length of the indentation mark in μm.

3. Results and discussion

Figure 1 displays XRD patterns for $BaSn_{1-x}Mn_xO_3$ with $0 \leq x \leq 0.4$. The major peaks indicate the formation of $BaSnO_3$ cubic perovskite with space group #221 (pm3m) up to x=0.1. For $x > 0.1$, $BaMnO_2$ peak was observed at $2\theta = 31.2°$. The lattice parameter *a* and the crystalline size *D* were estimated from Bragg's equation and Debye Scherrer's relation respectively [12], a and D are listed in table1. TEM and SEM for $BaSnO_3$ and $BaSn_{0.9}Mn_{0.1}O_3$ are presented in figure 2.

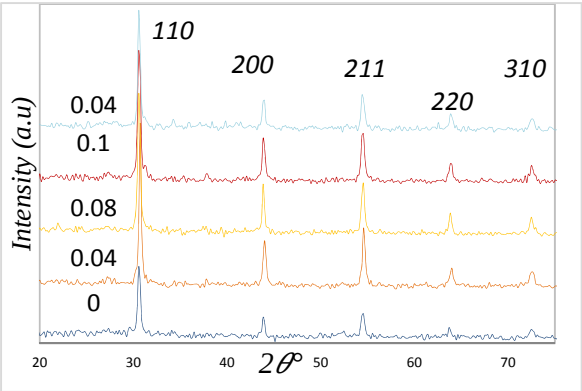

Figure 1. X-Ray diffraction patterns for $BaSn_{1-x}Mn_xO_3$ for x=0,0.04,0.08,0.1,0.4.

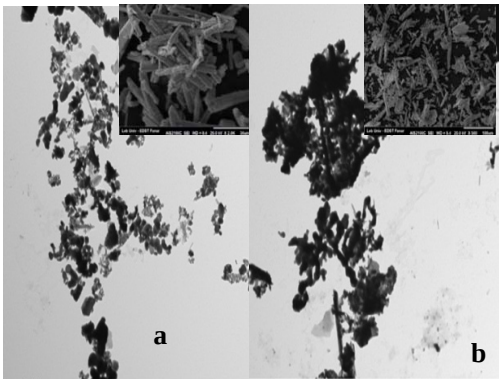

Figure 2. TEM and inserted SEM images for $BaSn_{1-x}Mn_XO_3$ samples for(a) x=0 and (b) 0.08.

The nano crystallites are of cuboidal shape with size ranging from 41-60 nm. The lattice parameter *a* fluctuates as x increases, where similar results were obtained by Ekaphan et al. [7] for $BaSnO_3$ doped by Fe. Figure 3 shows the variation of Vickers microhardness number H_v with the applied load F for $BaSn_{1-x}Mn_xO_3$ with x=0,0.04,0.08,0.1and 0.4. H_v decreases non-linearly as the applied loads increase till about 3.00 N, and it tends to attain saturation at F < 3.00 N. This behaviour can be explained on the basis of penetration depth of the indenter by Foerster et al. [14]. It is also noticed that H_v increases with the increase of x. This improvement can be attributed to the enhancement of resistance to crack propagation and due to the increase of cluster formation formed by Mn substitution.

The H_v results were analysed according to Elastic Plastic Deformation (EPD) and Modified Proportional Specimen Resistance (MPSR) models which are described by equations (2) and (3) respectively [15,16], the plots of the two models are represented in figures 4 a and b respectively. where A_1 is a constant, d_0 is the elastic component, $\alpha_1$corresponds to the minimum applied load to produce and indentation, $\alpha_2$and α_3 are related to the elastic and plastic properties of the material.

$$F = A_1(d + d_0)^2 \tag{2}$$

$$F = \alpha_1 + \alpha_2 d + \alpha_3 d^2, \tag{3}$$

Table 1. Lattice parameter (a), Crystallite size from XRD (DXRD), average particle size from TEM (DTEM) of $BaSn_{1-x}Mn_xO_3$ (x = 0,0.04,0.08,0.1 and 0.4) nanoparticles.

x	*a* (Å)	D_{XRD} (nm)	D_{TEM} (nm)
0	4.1118	50.0	60.0
0.04	4.1106	46.4	51.0
0.08	4.1148	44.2	48.0
0.1	4.1153	43.7	45.0
0.4	4.1176	42.4	41.0

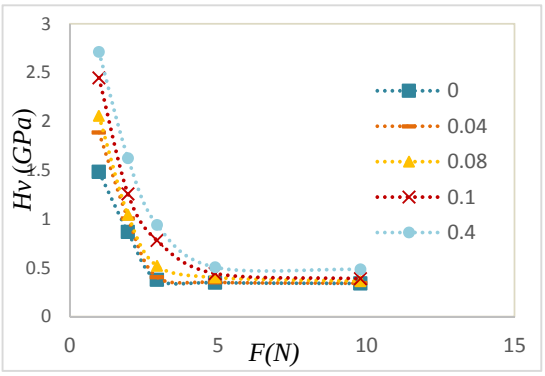

Figure 3. Variation of apparent H_v *with x= 0.00*, 0.04, 0.08, 0.1 and 0.4 at different applied loads.

We notice from the figures that the experimental results are well fitted according to the 2 models. The fitting parameters for all models are listed in table 2. It is noticed from table 2 that the values of α_1 are positive for all samples, which indicates that the applied load is enough to create both the elastic and plastic deformations [15]. Moreover the values of d_0 are positive for all values of x which indicates that elastic deformation is present for all values of x. The True microhardness values obtained from EPD and MPSR approaches are calculated according to equations (4) and (5) respectively, and listed in table 2.

It is clear from table 2 that the values of H_{MPSR} are comparable with those obtained from experimental results. Whereas, it is noticed that EPD model displays much lower values than the experimental values H_v. Thus, the MPSR Model is the best fitted model for $BaSn_{1-x}Mn_xO_3$ samples.

$$H_{EPD} = 1854.4 \times \frac{F}{(d_0+d^2)} \quad (4)$$

$$H_{MPSR} = 1854.4 \times \frac{\alpha_1+\alpha_2 d+\alpha_3 d^2}{d^2} \quad (5)$$

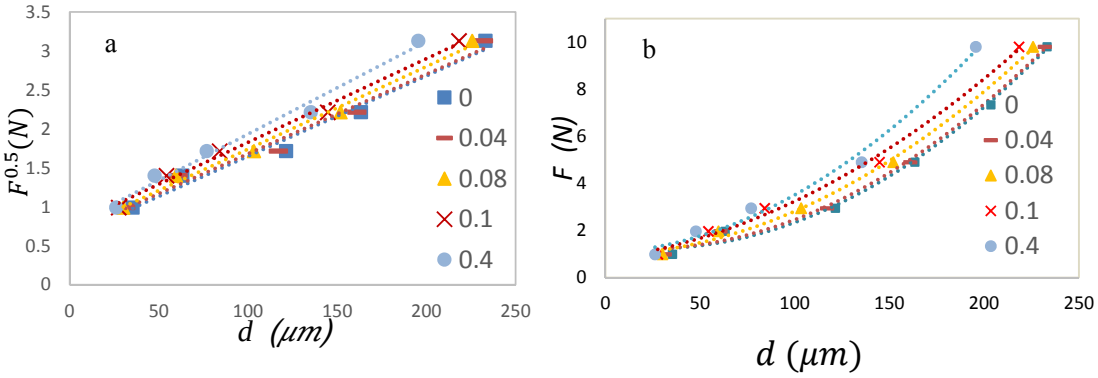

Figure 4. a. √F against d according to EPD model, b. F against d according to MPSR model.

Table2. Microhardness analysis results for different models and parameters for $BaSn_{1-x}Mn_xO_3$ samples with x= 0.00, 0.04, 0.08, 0.1, and 0.4; variation of Vickers microhardness values with respect to different applied models from experimental values calculated at t = 40 s.

	EPD model		MPSR model			Vickers microhardness values		
x	$A_1\ (\frac{N}{\mu m^2})$	$d_0\ (\mu m)$	$\alpha_1\ (N)$	$\alpha_2(\frac{N}{\mu m})$	$\alpha_3(\frac{N}{\mu m^2})$	Hv experimental	Hv (EPD)	Hv (MPSR)
0.0	0.00011	68.77670	0.00004	0.0291	0.0002	0.3555	0.1864	0.3632
0.4	0.00010	73.00980	0.00002	0.0330	0.0002	0.3668	0.1833	0.3953
0.8	0.00011	70.41509	0.00002	0.0343	0.0002	0.4286	0.2019	0.4273
0.1	0.00012	72.63889	0.00003	0.0361	0.0001	0.5373	0.2143	0.5106
0.4	0.00013	70.73684	0.00002	0.0398	0.0002	0.6442	0.2617	0.6037

4. Conclusion

$BaSn_{1-x}Mn_xO_3$ where $0.00 < x < 0.4$ were successfully prepared using co-precipitation method. XRD results indicated that the substitution of Mn to $BaSnO_3$ did not affect the cubic crystal structure but slightly increased the crystallite size. TEM and SEM images assure the increase of grain size of the particles and showed the Mn clusters that appear at high doping. The Vickers microhardness values increased as x increased. By analyzing Vickers microhardness according to different models, it was noticed that H_v results obeyed the Modified Proportional Specimen Resistance model.

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