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European Journal of Applied Engineering and Scientific Research, 2012, 1 (3):67-72 (http://scholarsresearchlibrary.com/archive.html)



# Raman studies of Rod-like Bismuth strontium manganites

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## ABSTRACT

The present investigation was aimed to synthesize bismuth strontium manganite of composition  $Bi_{0.6}Sr_{0.4}MnO_3$ ceramic by low cost solid state technique. The ceramic showed orthorhombic crystal structure with micro-rod like surface morphology. The crystallite size was 34nm, with preferential orientation in (111) plane with TC of 2.15. On the basis of Zener polaron model and conventional model, possible Raman vibrational modes in bismuth strontium manganites have been assigned.

Key words; Ceramics, XRD, Texture coefficient, SEM, Raman Spectroscopy

## INTRODUCTION

Mixed valence manganites with the perovskite structure have been studied for almost fifty years. The system offers a degree of chemical flexibility which permits the relation between the oxides' structure, electronic and magnetic properties to be examined in a systematic way. Research on the manganites has revealed new phenomena such as colossal [1] dense granular magnetoresistance [2], Jahn Teller polarons [3]. The intriguing physical properties and the potential technological applications of  $R_{1-x}A_xMnO_3$  pseudocubic manganites (where R is a rare-earth metal: La, Pr, Nd, Dy; and A is an alkaline earth: Sr, Ca, Ba, Pb) have led to a resurgence of interest in these and related materials [4]. In these systems colossal magnetoresistance commonly occurs near the Curie temperature Tc, when the system undergoes a paramagnetic (PM) to ferromagnetic (FM) transition. In the magnetic ordered state, the electron hopping process is favored by the spin arrangement, whereas for temperatures above  $T_c$  the conduction mechanism is semiconducting. This behavior is closely related to the double-exchange (DE) mechanism, which involves the transfer of  $e_g$  electrons between neighboring Mn ions when these are ferromagnetically coupled. This phenomenon is explained by "Double exchange (DE)" model proposed by Zener [5].

Rare-earth mixed-valence manganites  $(Ln_{1-x}A_xMnO_3)$  with perovskite structure have been focused on during the last years because of their colossal magnetoresistance (CMR) and charge ordering (CO) phenomena [6]. When A site is doped with divalent ions (alkaline earth: Sr, Ca, Ba, Pb) usually spatially ordered distribution of  $Mn^{3+}/Mn^{4+}$  ions in the lattice in a purely ionic picture accompanied by orbital ordering. As the ionic size of A-site cation is relatively small compared to the Mn–O bond length, the mobility of the itinerant  $e_g$  electrons is significantly suppressed due to the lattice distortion, and the CO is reinforced with the increase of the charge ordering temperature (TCO). A-site cation size is playing an important parameter for tuning the ground state of manganites system [7]. Sr doped BiMnO<sub>3</sub> have presented quite different properties from the other manganites, even though the ionic size of Bi<sup>3+</sup> (1.24 Å) is almost same as that of La<sup>3+</sup> (1.22 Å),the doping of Sr makes the BiMnO<sub>3</sub> extraordinary materials due to lattice distortion, which intern due to the Bi lone pair [8].

In this paper property of  $Bi_{0.6}Sr_{0.4}MnO_3$  ceramic synthesized by solid state reaction is reported. The structural, morphological and FT-Raman vibrational analysis assigned with the help of Zener polaron model and group theoretical analysis is reported.

## MATERIALS AND METHODS

#### a. Materials:

The synthesis of orthorhombic structured bismuth Strontium manganites have been done by simple solid state reaction, as shown in flowchart Fig.1 using proper amount of bismuth oxide, strontium chloride and manganese chloride as starting materials. These precursors were weighed in stoichiometric proportion, ground for 4 hour in acetone medium to get homogenous mixture. This mixture was pre-sintered at 900<sup>o</sup>C for 7 hour in a muffle furnace. Final sintering of samples was done at  $1050^{\circ}$ C, for 8 hour to get orthorhombic BSM samples. The chemical reaction at high temperature take place, through solid state reaction giving a stable sample product free of residual reactants as below,

$$Bi_2O_3 + SrCl_2 \cdot 6H_2O + MnCl_2 \cdot 4H_2O \longrightarrow Bi_{1-x}Sr_xMnO_3$$

In order to understand structural parameters, XRD, SEM, FT-Raman tools are used for analysis.

X-ray diffraction analysis was performed by a Philips (PW 3710) diffractometer using Cr-K<sub> $\alpha$ </sub> radiation)., The surface morphological study was carried out by scanning electron microscopy (JSM- 6360 JEOL, Japan), and Raman spectra was recorded in the spectral range of 35–4000 cm<sup>-1</sup> using Raman spectrometer (Bruker Multi RAM, Germany Make) Nd:YAG laser source with excitation wavelength of 1064 nm and resolution 4 cm<sup>-1</sup>.



Fig.1 Flowchart of Bi<sub>0.6</sub>Sr<sub>0.4</sub>MnO<sub>3</sub>

#### **RESULTS AND DISCUSSION**

The orthorhombic structure of the sample was confirmed from X-ray diffraction characterization as shown in figure 2. The X-ray diffraction patterns were indexed using JCPDS Card No. 49-0774. Using Debye -Scherer equation,[9] Where D is the diameter of the crystallites of powder,  $\lambda$  is the wavelength of the Cr-K $\alpha$  line,  $\beta$  is the FWHM in radians and  $\theta$  is Bragg's angle.

$$D = \frac{0.9\,\lambda}{\beta\,\cos\,\theta}$$

The lattice parameters of orthorhombic bismuth strontium manganite sample are  $a=5.569(A^0)$ ,  $b=5.452(A^0)$ , and  $c=3.758(A^0)$ . The cell volume and crystallite size was calculated 114.101  $(A^0)^3$  and 34nm respectively. In order to understand the degree of orientation of planes, the texture coefficient was calculated which is nothing but preferred orientation of planes.



Fig.2. XRD pattern of Bi<sub>0.6</sub>Sr<sub>0.4</sub>MnO<sub>3</sub>

Quantitative analysis depends on intensity ratios which are greatly distorted by preferred orientation. Quantitative information concerning the preferential crystal orientation can be obtained from the texture coefficient, TC, defined as where TC(hkl) is the texture coefficient, I(hkl) is the XRD intensity and n is the number of diffraction peaks considered.  $I_o(hkl)$  is the intensity of the XRD reference of the randomly oriented grains.

The texture coefficient of each planes were tabulated as shown in Table.2.

Texture Coefficient of all planes of bismuth strontium manganite								
$TC(hkl) = \frac{I(hkl) / I_o(hkl)}{(1/n) \sum_n I(hkl) / I_o(hkl)}$								
hkl planes	(110)	(200)	(111)	(201)	(220)	(002)	(130)	(131)
TC(hkl)	0.16	0.032	2.15	1.34	1.53	1.26	0.45	1.06

From table it is clear that the grains are more intensely orientated in the (111) plane, nevertheless we also find that grain oriented in (110) is the least. The values 0 < TC (hkl) <1 indicate the lack of grains oriented in that direction. As TC (hkl) increases, the preferential growth of the crystallites in the direction perpendicular to the hkl plane is the greater.

The sintered density was calculated using the formula,

$$\rho_{s} = \frac{m}{\pi r^{2} h}$$

where 'm' is the mass of the pellet, 'r' is the radius of the pellet and 'h' is the thickness of the pellet.

The sintered density of the sample is  $3.33 \text{ g/cm}^3$ .



Fig.3. Micro-rod like morphology of Bi<sub>0.6</sub>Sr<sub>0.4</sub>MnO<sub>3</sub>

The surface morphology of the sample is shown in Fig.3.The scanning electron micrograph image reveals that the rod-like nature of the sample without any ambiguity. We observed non-agglomerated micro-rods, of different sizes. Micro-rods length varies in the range of  $5\mu$ m to  $34\mu$ m. To the author's knowledge micro-rods like morphologies of BSM has been reported for the first time.

Generally perovskite-like manganites  $R_{1-x}A_xMnO_3$ , where R is a trivalent rare earth and A is a divalent alkaline element, are characterized by a strong interplay of magnetism, electric transport and crystallographic distortion. The perovskite distortions can be divided into two groups: distortions changing Mn-O-Mn bond angles governed by the tolerance factor and distortions changing the Mn-O distances governed by the magnitude and the spatial coherence of the Jahn-Teller distortions of the Mn<sup>3+</sup>O<sup>2-</sup><sub>6</sub> octahedra.

K. Yamamoto, *et al* [10] from lattice dynamical calculation on LaMnO<sub>3</sub>, which gives the frequencies of the modes corresponding to the JT and breathing modes as about 580 and  $670 \text{ cm}^{-1}$ . The group theoretical point of view that both breathing modes and Jahn-Teller type modes are likely responsible for these phonon peaks with assumption of the lattice distortion since detailed crystal structure and symmetry in the charge-orbital ordered state is unknown. The band observed in the range500-700 cm<sup>-1</sup> likely to be due to likely assigned to the in-plane Mn-O bond stretching modes.



Fig.4.FT-Raman spectra of Bi<sub>0.6</sub>Sr<sub>0.4</sub>MnO<sub>3</sub>

According to M. V. Abrashev *et al* [11] major peaks are assigned in BSM with group theoretical technique using two models, conventional checkerboard ordering and Zener polaron ordering. Thus on the basis of Zener polaron model in bismuth strontium manganites the possible Raman vibrational modes are , Zener pair Jahn-Teller type mode(~480 cm<sup>-1</sup>), Zener pair rotational modes(~200-300 cm<sup>-1</sup>), Zener-pair breathing mode(~630 cm<sup>-1</sup>) and Zener-pair bending mode(~470 cm<sup>-1</sup>). According to the group theoretical analysis, under the assumption of the conventional model, for bismuth strontium manganites there are two A<sub>g</sub> and two B<sub>1g</sub> modes are possible, which are namely can be assigned to A<sub>g</sub>(1), A<sub>g</sub>(2), B<sub>1g</sub>(1), and B<sub>1g</sub>(2), respectively. The Breathing mode A<sub>g</sub>(1) at (~630 cm<sup>-1</sup>), Jahn Tellar A<sub>g</sub>(2) at (~480 cm<sup>-1</sup>), Breathing mode B<sub>1g</sub>(1) at (~630 cm<sup>-1</sup>), and Jahn Tellar B<sub>g</sub>(2) at (~470 cm<sup>-1</sup>) which are good agreement with result.[12]

The Raman spectra exhibits additional high frequency modes attributed to the local breathing vibration of oxygen surrounding the substituent ion [13].

## CONCLUSION

 $Bi_{0.6}Sr_{0.4}MnO_3$  ceramic having orthorhombic structure with crystallite size 34nm and micro-rod like morphology has been synthesized by low cost, simple solid state reaction. Preferential orientation of grains in (111) plane is more prominent. FT-Raman vibrational analysis, shows Breathing mode  $A_g(1)$  at (~630 cm<sup>-1</sup>), Jahn Tellar  $A_g(2)$  at (~480 cm<sup>-1</sup>), Breathing mode  $B_{1g}(1)$  at (~630 cm<sup>-1</sup>), and Jahn Tellar  $B_g(2)$  at (~470 cm<sup>-1</sup>) prominent.

## Acknowledgments

One of the authors Vijaya Puri gratefully acknowledges the UGC India for Award of Research Scientist 'C'. S.N.Mathad very much thankful to Management, and Principal K.L.E Institute of Technology, Hubli, pursue for his Ph.D. thesis. R. N. Jadhav would like to express thanks to DST for WOS-A. All authors acknowledge the UGC-SAP and DST-PURSE.

## REFERENCES

[1] Jin, S., Tiefel, T. H., McCormack, M., Fastnacht, R. A., Ramesh, R., and Chen, L. H., Science, 264, 413 1994.

[2] Hwang, H. Y., Cheong, S. W., Ong, N. P., and Batlogg, B., Phys. Rev. Lett., 77, 2041 1996.

[3] Zhao.G., Conder.K., Keller.H., and Muller, K. A, Nature, 381, 676 1996.

[4]. A.J. Millis, Nature, 392, 147 1998.

[5] Z. Zener, *Phys. Rev.* 82 403. 1951.

[6] Y. Tokura, Y. Tomioka, J. Magn. Magn. Mater. 200, 1-23 1999.

[7] C.N.R. Rao, A. Arulraj, P.N. Santosh, A.K. Cheetham, Chem.mater 10,2714 1998.

[8] A. Kirste, M. Goiran, M. Respaud, J. Vanaken, J.M. Broto, H. Rakoto, M. von Ortenberg, C. Frontera, J.L. García-Muñoz, *Phys. Rev.* B 67 134413 2003.

[9] S. N. Mathad and Vijaya Puri, Archives of Physics Research, , 3 (2):106-115 2012.

[10] K. Yamamoto, T. Kimura, T. Ishikawa T. Katsufuji, and Y. Tokura "Raman spectroscopy of the charge-orbital ordering in layered manganites", 61, 21 **2000.** 

[11] M. V. Abrashev, J. Bäckström, L. Börjesson, M. Pissas, N. Kolev, and M. N. Iliev, *Phys. Rev.* B 64, 144429 2001.

[12] T. Kawasaki, Y. Ogimoto, N. Ogawa and K. Miyano, H. Tamaru, M. Izumi, J. Appl. Phys. 101, 123714 2007.

[13] N. V. Minh, Journal of Physics: Conference Series 187,012011 2009.