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Hydroxide co-precipitation route for synthesis of $La_{0.7}Sr_{0.3}MnO_3$ - $BaTiO_3$ nanocomposites

S.S. VEER, D.J. SALUNKHE, S.V. KULKARNI, S.B. KULKARNI and P.B. JOSHI

Department of Physics, Solapur University Solapur 413 255 (India)

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ABSTRACT

The paper deals with synthesis of nanocrystalline $La_{0.7}$ $Sr_{0.3}$ Mn O_3 (LSMO) and $BaTiO_3$ (BT) powder via hydroxide co-precipitation route. The particle size of the powder is determined using Williamson Hall method and is observed to be nearly 35 nm for LSMO and 120 nm for BT. To avoid occurrence of impurity phases the composites of LSMO and BT are formed at 1273 K using Bi_2O_3 as a sintering aid. The paper focuses mainly on synthesis and dielectric properties of LSMO and BT composites.

Key words: Synthesis of nanocrystalline $La_{0.7}Sr_{0.3}MnO_3$.

INTRODUCTION

The Ferroic materials have regained a renewed interest in the recent years; owing to the useful magnetoelectric (ME) susceptibility χ^{ME} exhibited by the ferrite-Pb (TiZr) O_3 (PZT), ferrite-$BaTiO_3$ (BT) composites and multilayer laminates[1-3].

The manganites e.g. $La_{0.7}$ $Sr_{0.3}$ Mn O_3 (LSMO), are potential candidates to form ME composites for various reasons as elaborated in the literature[1,2]. The ME composites are expected to be mechanically sturdy as compared to the laminated composites[4]. Therefore we have opted to investigate the ME properties on particulate composites of LSMO and BT. To have well dispersed particles of LSMO and BT nanopowders of LSMO and BT are used as starting materials. Here, the hydroxide co-precipitation route is used for synthesis of LSMO and BT nanopowders[5-7].

The paper reports synthesis of LSMO and BT nanopowders and formation of following series of composites.

x LSMO + (1-x) BT + 2 wt % Bi_2O_3, for x = 0.05, 0.1, 0.15 and 0.2 ……series 1.

x LSMO + (1-x) BT + 3 wt % Bi_2O_3, for x = 0.05, 0.1, 0.15 and 0.2 ……series 2.

It has been reported that the use of sintering aid allows formation of dense ceramic bodies at relatively low sintering temperature[8]. The need of low sintering temperature is needed to avoid formation of impurity phases in case of LSMO based composites (2). Here, the paper additionally reports structural investigations, dielectric and ME properties of nanopowders LSMO and BT and their composites.

EXPERIMENTAL

Hydroxide co-precipitation route has been used for synthesis of LSMO and BT nanopowders.

Synthesis of LSMO

La $(NO_3)_3$.6H2O, $Sr(NO_3)_2$, $MnCl_2.4H_2O$, $KMnO_4$ of AR grade are used as precursors for synthesis of LSMO by hydroxide co-precipitation route. The weight proportions of $MnCl_2.4H_2O$ and $KMnO_4$ is selected to be 3.56:1 so that the valencies of the hydroxide residues of Mn in state 3+ and 4+ would be 7:3(7). A combination of NH_4OH and KOH is used as mineralizer. The dried precipitate is subjected to pre and final sintering process at 1223 K and 1473 K.

Synthesis of BT

High purity (> 99.9%) Barium nitrate [$Ba(NO_3)_2$] and Pottassium Titanium Oxalate [$K_2TiO(C_2O_4)_2.2H_2O$] are used as precursors. The KOH has been employed as a mineralizer. For complete precipitation of Ba $(OH)_2$ and Ti O $(OH)_2$, the molar ratio of KOH to (BaTi) of 1.6 has been used, based on the earlier reports(9). It has been observed that the Ba $(OH)_2$ is fractionally soluble in water but insoluble in alkaline medium[10]. Therefore the precipitates are washed in dilute NH_4OH solution with $p^H \sim 8$. The remaining procedure of co-precipitation is similar to that of LSMO. The precipitates are subjected to TG analysis to examine the validity of proposed precipitation reactions and to determine the minimum required sintering temperature. Considering TG analysis the precipitates of $Ba(OH)_2$ and $TiO(OH)_2$ are subjected to the pre sintering process at 1473 K and the final sintering has been carried out at 1553 K for 4 hrs.

The nano powders of LSMO and BT are used to form composites using formulae of series 1 and series 2 as above. The Bi_2O_3 is used as sintering aid to lower the temperature of sintering and achieve higher levels of densification[8]. The composites are pressed in the form of pellets for further process of investigations. The composites are sintered at 1273 K for 8 hours. The HP4284A LCR-Q meter is used for the purpose of the measurement of dielectric constant and a custom built setup is used for the measurement of magneto-electric properties.

RESULTS AND DISCUSSION

XRD and particle size

The X-ray spectra of LSMO are observed to be in accordance with the standard data (ICDD card # 89-4461). The observed peak widths of X-ray spectra are used to determine the particle size using Williamson Hall method. The analysis shows that LSMO posses particle size of nearly 35 nm. The XRD spectrum of BT is observed to reproduce the JCPD data and earlier reports[11]. Here the particle size estimated using Williamson Hall method is observed to be nearly 120 nm. Therefore it appears that the hydroxide co-precipitation route could be used to produce nano scale ceramics. The particle size is also confirmed by using SEM pictures. Figure 1 shows the SEM pictures of LSMO,

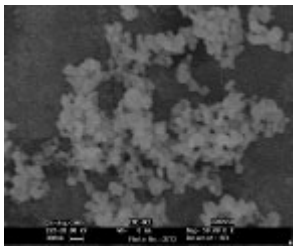

Fig. 1(a): SEM picture of LSMO

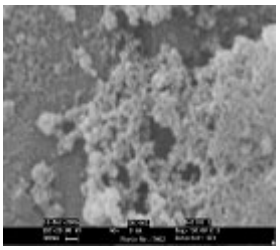

Fig. 1(b): SEM picture of BZT

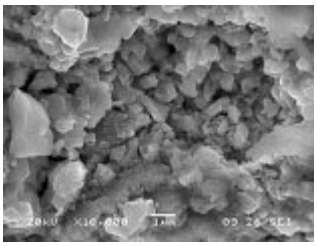

Fig. 1(a): SEM picture of COMP

BT and composite respectively

The XRD spectra on pellets of the composites are observed to show the reflections corresponding to both the LSMO and BT phases and confirm formation of the desired composite form.

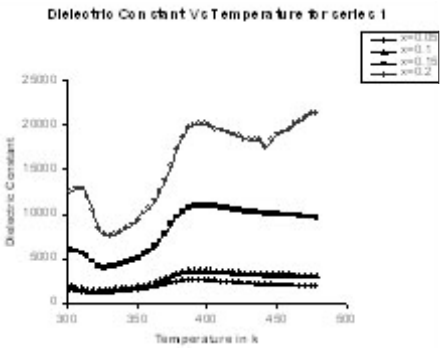

Fig. 2 : Variation of ε_r with Temperature of series 1 at f= 1 KHz.

Fig.2 shows the variation of the dielectric constant ε_r, at excitation frequency f = 1 KHz, as a function of T for series 1. The overall behavior for series 2 also is similar to these observations except for the magnitude of ε_r. It is observed that the ε_r, ε_{rmax} (the maximum value of ε_r at $T=T_c$) and Q for series 2 are lower as compared that of series 1. Now, the features common for series 1 and series 2 could be summarized as (i) the ε_r passes through a diffused phase transistion (DPT) at T ~ 387 K, (ii) for frequencies less than 100 KHz, the ε_r shows possibility of another DPT for T ~ 300 K or less, but for f = 100 KHz and 1 MHz, ε_r do not show any significant DPT behavior in this temperature range as shown in fig. 1 and (iii) The ε_{rmax} is observed to increase with increasing x, while the Q reduces with increasing x.

The frequency variation of å$_r$ shows a characteristic behavior indicating a presence of interfacial/space charge polarization. Fig. 3 shows variation of ε_r as a function of T for varying f for *x* = 0.15 of series 2. From fig. 3 it could be seen that the

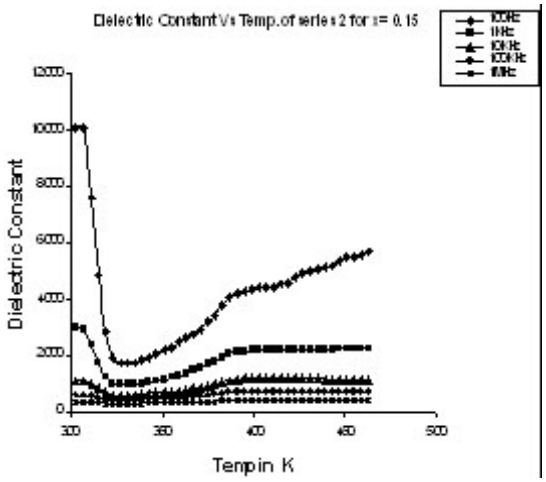

Fig. 3 Variation of ε_r with Temperature of series 2 for x= 0.15.

ε_r and ε_{rmax} reduce sharply with increasing f. The behaviour for other compositions is observed similar to the one shown in fig. 3.

These observations of ε_r could be understood by assuming two contributions to the $\varepsilon_{r,}$ one due to the parent BT particles and other due to interfacial/space charge polarization at grain boundaries of LSMO and BT, occurring because of very large difference in the conductivities of these two sub-systems. A DPT that is seen near room temperature is significant only at low frequencies (f <10 KHz) and for *x* > 0.15. This feature could be attributed to a small percentage of impurity phases at grain surface of BT (2).

For the measurements of longitudinal magnetoelectric coefficient α_{33}, the samples are polled at an electric field of 1.5 KV/cm for 8 hours, which is sufficient to poll the BT particles. The α_{33} is

Table 1: The values of α_{33} for series 1 and 2

X	α_{33} in m V/cm/oes.			
	0.05	**0.1**	**0.15**	**0.2**
Series 1	1.35	1.56	1.87	3.88
Series 2	4.55	2.847	2.606	1.14

measured at 800 Hz, with zero dc bias fields, using a laboratory scale setup. Table I shows the observed values of a_{33} for series 1 and series 2.

It is observed that α_{33} is higher for composites of series 2 as compared to corresponding composites of series 1 except for x=0.2. The observed magnitudes of α_{33} are within the range of values reported earlier for composites of ferrite-BT and LSMO-PZT (1, 2).

Conclusions

Hydroxide co-precipitation route has been successfully used for synthesis of nanocrystalline LSMO and BT powders. To form dense composites of LSMO-BT at lower temperatures (1273 K), Bi_2O_3 could be used as a sintering aid. The preliminary investigations on ε_r and α_{33} indicate that LSMO-BT composites will also posses a useful figure of merit for the device applications of ME materials.

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