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Synthesis and characterization of $La_{0.7}Sr_{0.3}MnO_3$ and $PbZr_{0.5}Ti_{0.5}O_3$ nanopowders using hydroxide Co-precipitation route

D.J. SALUNKHE, S.S. VEER, 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 reports details on synthesis of nanopowders of $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) and $PbZr_{0.5}Ti_{0.5}O_3$ **(**PZT) via hydroxide co-precipitation route. The method is found advantageous in respect of possibilities of chemically stabilizing the average valences of the divalent Mn ions in the LSMO product. Further the hydroxide precipitates are subjected to the thermo gravimetric studies to understand the temperature of the desired phase formation. It is observed that the single phase LSMO and PZT nanopowders could be synthesized at lower temperatures with average particle size of ~ 35nm and 50 nm respectively using this method. The particle size is calculated using Williamson-Hall plots and confirmed using SEM pictures.

Key words: Nanopowders of $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) and $PbZr_{0.5}Ti_{0.5}O_3$ **(**PZT).

INTRODUCTION

The present paper deals with the synthesis of nanoparticles of $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) and $PbZr_{0.5}Ti_{0.5}O_3$ **(**PZT) for use as starting materials for formation of magnetoelectric composites. The literature indicates that the LSMO and PZT nano powders could be synthesized using sol-gel process, Pechini method and hydrothermal reaction[1-5]. These methods need either costly precursors or sophisticated reaction setups. Also yields of single batch are usually limited to 3 to 5 gms. Further, the hydroxide coprecipitation route is found to be a cost effective and scalable alternative over other methods of synthesis of nanocrystalline LSMO and PZT. Therefore, owing to the discussion above the present paper reports mainly studies on synthesis of LSMO and PZT via hydroxide co-precipitation route.

EXPERIMENTAL

Synthesis of LSMO

High purity (>99%) of $La(No_3)_3.6H_2O$, $Sr(NO_3)_2$, $MnCl_2.4H_2O$, $KMnO_4$ of AR grade are used as precursors for hydroxide co-precipitation. The weight proportions of $MnCl_2.4H_2O$ and $KMnO_4$ is selected to be 3.56: 1 so that the valances of the hydroxide residues of Mn in state 3+ and 4+ would be 7:3[1-3]. The NH_4OH has been used as a mineralizer. For complete mineralization of Sr, KOH has been used as additional mineralizer. The precipitates were thoroughly washed and dried under IR lamp. The dried precipitate has been subjected to pre and final sintering process at 950°C and 1200°C.

Synthesis of PZT

The nanopowder of PZT has been synthesized using a similar procedure, but employing $Pb(NO_3)_2$, $K_2OTi(C_2O_4)_2.2H_2O$ and $ZrO(NO_3)_2$ as precursors. NH_4OH appeared to be only mineralizer for the PZT. The precipitates are washed in NH_4OH at p^H between 8.7 to 10^5. To minimize the loss of PbO due to evaporation from the PZT matrix, during the process of sintering, the PZT was sintered at 850°C for 12 hours. The resulting PZT is observed to possess average particle size of 35nm.

RESULTS AND DISCUSSIONS

The dried precipitate is used for TGA, DTG and DTA investigations. Fig. 1 shows the TGA, DTG and DTA observations carried out using Rheomatic Scientific, 1500 STA setup. The TGA shows that there exist two discontinuities, one at 270°C and other at ~ 880°C. Additionally two separate segments of weight loss with different slopes are observed between 270°C and 880°C. The DTA indicates a continuous heat loss from nearly 200°C onwards. Here the first discontinuity in TGA could be attributed to the onset of conversion from hydroxide to the oxides. The process appears second order and continuous up to ~ 880°C. The total weight loss during this temperature interval is nearly equal to the theoretically expected weight loss of hydroxide to oxide conversion (18%). The weight gain at 880°C may correspond to the oxidation of Mn^{2+} yet not oxidized completely to state Mn^{3+} and formation of crystalline phase. The present observations are similar to the earlier observations on $La_{0.5}Sr_{0.5}MnO_3$ synthesized using Pechini method[4].

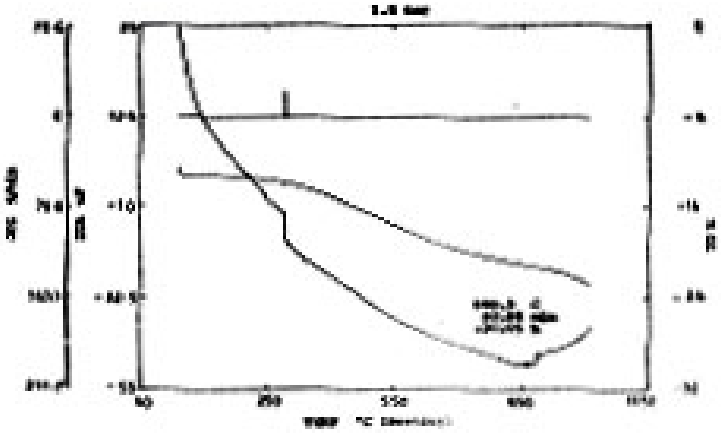

Fig. 1: TGA/DTG data for $La_{0.7}Sr_{0.3}MnO_3$

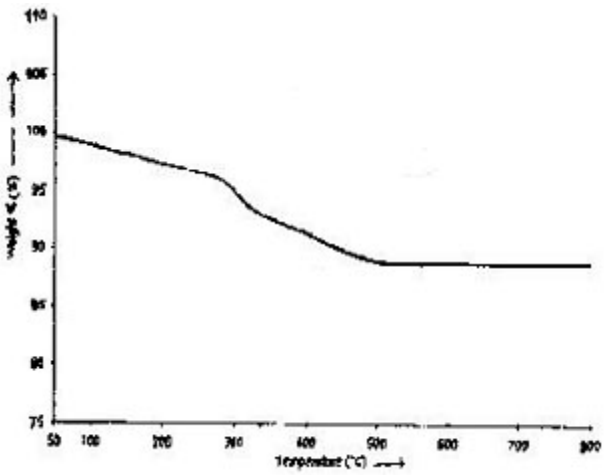

Fig. 2: TG analysis curve for PZT

The fig. 2 shows TGA data on PZT residue. The weight loss (~10.1%) is as expected from the precipitation reaction. It appears that PZT phase is formed at T ~ 600°C itself[4]. No additional weight loss is secures above 600˚C to 856°C. This observation is not in confirmation with the earlier report[5]. The present observation appears more legitimate as the boiling point of PbO is 856˚C[6].

The X ray diffractographs on the LSMO and PZT nanopowders are determined for the confirmation of phase formation and determination of the particle size. The x ray investigations show that no LSMO phase formation occurs at room temperature, while the XRDs at 950°C and 1200°C indicate complete phase formation at 950°C itself, without any additional crystalline phase and reproduce JCPD standard data of LSMO. The particle size is determined by making use of Williamson Hall (W-H) plot. The particle size for sintering at 1200˚C is nearly 35 nm. The W-H plot shows that no additional strains are present in the LSMO particles. The XRD spectra of PZT shows a tetragonal crystal structure with c/a = 1.028 as expected for the selected composition[6]. The particle size for PZT is also determined using W-H method and it is observed to be ~50 nm.

SEM studies are performed on LSMO and PZT to confirm formation of nanocrystalline powder. Figs. 3 and 4 show SEM picture of LSMO and PZT powder dispersed in ethanol. It is observed that the

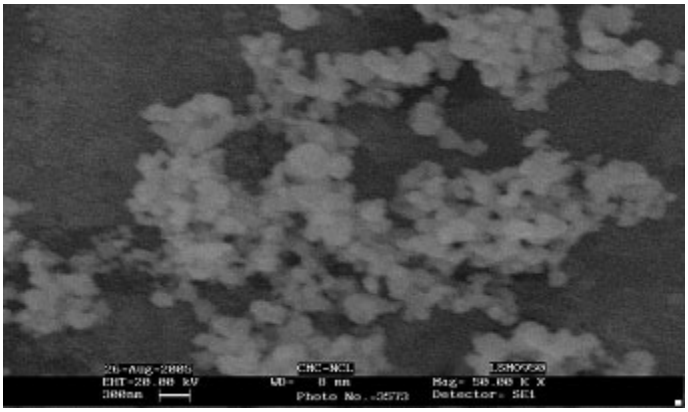

Fig. 3: SEM LSMO powder sintered at 950°C

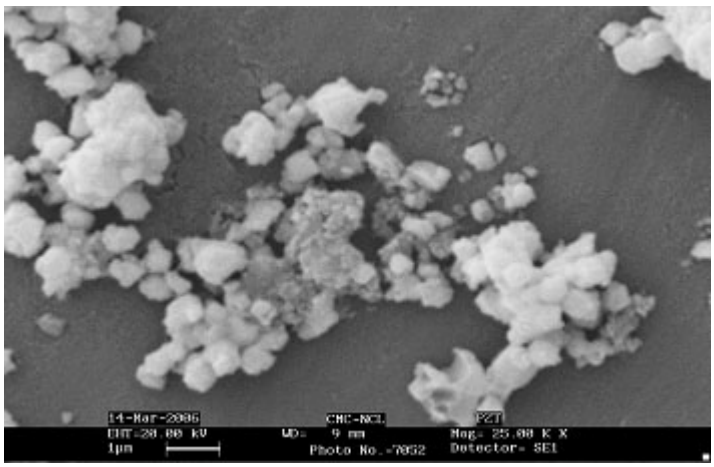

Fig. 4: SEM of PZT sintered at 1200°C

particles of LSMO are well dispersed and possess average particle size of nearly 35 nm as determined from the W_H method. The PZT on the other hand could not be dispersed completely and the fig. 4 shows aggregates of the PZT particles possessing average size of 150 nm, as against the 50 nm particle size determined using W-H method.

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