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Synthesis of pyrochlore free PMN-PT powder by partial oxalate process route

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Abstract

Pyrochlore phase free PMN-PT powder of morphotrophic phase boundary (MPB) composition has been prepared using the partial oxalate method. The synthesis process has been optimized by thorough characterization of the intermediate compounds such as columbite and $(Mg_{1/3}Nb_{2/3})_{0.675}\ Ti_{0.325})O_2$ by XRD analysis, particle size analysis, surface area measurement and morphological studies. Lead oxalate produced by *in situ* precipitation in a suspension of $(Mg_{1/3}Nb_{2/3})_{0.675}Ti_{0.325})O_2$ powder expected to coat on the particle surface, which improved the homogeneity of the precursors and resulted in the formation of pure PMN-PT phase during calcination at 750 °C. The PMN-PT powder contains more than 95% submicron particle with D_{50} 0.4 μm. The process eliminates the formation of detrimental pyrochlore phase from the PMN-PT powder.

Keywords: A. Calcination; PMN-PT; Powder; Synthesis

1. Introduction

Lead magnesium niobate $(Pb(Mg_{1/3}Nb_{2/3})O_3)$ is a relaxor ferroelectric material having a perovskite structure [1–7]. The comprehensive review of the synthesis and dielectric properties of lead magnesium niobate is reported elsewhere [8]. Lead magnesium niobate forms a solid solution with lead titanate [PMN-PT] for a reported morphotrophic phase boundary (MPB) in the composition range of 32–35 mol% of PT [9–11]. The PMN-PT compositions near the MPB exhibit superior dielectric and piezoelectric properties and a Curie temperature of 160–175 °C [12,13]. The piezoelectric properties in this region are better than those of the best compositions of PZT. Owing to the excellent dielectric and electromechanical properties, the piezoelectric PMN-PT is a better substitute for PZT in many actuator and sensor applications [14,15]. The PMN-PT in the form of single crystals and thin films has been used for MEMS/NEMS, smart structures, multi layer actuators (MLA) for active vibration control and noise cancellation. It also finds application in micro and nano positioning, chip manufacturing and testing, semiconductor equipment, telecommunication, laser tuning, precision mechanics and piezomotors [16–18]. Piezocomposites with PMN-PT elements in the form of micro and nanofibers (dense/hollow/transparent) have been used for high frequency ultrasonic transducers in high resolution medical imaging, energy harvesting, microfluidic pumping and modulators [19–21].

Formation of pyrochlore phase which decreases the dielectric constant of the materials is the main problem observed in the synthesis of PMN-PT. Much effort has been made by the researchers to eliminate the pyrochlore phase during synthesis but most of them leave residual pyrochlore phase in the sintered product [22,23]. Conventionally, PMN-PT powder has been synthesized by the solid state (columbite precursor) mixed oxide method [24–26]. Soft mechanochemical pulverization, sol–gel method, KCl molten salt method, hot pressing, and B-site precursor method have also been reported for synthesis of PMN-PT [27–31].

Partial oxalate route is a well known method for preparation of lead based electro-ceramics. The method has been successfully used for the synthesis of PZT, PLZT and lead magnesium niobate (PMN) [32–35]. Santos et al. [36] reported a partial oxalate method for preparation of pure nano PMN-PT particles. In this process, crystalline magnesium niobate and amorphous lead titanate powders were coated with required amount of lead oxalate followed by calcination to form the

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PMN-PT. In the present paper, we report preparation of PMN-PT powder by coating $(Mg_{1/3}Nb_{2/3})_{0.675}Ti_{0.325})O_2$ powder, prepared from columbite and titania, with lead oxalate followed by calcination. The primary composition used in this present study is 0.675PMN-0.325PT for which maximum piezoelectric properties has been reported by Choi et al. [37]. The PMN-PT powder free of pyrochlore phase could be prepared with excellent reproducibility by this partial oxalate method.

2. Experimental

Analytical reagent grade magnesium carbonate (Thomas Baker India, 98.5%) niobium pentoxide (Merck Germany, 99%), titanium dioxide (Merck Germany, 99%), lead nitrate (Merck Germany, 99.5%) and oxalic acid (Merck Germany, 99.95%) were used as starting materials. Flow diagram for the preparation PMN-PT powder by the partial oxalate method is shown in Fig. 1. The stoichiometric amounts of $MgCO_3$ and Nb_2O_5 were mixed in methanol for 6 h by planetary ball milling (RETSCH, PM400, Germany) and then dried at 120 °C in an oven. The mixture was calcined at 1100 °C for 4 h in a muffle furnace. The columbite powder thus obtained was sieved through 150 mesh. The columbite powder was then mixed with required amount of titania by planetary ball milling for 6 h. The columbite–titania powder mixture was calcined at 1100 °C for 4 h to form $(Mg_{1/3}Nb_{2/3})_{0.675}Ti_{0.325})O_2$ (MNT). The MNT powder was sieved through 150 mesh. The lead oxalate coating procedure reported in the literature for preparation of PZT, PLZT, PMN is adopted here for coating of MNT particles with lead oxalate [30–32]. The MNT powder was dispersed in a 2 M oxalic acid solution by stirring mechanically for 2 h to form a 15 wt% suspension. Required amount of lead in the form of 1.5 molar aqueous solution of $Pb(NO_3)_2$ was added drop wise to the MNT powder suspension in the oxalic acid solution under stirring. The molar ratio of lead nitrate to oxalic acid used was 1:1.5. After completion of the addition of the lead nitrate, the suspension was stirred mechanically for another 3 h to ensure complete coating of lead oxalate over MNT particles. The coated MNT powder was washed several times with distilled water and then with methanol before separation by filtration. The oxalate coated MNT was dried at 120 °C and then calcined at 750 °C for 4 h. The calcined powder was crushed and attrition milled (Union Process Model-01 HD, USA) using methanol as a milling medium for 12 h. The powder obtained by evaporating off the methanol in an oven was calcined again at 750 °C for 4 h.

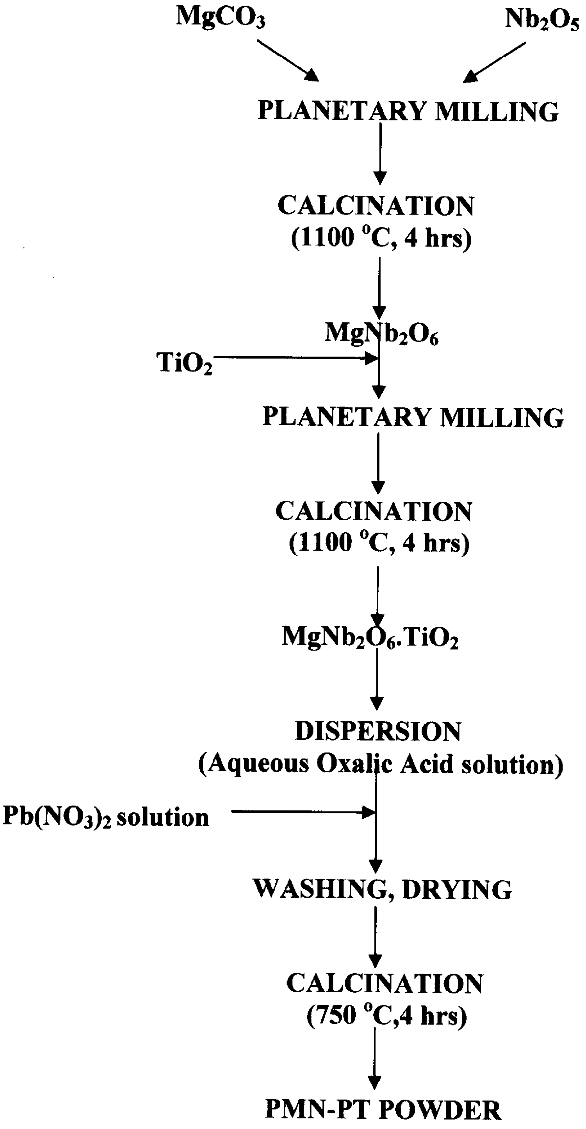

Fig. 1. Flow diagram for the preparation PMN-PT powder by the partial oxalate method.

The MN, MNT and PMN-PT powders were characterized for phase formation by XRD (Philips, Netherlands) analysis using Cu Kα radiation. The surface area (Sorptomatic 1990, Thermo Fennigan, Italy) and particle size (Malvern Master Size Analyzer 2000, UK) analysis of the powders were carried out. The morphology of the MN, MNT, and PMN-PT powders were observed using a scanning electron microscope (LEO 1455, UK).

3. Results and discussion

The magnesium carbonate–niobium pentoxide mixture prepared by planetary ball milling produced magnesium niobate (columbite) on calcination at 1100 °C for 4 h. Fig. 2

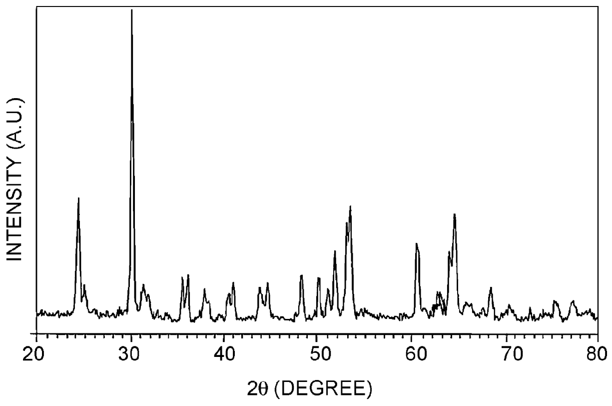

Fig. 2. XRD spectrum of magnesium niobate.

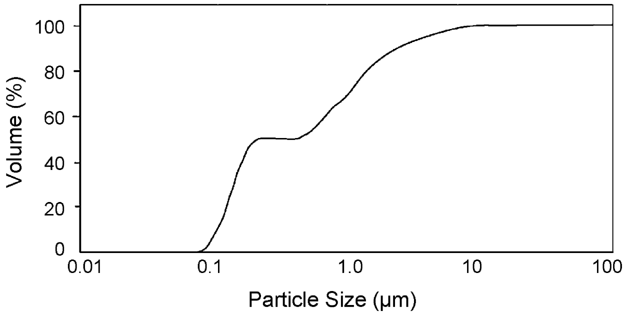

Fig. 3. Particle size distribution of the magnesium niobate powder.

shows XRD spectrum of the columbite. No peak other than the columbite peaks is observed in the XRD spectrum indicating the formation of phase pure columbite. The surface area of the columbite powder is 3.9 m^2/g. Fig. 3 shows the particle size distribution of the columbite powder. The columbite powder contain particles with size in the range of 0.1–10 μm with D_{50} value of 0.43 μm. More than 90% of the particles are having size less than 2.7 μm. Fig. 4 shows the SEM photograph of the columbite powder wherein the particles are having near spherical shape.

Fig. 5 shows XRD spectrum of the $(Mg_{1/3}Nb_{2/3})_{0.675}Ti_{0.325})O_2$ obtained by calcinations of columbite–titania powder mixture at 1100 °C. Suh et al. [31] reported the difficulty of complete solid solution formation of columbite and TiO_2 due to their dissimilar crystal structure. The XRD spectrum of the columbite–titania mixture calcined at 1100 °C showed peaks corresponding to the columbite and titania along with peaks corresponding to the phase obtained by Ti substitution of $Mg_{1/3}Nb_{2/3}$ complex as observed by Suh et al. [31]. The surface area measurement of the $(Mg_{1/3}Nb_{2/3})_{0.675}Ti_{0.325})O_2$ showed a value of 1.3 m^2/g. The SEM study indicated that the powder contain aggregate of fine particles. Particles with near spherical geometry can be clearly seen on enlarged version of single agglomerate. Fig. 6A and B shows SEM photograph of the $(Mg_{1/3}Nb_{2/3})_{0.675}Ti_{0.325})O_2$ powder. Particle size analysis of the $(Mg_{1/3}Nb_{2/3})_{0.675}Ti_{0.325})O_2$ shows that the powder contain particles in the size range of 0.09–11.5 μm with a D_{50} value of 0.177 μm. Only 10% of the particles are having size more than 5 μm. This indicates that the agglomerates observed in SEM could easily be broken in to primary particles by stirring in water medium. Fig. 7 shows particle size distribution of the $(Mg_{1/3}Nb_{2/3})_{0.675}Ti_{0.325})O_2$ powder.

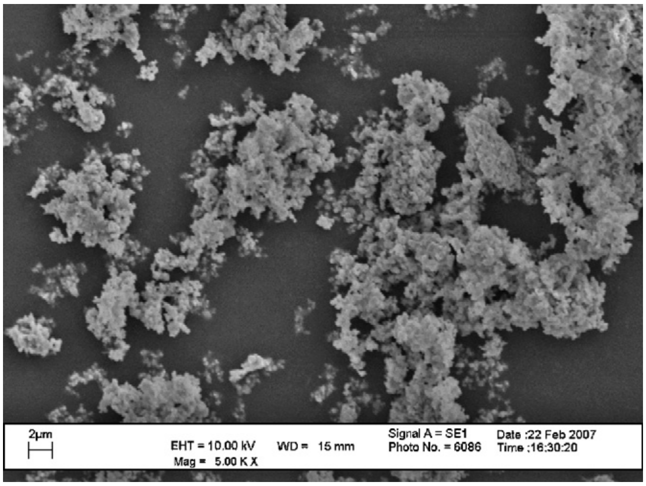

Fig. 4. SEM photograph of the magnesium niobate powder.

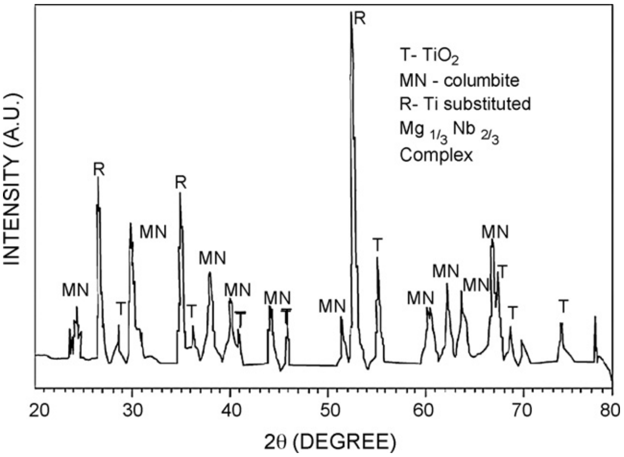

Fig. 5. XRD spectrum of the $(Mg_{1/3}Nb_{2/3})_{0.675}Ti_{0.325})O_2$ powder.

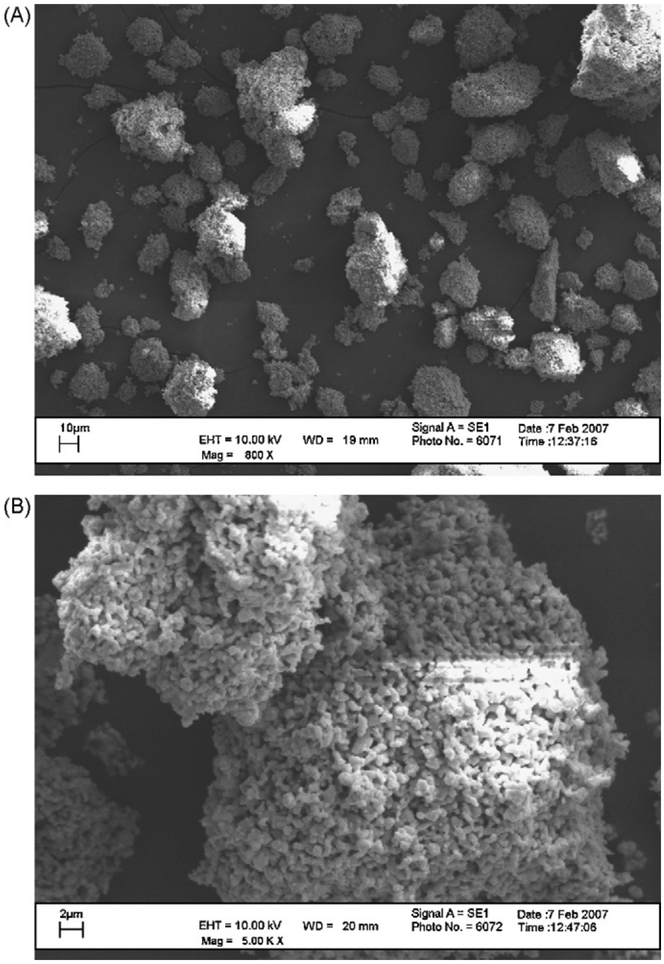

Fig. 6. SEM photograph of the $(Mg_{1/3}Nb_{2/3})_{0.675}Ti_{0.325})O_2$ powder (A) agglomerate of particles (B) enlarged version of a single agglomerate.

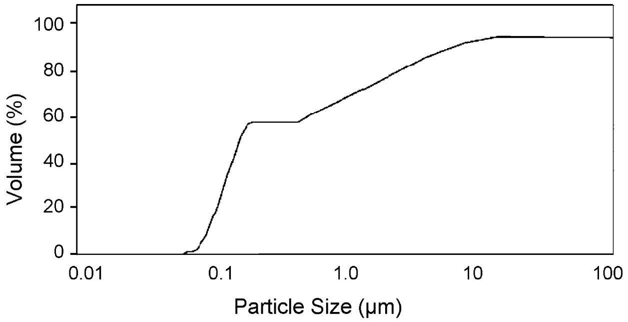

Fig. 7. Particle size distribution of the $(Mg_{1/3}Nb_{2/3})_{0.675}Ti_{0.325})O_2$ powder.

It is well known that oxalic acid and lead nitrate react to form lead oxalate precipitate. It is expected that when lead nitrate solution is added to the dispersion of $(Mg_{1/3}Nb_{2/3})_{0.675}Ti_{0.325})O_2$ powder in oxalic acid the lead oxalate precipitate form a coating on the $(Mg_{1/3}Nb_{2/3})_{0.675}Ti_{0.325})O_2$ particle surface [30–32]. Fig. 8 shows TGA plot of the lead oxalate coated $(Mg_{1/3}Nb_{2/3})_{0.675}Ti_{0.325})O_2$ powder. The thermogram showed complete burnout of the organics at temperature below 620 °C. Nearly 20% weight loss was observed in the temperature range of 340–390 °C. Further 2% weight loss was observed in the temperature range of 390–620 °C. It appears that decomposition of oxalate at temperature below 390 °C leave some carbon residue that burn off in the temperature range of 390–620 °C.

Though the TGA shows complete weight loss at 620 °C the lead oxalate coated $(Mg_{1/3}Nb_{2/3})_{0.675}Ti_{0.325})O_2$ powder on calcination at 750 °C for 4 h showed slight black color after attrition ball milling. This indicates the presence of traces of carbon residue within the particle aggregates that got exposed during the deagglomeration. Therefore, the deagglomerated powder is further calcined at 750 °C for another 4 h to remove the carbon residue. The XRD spectrum of the calcined powder completely matching with the JCPDS standard for perovskite PMN-PT phase. Fig. 9 shows XRD spectrum of the PMN-PT powder. Surface area of the PMN-PT powder was 3.08 m^2/g. The PMN-PT powder contain particle in the size range of 0.05–6 μm with a D_{50} value of 0.40 μm. Nearly 95% particles are in the submicron range. Fig. 10 shows particle size distribution of the PMN-PT powder. SEM analysis of the PMN-PT powder indicated that the particles are having near spherical shape. Fig. 11 shows SEM photograph of the PMN-PT powder.

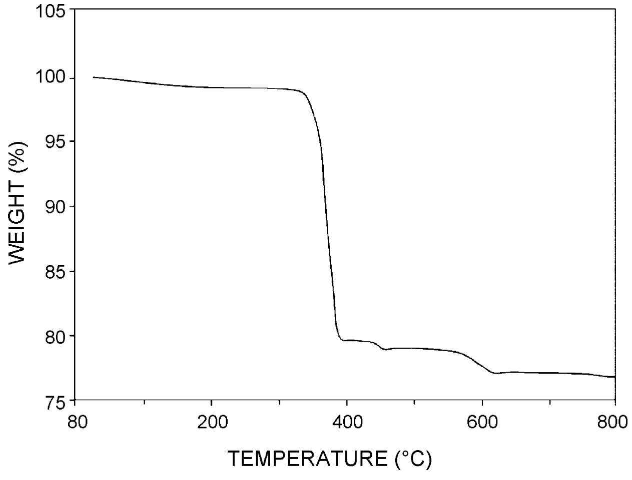

Fig. 8. TGA plot of the lead oxalate coated $(Mg_{1/3}Nb_{2/3})_{0.675}Ti_{0.325})O_2$ powder.

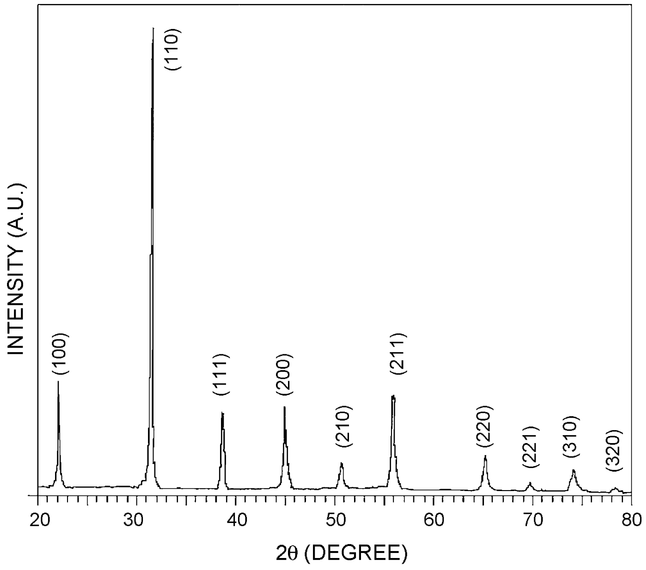

Fig. 9. XRD spectrum of the PMN-PT powder.

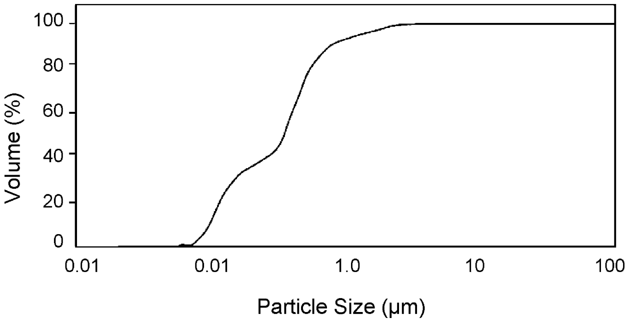

Fig. 10. Particle size distribution of the PMN-PT powder.

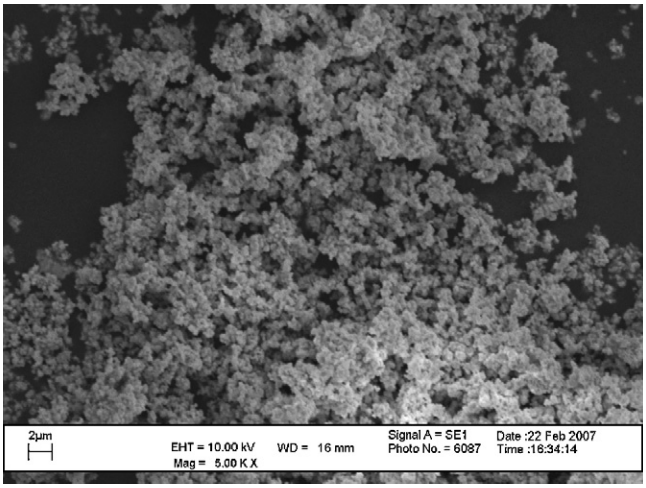

Fig. 11. SEM photograph of the PMN-PT powder.

It is well known that formation of pyrochlore phase is the main problem associate with the synthesis of PMN-PT powder. The formation of pyrochlore is a result of the poor reactivity of the starting material [38]. Also, the pyrochlore forms readily whenever there is a considerable deviation of Mg/Nb ratio from the stoichiometry and lead deficiency [39]. Therefore, the reaction of MgO with Nb_2O_5 to form the columbite without leaving unreacted MgO and Nb_2O_5 has to be ensured. It is worthy to note that in the present case, the product is fully free from the detrimental pyrochlore phase The XRD spectrum did not show any peak corresponding to the pyrochlore phase. This indicates the better control over the achieved Mg/Nb stoichiometric ratio and higher reactivity due to uniform coating of lead oxalate on $(Mg_{1/3}Nb_{2/3})_{0.675}Ti_{0.325})O_2$ particles.

4. Conclusion

PMN-PT powder of morphotrophic phase boundary (MPB) composition has been prepared using the partial oxalate method. Coating of lead oxalate on the $(Mg_{1/3}Nb_{2/3})_{0.675}Ti_{0.325})O_2$ particles resulted in higher homogeneity of the precursors and resulted in phase pure PMN-PT on calcination at 750 °C. The process eliminates the detrimental pyrochlore phase from the PMN-PT. The PMN-PT powder prepared contains more than 95% submicron particles with D_{50} value of 0.4 μm.

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