

INFLUENCE OF Pb ON SOL-GEL SYNTHESIS OF PFN PRECURSORS

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Abstract

Lead iron niobate $Pb(Fe_{0.5}Nb_{0.5})O_3$ (PFN) precursors were prepared using sol-gel synthesis by mixing acetates Pb and Fe with Nb-ethylene glycol-tartarate (Pechini) complex at 80°C and calcination of gels at 600°C. Single pyrochlore phase with structure close to $Pb_3Nb_4O_{13}$ was formed in the stoichiometric precursor. Nonstoichiometric gel with excess of Pb in molar ratio (Pb:Fe:Nb = 1.2:0.5:0.5) was transformed to a two phase system of PFN powder with major pyrochlore $Pb_3Nb_4O_{13}$ phase and a small amount of the perovskite $Pb(Fe_{0.5}Nb_{0.5})O_3$ phase. Average particle sizes of PFN calcined powders were ~ 120 nm.

Keywords: Pechini complex, sol-gel, calcination, PFN precursor, pyrochlore, perovskite phase

INTRODUCTION

Lead iron niobate $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN) is synthesized by various wet chemical processing routes such as sol-gel [1], semi-wet hydroxide [2] and coprecipitation [3]. The Pechini method is based on the formation of metallic complexes (Nb complex) with carboxylic acid as ligand, followed by a polymerization reaction with a polyalcohol generating polyester. Besides the sol-gel synthesis, the calcination temperature and pyrolysis conditions influence the formation of the final perovskite phase. Fine lead iron niobate powders with average particle size of 500 nm were prepared by the precipitation of Nb precursor in solution [3].

Excess of Pb in the sol-gel process compensates the evaporation of PbO during sintering of PFN ceramics [1]. The pyrochlore phase is first formed at 500°C and the perovskite phase begins to appear above 500°C. It is very difficult to fabricate the pure perovskite ABO_3 (pv) PMN and PFN phases without the formation of the undesirable pyrochlore $A_2B_2O_6$ (py) phase, which degrades the physical properties of ceramics.

The present paper describes the preparation of PFN precursors using sol-gel synthesis by mixing acetates Pb and Fe with Nb-ethylene glycol-tartarate complex. The influence of excess Pb on the phase composition and average particle sizes of PFN powders calcined at temperature of 600°C for 2 hours are reported.

EXPERIMENTAL

The niobium precursor solution for $Pb(Fe_{0.5}Nb_{0.5})O_3$ (PFN) synthesis has been prepared by Pechini-type polymerizable complex method [4]. The acetate solutions of Pb and Mg were mixed at 80°C with the Pechini Nb-complex to obtain the organic mixtures (sols) with molar ratio of Pb:Fe:Nb = 1:0.5:0.5 or 1.2:0.5:0.5 (stoichiometric and nonstoichiometric PFN) [4]. Viscous PFN gels were calcined at 600°C for 2 hours.

The phase composition of PFN precursors was analysed by the X-ray diffraction technique (XRD, a model Philips X Pert Pro) using $\text{CuK}\alpha$ radiation. The size and morphology of powder particles were observed using a scanning electron microscope (SEM, TESLA BS 340 model) and by a transmission electron microscopy (TEM, TESLA BS 500 model).

RESULTS AND DISCUSSION

Using the sol-gel synthesis, two different types of $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ (PFN) precursors were prepared with molar ratio of $\text{Pb}:\text{Fe}:\text{Nb} = 1:0.5:0.5$ or $1.2:0.5:0.5$ (stoichiometric and nonstoichiometric PFN). Table 1 summarizes the properties colours and efficiency of PFN powders (denoted as 1 and 2), where efficiency $w = (x/y) \times 100$, x is mass of obtained powder after calcination of gel and y is the theoretical mass of powder phase according to initial stoichiometry of PFN.

Tab.1. The properties (colors and efficiency w [wt.%]) of the $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ (PFN) powders obtained sol-gel synthesis.

sample	type of PFN	mole ratio Pb:Fe:Nb	sol at 80°C	gel at 25°C	dried gel at 100°C	powder at 600°C	w^* [wt.%]
1	stoichiometric	1:0.5:0.5	red	orange	green	red	42
2	nonstoichiometric	1.2:0.5:0.5	brown	yellow	beige	brown	48

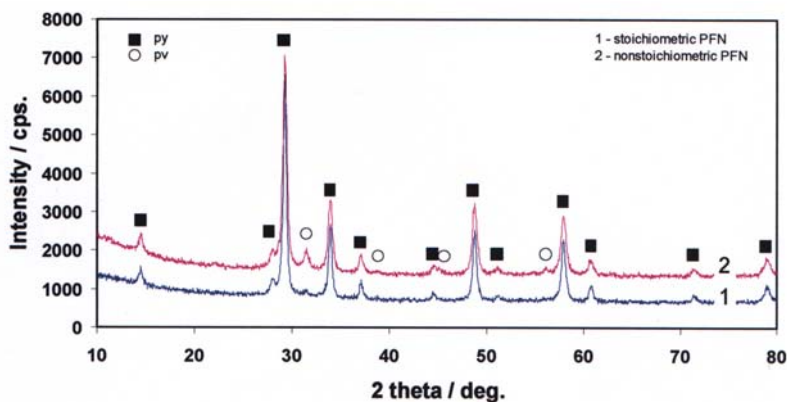


Fig.1. XRD diffractograms of the PFN powders calcined at 600°C: stoichiometric PFN (sample 1) and nonstoichiometric PFN (sample 2).

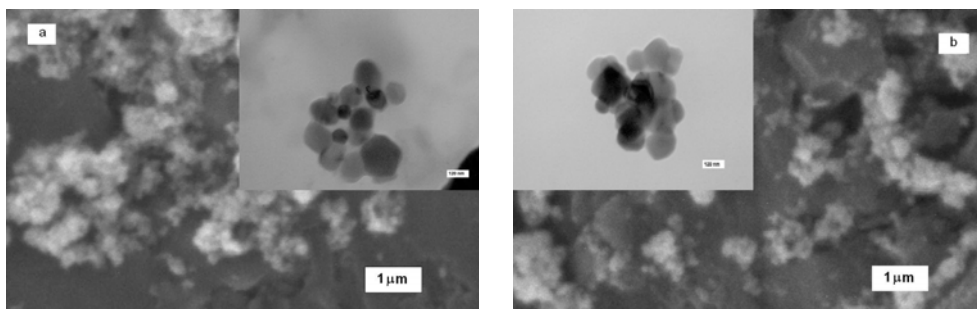


Fig.2. REM and TEM micrographs of the calcined PFN powders: (a) stoichiometric (sample 1) and (b) nonstoichiometric (sample 2), (bar (TEM micrographs) = 120 nm).

The SEM and TEM images of calcined powders (samples 1 and 2) are shown in Figs.2a,b. The particles have almost spherical shape with the particle size between 100-130 nm in both PFN precursors. Excess of Pb caused wrapped core-shell structure [3] in the powder with fine particles.

CONCLUSION

$\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ (PFN) precursors were prepared using sol-gel synthesis by mixing acetates Pb and Fe with Nb-ethylene glycol-tartarate (Pechini) complex at 80°C and calcining of gels at 600°C.

The pyrochlore phase with structure close to pure pyrochlore $\text{Pb}_3\text{Nb}_4\text{O}_{13}$ phase was created by the calcination of stoichiometric PFN gel. Nonstoichiometric gel with excess of Pb in molar ratio (Pb:Fe:Nb = 1.2:0.5:0.5) was transformed into two phase system with major pyrochlore $\text{Pb}_3\text{Nb}_4\text{O}_{13}$ phase and a small amount of the perovskite $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ phase. Average size of particles in PFN calcined powders were ~ 120 nm.

Acknowledgement

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REFERENCES

- [1] Jenhi, M., Ghadraoui, EHE., Balli, H., Aatmani, ME., Rafiq, M.: *Annal. Chim. Science. Mater.*, vol. 23, 1998, p. 151
- [2] Mohan, D., Prasad, R., Banerjee, S.: *Ceram. Int.*, vol. 27, 2001, p. 243
- [3] Tang, J., Zhu, M., Zhong, T., Hou, Y., Wang, H., Yan, H.: *Mater. Chem. Phys.*, vol. 10, 2007, p. 475
- [4] Bruncková, H., Medvecký, L., Mihalik, J.: *Eur., Ceram. Soc.*, vol. 28, 2008, p. 123
- [5] Chiu, CC., Desu, SB.: *Mater. Science Engen, B*, vol. 26, 1993, no. 2