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Journal of the European Ceramic Society 24 (2004) 1041–1044
www.elsevier.com/locate/jeurceramsoc

Fabrication of transparent lead lanthanum scandium niobate ceramics by two-stage atmosphere sintering

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Abstract

Transparent lead lanthanum scandium niobate (PLSN) ceramics were fabricated from fine powders using a two-stage atmospheric sintering technique. A method for preparing clear aqueous solutions with lead, lanthanum, scandium and peroxo–niobium complex ions has been developed by mixing a niobium precursor solution with the corresponding nitrates. The coprecipitation process of the solution produced chemically homogeneous powders. Biaxially pressed green pellets were sintered in an oxygen gas in an alumina setter containing an atmosphere powder at 1100 °C and were then reheated in air. Transparent ceramics with an average grain size of 0.54 μm was obtained.

Keywords: Niobates; Perovskite; Powder-chemical preparation; Optical properties; Sintering

1. Introduction

Pb-containing relaxor ferroelectrics are interesting alternative high permittivity materials as they possess broadened phase transitions, high dielectric constants over a wide temperature range, and comparatively low firing temperatures.[1] The lead lanthanum scandium niobate ($Pb(Sc_{0.5}Nb_{0.5})O_3$, PSN) compound with a rhombohedral perovskite structure was first prepared by Smolenskii et al.[2] as part of a synthesis program for the general formula A_2^{2+} (B_I^{3+} B_{II}^{5+}) O_6 series. They reported that the PSN is a ferroelectric relaxor material with a diffuse maximum at 90 °C in the dielectric constant measured from a ceramic sample. In the X-ray diffraction pattern of their PSN samples, Ismailzade[3] found a partially ordered arrangement of Sc and Nb cations. Stenger and Burggraaf[4] reported that this ordering can be varied by suitable annealing and the degree of ordering strongly affects the character of the ferroelectric–paraelectric phase transition. Dambekalne et al.[5] reported an improved technology for the fabrication of transparent materials for optoelectric devices, PSN, PSN–$Pb(Zn_{1/3}Nb_{2/3})O_3$, and PSN–$Pb(Mg_{1/3}Nb_{2/3})O_3$ obtained by them in 1973–1980. It was a combination of a two-step calcination and hot pressing. 0.9PSN–0.1PZN and 0.7PSN–0.3PMN had the best transmittance value of 50% while pure PSN had a transmittance of 43% for 628 nm light. They also reported only the hot pressing techniques could provide transparent ceramics. Recently, Dambekalne et al.[6] doped lanthanoids elements (Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Tm, Yb and Lu) into the PSN ceramics. The best characteristics have been obtained in the case of PSN + 1 wt.% Lu_2O_3 (1060 °C), having a transmittance which was only slightly less compared to pure PSN (1350 °C). All the rare-earth dopants decreased the temperatures of the hot pressing.

Conventional routes for fabricating such transparent ceramics involve preparing the powders by the solid-state reactions of mechanically mixed oxides above 1000 °C with subsequent milling, packing and hot-pressing. Often, however, undesirable impurities are introduced during the repeated millings and firings of the powders required to complete the reactions. Moreover, steps involving high temperature tend to produce chemically nonhomogeneous powders and non-homogeneous microstructures due to grain coarsening and the volatility of lead oxide. These problems make it impossible to reproduce the physical properties and lead to poor optoelectric characteristics. This suggests the importance of the chemical homogeneity of the powder and powder sinterability for low processing temperatures when fabricating high-quality ceramics. A chemical preparation method was developed for the synthesis

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0955-2219/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0955-2219(03)00547-8

of typical relaxor compounds from a nitrate solution.[7] The PSN precursor powders calcined at 800 °C for 1 h formed a single perovskite phase. The submicronmeter-sized powders would apparently allow a lower sintering temperature.

The purpose of the present study is to combine the chemically prepared fine powder with a two-stage sintering technique and fabricate high-quality, highly transparent PLSN ceramics at low cost.

2. Experimental

The raw materials used to prepare the aqueous nitrate mixtures were $Pb(NO_3)_2$, $Sc(NO_3)_3 4H_2O$, $La(NO_3)_3$ and a niobium precursor solution. The precursor solution was prepared as follows:[7] (1) Hydrated niobia were prepared from aqueous niobium oxalate solutions by hydrolysis with ammonia water. The resulting precipitate was washed with water and then dissolved in a nitric acid solution with hydrogen peroxide. It is an oxalate-free niobium precursor solution. Niobium will exist as peroxo-complex ions in the solution. (2) The concentration of nioba was determined by gravimetric analyses; (3) the solution was stored at 5 °C to avoid self hydrolysis.

Clear aqueous solutions (0.03 mol/l) of the composition Pb_{1-x} $La_x(Sc_{0.5}Nb_{0.5})O_3$ ($x = 0$–0.1) were prepared by mixing the niobium precursor solutions with the corresponding nitrates for subsequent precipitation. An excess of lead oxide PbO (0–20 wt.%) was added to the solution as lead nitrate to enhance the densification of the ceramics during sintering. The mixed solutions were hydrolyzed by pouring ammonia water into 1000 ml of the PLSN precursor solution. All the components were successfully precipitated from the precursor solutions by maintaining the final pH value of 10.5–10.6. The precipitates were washed with 500 ml of water and/or rinsed with acetone, and then dried at 80 °C for 12 h.

The as-dried powders were calcined at 800 °C for one hour and then wet ball-milled for 1 h. Pellets 1.3 cm in diameter and 0.1 cm thick were formed by biaxial cold-pressing at 0.29 GPa. The pellets were first sintered at 1100 °C for 12 h; the pellets were placed in a platinum crucible lined alumina setter. The platinum crucible was surrounded by atmospheric powder (0.2 mole rate of $PbO/PbZrO_3$). Oxygen flow into the furnace cavity was initiated when the furnace heat-up was started. To remove the free-lead oxide in the sintered bodies, the platinum crucible was replaced in another alumina setter and then reheated at 1100 °C for 10 h in air.

The as-dried, calcined powders and sintered samples were analyzed by powder X-ray diffraction (XRD) and observed by scanning electron microscope (SEM). The powders were also subjected to differential thermal analysis (DTA) and thermogravimetric analysis (TGA). The specific area was determined by the single point Brunauer–Emmett–Teller (BET) method.

3. Results and discussion

The coprecipitates prepared by hydrolysis were reddish-yellow and the XRD analysis revealed that they were amorphous. Table 1 shows the surface area, particle size and agglomerate state of the as-dried powders. The diameters of these particles of the as-dried powder which was rinsed with acetone were ranged 30 μm. The acetone-rinse was useful during the coprecipitated hydroxide gel washings to prevent the formation of a strong particle agglomerate. Density comparisons of calinced powders were made on the green compacts by identical processes (i.e., calcining at 800 °C, ball-milling, pressing, etc.) except for variations in washing, rinsing and drying procedures. An improvement in the green density of 2.9% was found. The weak agglomerates in the acetone-washed powder after calcination were broken down during ball-milling and compaction, as indicated by the higher density.

Fig. 1 shows the TGA–DTA curves for the as-dried PLSN powders (La = 5 at.%, excess PbO = 5 wt.%). The first endothermic peak, near 100 °C, is due to the removal of residual water. The exothermic peaks at 200–280 °C correspond to the exothermic pyrolysis of the acetone trapped inside the powders. A weight loss due to the pyrolysis of the organics and dehydration of the hydrated precipitates continued to 485 °C on the TGA curve and then an exothermic peak appeared at 507 °C on the DTA curve. An XRD analysis of the controlled samples that were heated to the exothermic peak was performed. The XRD pattern of the sample heated to 450 °C shows only a broad peak around $2\theta = 29°$, while a perovskite phase was detected for the powders quenched from 560 °C to room temperature (Fig. 2a and b). Thus, the exothermic effects essentially

Table 1
Characterization of as-dried powders and calcined powders

	BET specific surface area (m^2/g)	SEM observation		Green compact density (g/cm^3)
		Particle size (nm)	Agglomerate state	
Water-washed powder	130	30–200	Strong	5.42–5.58
Acetone-rinsed powder	150	25–35	Weak	5.58–5.74

show the heat of crystallization of the perovskite phase from the amorphous powders.

The as-dried powders were calcined at 800 °C for 1 h. An X-ray pattern of the calcined PLSN powders (La = 5 at.%, excess PbO = 5 wt.%) in Fig. 2c shows that a single perovskite phase could be readily obtained. This is a significantly lower processing temperature than that required for the conventional mixed oxide process. The percentage of the perovskite phase for the powders was determined from the relative intensities of the (110) perovskite peak and the (222) pyrochlore peak (Table 2). For the powders (excess PbO = 0 wt.%), a pyrochlore phase is seen when the solubility limit of La was exceeded. The addition of 5 wt.% excess PbO promoted the formation of the perovskite phase. However, the percentage of perovskite for the powders with 10 wt.% excess PbO was lowered again. This may be attributed to the preferential formation of lead niobate with the pyrochlore structure during the solid-state reaction kinetics. Densification in the present two-stage sintering technique is based on a rapid particle rearrangement in the liquid matrix during the first stage and removal of the liquid by vaporization during the second stage.[8] The first sintering thus must be set at a temperature at which the liquid stably exists. Lead oxide in calcined powders began to vaporize around 1000 °C.

PLSN pellets (La = 5 at.%, excess PbO = 0, 5 and 10 wt.%) were sintered. They were dull red after the first stage. During the early second stage, the residual lead oxide in the pellets was rapidly lost and later grains grew. Typical polished pellet with 5 wt.% initial excess lead oxide is shown in Fig. 3 and the density of the transparent pellets was ~7.81 g/cm^3. A microstructure obtained by SEM is shown in Fig. 4. The transmittances of sintered pellets (thickness 0.3 mm) for 0, 5 and 10 wt.% initial excess lead oxide were 2, 29 and 1%, respectively, for 600 nm wavelength. The pellets with 10 wt.% initial excess lead oxide were dense but translucent. The lower transparency indicated that the removal of liquid phase of lead oxide during the second stage was far from complete.

Some samples were fabricated without the addition of lanthanum. The powder processing was the same as that used for PLSN and the pellets containing 5 wt.% excess PbO. After the second stage, the pellets were yellow in color and opaque. Although the true crystal symmetry of the PLSN system could not be determined, it was assumed that the basic perovskite lattice of the materials is rhombohedral. The lattice spacing and parameters were obtained from the (201) and (211) values. Table 3 shows the lattice parameters and grain sizes of the ceramics from the PLSN and PSNs. The unit-volume of PLSN shrunk by the substitution of lanthanum ions

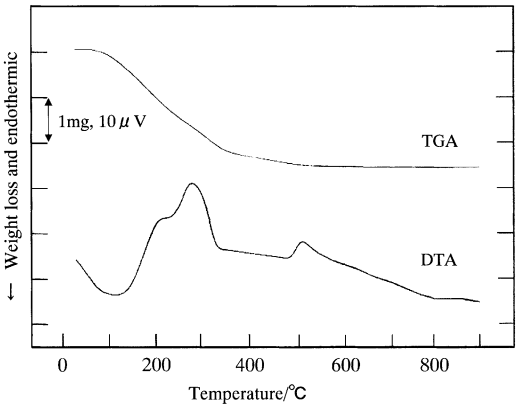

Fig. 1. Thermogravimetric analysis and differential thermal analysis of as-dried powders (La = 5 at.%, excess PbO = 5 wt.%) treated by rinsing with acetone. 54.5 mg of powder was measured at a heating rate of 10 °C /min in air.

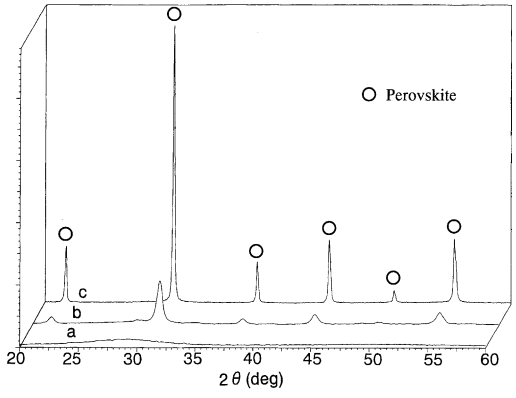

Fig. 2. X-ray diffraction patterns of calcined powders (La = 5 at.%, excess PbO = 5 wt.%): (a) quenched from 450 °C; (b) quenched from 560 °C; (c) calcined at 800 °C for 1 h.

Table 2
Percentage of perovskite phase for powders calcined at 800 °C for 1 h

Excess PbO (wt.%)	La (atm.%)				
	0	2.5	5	7	10
0	100	100	98.5	–	92.0
5	100	100	100	100	98.0
10	100	100	99.7	–	96.7

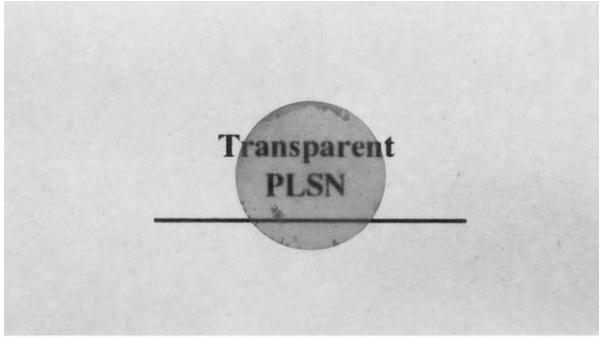

Fig. 3. Polished PLSN ceramics (La = 5 at.%, excess PbO = 5 wt.%), 11.2 mm in diameter and 0.5 mm thick.

Table 3
Lattice parameters and grain size

	La (at.%)	Excess PbO (wt.%)	Lattice parameter			Grain size (μm)
			α (degree)	a (nm)	Unit-volume (cm^3)	
PLSN	5	5	89.93±0.02	0.4078±0.0001	6.782×10^{-23}	0.54
PSN	0	5	89.94±0.02	0.4086±0.0001	6.822×10^{-23}	5.43
PSN	0	0	89.80±0.02	0.4088±0.0001	6.832×10^{-23}	0.33
PSN Ref. 10			89.88	0.40728	6.756×10^{-23}	
Ref. 4			89.89	0.4080	6.792×10^{-23}	

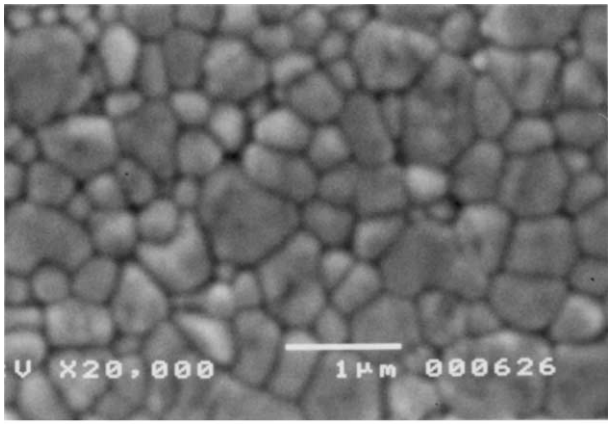

Fig. 4. Scanning electron micrograph of microstructure of PLSN ceramics (La = 5 at.%, excess PbO = 5 wt.%).

with lead ions in the A sites. Also the addition of excess PbO or lanthanum converted the rhombohedral structure of PSN to a cubic structure.

The grain size of the PSN ceramics was as large as the particle size in the calcined powders and was the smallest of the three kinds of ceramics. There were many large pores in the PSN ceramics. On the other hand, the grain size of the PSN from the powder with excess PbO is the largest, indicating the rapid rearrangement of the fine particles in the liquid matrix and increases in the particle contacts. The grain size of PLSN again significantly decreased. The grain growth rate was reduced when La is present. Similar grain-growth inhibition has been reported for $Pb(Zr,Ti)O_3$ doped with La^{3+} (A site).[9] After the removal of the liquid by vaporization for a long time (10 h) at 1100 °C during the second stage, the grains began to grow at the late of 0.02 μm/h.

4. Conclusions

Transparent lead lanthanum scandium niobate (PLSN) ceramics were fabricated from fine powders by a two-stage atmospheric sintering technique. The powders were prepared by hydrolysis from low-cost inorganic precursors. By using adequate postcoprecipitation processing, rinsing with acetone, nanometer-scaled coprecipitates were retained and the agglomeration state of the particles in the calcined powders was weak to enough to broken down by moderate milling. Upon calcination, the as-dried powders began to crystallize into a perovskite phase from an amorphous powder at 500 °C and yielded a 100% perovskite phase at a temperature as low as 800 °C. As long as the sinterable powders such as those in the present study are available, this two-stage sintering technique densified the powders to nearly theoretical values in an oxygen gas atmosphere at 1100 °C and transparent ceramics with an average grain size of 0.54 μm were obtained.

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