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Densification and anisotropic grain growth in $Sr_2Nb_2O_7$

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Sr : Nb stoichiometry and donor-doping with La were found to affect densification behavior and anisotropic grain growth in $Sr_2Nb_2O_7$ ceramics. La-doping improved the high temperature a.c. resistivity, but inhibits grain growth by grain boundary pinning. The presence of excess Nb was found to promote anisotropic grain growth by forming a liquid at the grain boundaries in both undoped and doped $Sr_2Nb_2O_7$. Anisotropic grain growth in La-doped $Sr_2Nb_2O_7$ can be controlled by incorporating large template particles in a Nb-rich matrix. High sintered densities (~98% of theoretical) were achieved in both undoped and La-doped samples. *© 2000 Kluwer Academic Publishers*

1. Introduction

$Sr_2Nb_2O_7$ has a ferroelectric Curie temperature of 1342°C and shows high temperature piezoelectric behavior in single crystal form which makes it a candidate for device applications in high temperature environments [1, 2]. Although piezoelectricity has been reported in single-crystal $Sr_2Nb_2O_7$, polycrystalline samples have never been successfully poled. This has been attributed to the low crystal symmetry which offers very few equivalent directions to thread the polarization across the bulk of the sample by the application of an electric field at low temperatures (<200°C) [3]. Also, a low sintered density, resulting from exaggerated grain growth, makes it impossible to apply large electric fields across the sample without causing dielectric breakdown in the pores. It is reasonable to propose that $Sr_2Nb_2O_7$ could be poled by fabricating dense, insulating polycrystalline $Sr_2Nb_2O_7$ with preferred grain orientation.

One approach to producing a textured ceramic is to take advantage of intrinsic anisotropic grain growth by templating the growth of oriented grains in a preferred direction. This technique, templated grain growth, depends on orienting single-crystal template particles in a fine-grained matrix to initiate and promote grain growth [4–7]. Potential applications and especially poling require the ceramic to be electrically insulating, therefore the resistivity was increased by donor doping with La^{3+} on the A-site [3]. The understanding developed about the intrinsic sintering behavior of pure and doped $Sr_2Nb_2O_7$ was coupled with studies conducted on samples templated with large, single-crystal particles to determine the conditions required to produce textured $Sr_2Nb_2O_7$ and La^{3+} doped $Sr_2Nb_2O_7$.

2. Experimental procedure

Coprecipitated $Sr_2Nb_2O_7$ powder was prepared by the drop-wise addition of an aqueous precursor solution consisting of 0.05 M $Sr(NO_3)_3$ and 0.05 M Nb-oxalate* in excess oxalic acid to a solution of ammonium hydroxide and excess oxalic acid maintained at pH 8. The precipitate, composed of SrC_2O_4 and hydrated niobium oxide, was calcined at 1100°C for 2 h and ball milled for 12 h to obtain phase pure, 0.5–0.7 μm $Sr_2Nb_2O_7$. La-doped powder was prepared by adding $La(NO_3)_3$ to the aqueous precursor solution, and subsequent precipitation as lanthanum hydroxide.

Solid state reacted powder was prepared by calcining a ball-milled stoichiometric mixture of $SrCO_3$† (99.994%) and Nb_2O_5‡ (99.9%) at 1100°C for 2 h. The starting powder was milled for 24 h in 2-propanol with a commercial dispersant KD-2§ in a vibratory mill. The calcined powder was milled in 2-propanol for 12 h in a vibratory mill to obtain $Sr_2Nb_2O_7$ powder with an average particle size of 0.6 μm. La-doped powder was prepared by the addition of La_2O_3¶ to the starting powder.

Samples with relative green densities of 58–60% of theoretical density were selected for sintering studies. These samples were first formed by uniaxially pressing 0.625 cm and 1.27 cm diameter pellets at ~70 MPa. This was followed by isostatic pressing at 250 MPa to obtain high green density samples with randomly oriented crystallites.

Samples were sintered isothermally in air from 1300°C to 1550°C for 1–100 min in a horizontal tube furnace. The typical loading and unloading times were 1–2 s, and the samples were estimated to reach the sintering temperature in ~15–20 s. After sintering, the samples were quenched in air. Therefore, the uncertainty in sintering time measurement is very low for

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§ ICI Surfactants, Wilmington DE, USA.
¶ Unocal Molycorp, White Plains NY, USA.

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hold times >1 min. Hence, hold times of 1, 3, 10, 30, and 100 minutes were chosen. Sintered samples were air quenched. The bulk density of sintered samples was measured by Archimedes' technique. The theoretical density of doped samples was estimated by measuring the unit cell parameters by slow scan X-ray diffraction of powder crushed from the sintered samples using Si as the reference standard. Peaks in the 5–65° 2θ range were indexed and used for these measurements. For stereological measurements, samples were first polished with 0.1 μm diamond paste and then annealed 100–200°C below the sintering temperature. SEM micrographs with 250–1000 grains from 2–5 random cross-sections were used for stereological measurements. Grain size statistics were computed using the NIH image analysis software [8].

Dielectric permittivity and loss were measured as a function of temperature with a multi frequency LCR meter (Hewlett Packard HP 4274) from 25°C to 425°C at 1 MHz under a field of 1 KV/m.

3. Results and discussion

3.1. Sintering

Earlier studies on the sintering of solid state reacted $Sr_2Nb_2O_7$ reported an inability to obtain densities >92% by pressureless sintering as a result of dedensification caused by anisotropic grain growth. This leads to wrenching apart of grains and the creation of voids due to a combination of thermal expansion anisotropy and the large grain size which favors fracture in $Sr_2Nb_2O_7$ [9]. In contrast to this work, samples of coprecipitated $Sr_2Nb_2O_7$ and solid state reacted $Sr_2Nb_2O_7$ attained a sintered density of ~97–98% after 1 min at 1500°C as seen in Fig. 1. The presence of large anisotropic grains can be seen in the samples sintered at 1550°C (Fig. 2).

Donor doping with La was found to decrease the dielectric loss. Lanthanum incorporates into the $Sr_2Nb_2O_7$ lattice at a temperature >1250°C. Thus, the theoretical density was calculated for each sintering temperature using lattice parameters measured by X-ray diffraction (Table I). The results of the isothermal sintering experiments are summarized in Figs 3 and 4. A density of 99% was obtained at temperatures >1400°C.

The dielectric permittivity and loss data for pure $Sr_2Nb_2O_7$ and $(Sr_{0.99}La_{0.01})_2Nb_2O_7$ are presented in Fig. 5, where the addition of La is seen to suppress the dielectric loss up to 400°C. This demonstrates the efficacy of La-doping in increasing the a.c. resistivity of $Sr_2Nb_2O_7$ which can be explained by a change in the defect chemistry of the system [3]. Also, from the data in Table I, it is observed that for the sintering conditions used in this study, a small amount of unreacted La_2O_3 (~15% of the total available La) is present at the grain boundaries.

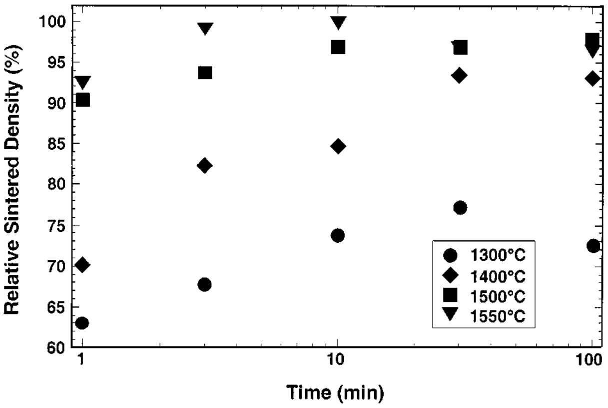


Figure 1 Isothermal sintered density as a function of time at different temperatures for $Sr_2Nb_2O_7$.

TABLE I Calculated lattice parameters and fraction of total available La (2 mol%) incorporated in to the $Sr_2Nb_2O_7$ lattice as a function of temperature

T (°C)	t (min)	a (nm)	b (nm)	c (nm)	Fraction of La in the lattice
1250	120	0.3955	2.6770	0.5699	0.00
1350	120	0.3957	2.6734	0.5694	0.75
1450	120	0.3958	2.6719	0.5691	0.85
1550	1	0.3958	2.6708	0.5691	0.85
1550	120	0.3961	2.6704	0.5689	1.00

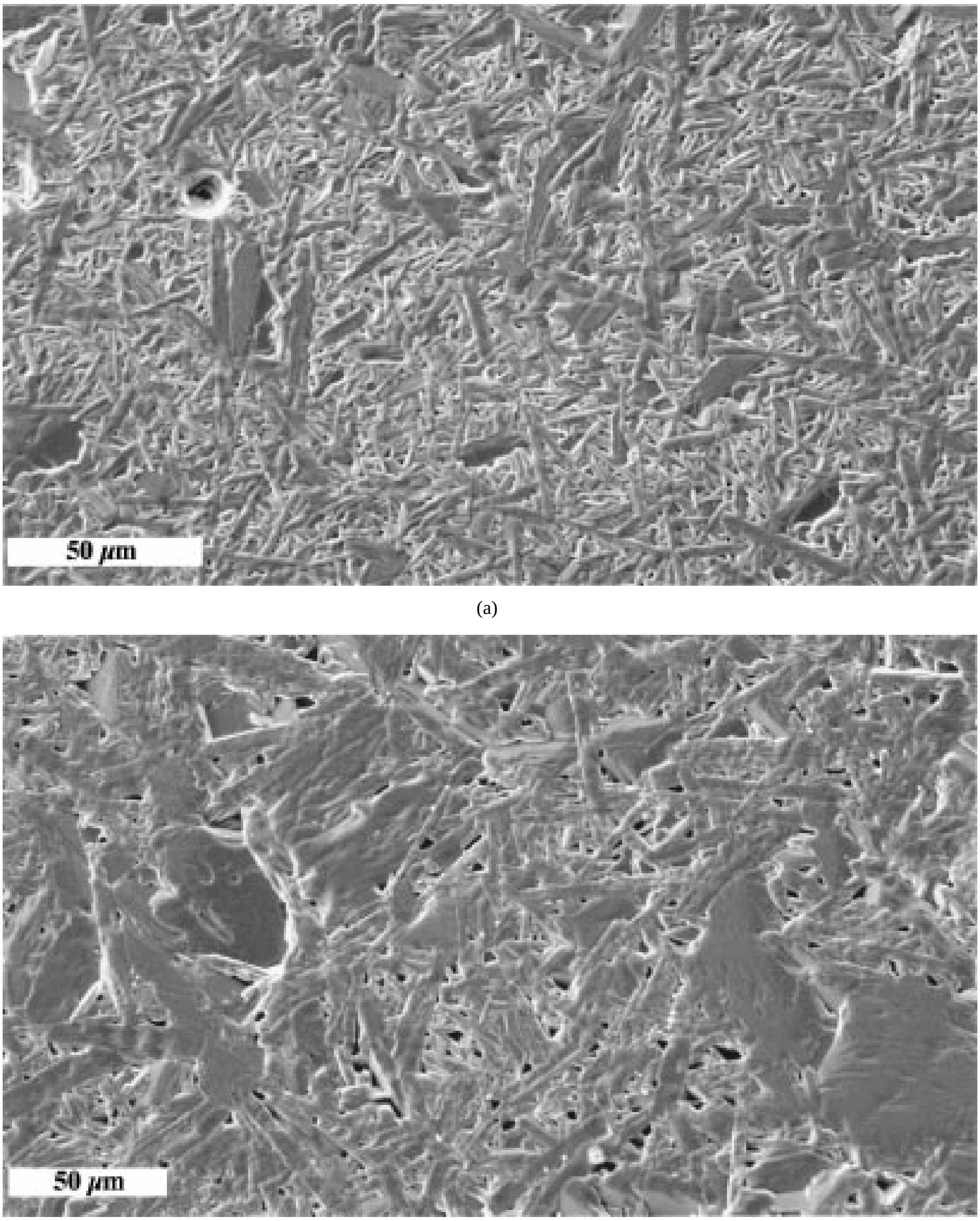
3.2. Grain growth in undoped $Sr_2Nb_2O_7$

On examining the SrO-Nb_2O_5 phase diagram reported by Leschenko *et al.* [10] (Fig. 6), it can be seen that phase pure $Sr_2Nb_2O_7$ exists only at a molar ratio of $Sr : Nb = 1$. For $Nb_2O_5 : SrO > 0.5$ a liquid can form above 1330°C. For $Nb_2O_5 : SrO < 0.5$ no liquids form at any of the sintering temperatures in this study.

The presence of a liquid layer has been reported to enhance anisotropic grain growth in other ceramic systems [11, 12]. The presence of a thin liquid film increases the grain boundary mobility by providing a path for rapid diffusion. The boundary migration rate can be determined by the relative kinetics of diffusion through the liquid film and the surface reaction (dissolution). In order to understand the effect of a liquid on the grain growth and densification kinetics, coprecipitated compositions with Sr : Nb ratios of 1.05, 1, 0.95 and 0.9 were studied.

Samples of undoped, coprecipitated powder were sintered at 1300, 1400, and 1500°C. There is substantial anisotropic grain growth in samples heated between 1300°C and 1400°C in Nb-rich samples. Large anisotropic grains were observed to form in samples which were at least 90% dense. This implies that the formation of a continuous liquid film between particles is required for the growth of anisotropic grains. From the phase diagram (Fig. 6) it is apparent that the liquid responsible for this growth does not form between $Sr_2Nb_2O_7$ and $SrNb_2O_6$ because the grain growth is observed well below their eutectic point at 1450°C. This suggests that the liquid is a result of the reaction between $SrNb_2O_6$ and $Sr_2Nb_{10}O_{27}$, or $Sr_2Nb_{10}O_{27}$ and Nb_2O_5 which form eutectic liquids at 1340°C and 1330°C, respectively.

The homogeneous microstructures obtained at 1300°C for different Sr/Nb ratios (Fig. 7), show a narrow grain size distribution. There were no grains larger than 2 times the average grain size. Thus, the Hillert criterion [13] for a size ratio which is required for the



(a)

(b)

Figure 2 SEM micrographs of $Sr_2Nb_2O_7$ sintered at 1550°C for (a) 10 min, (b) 100 min.

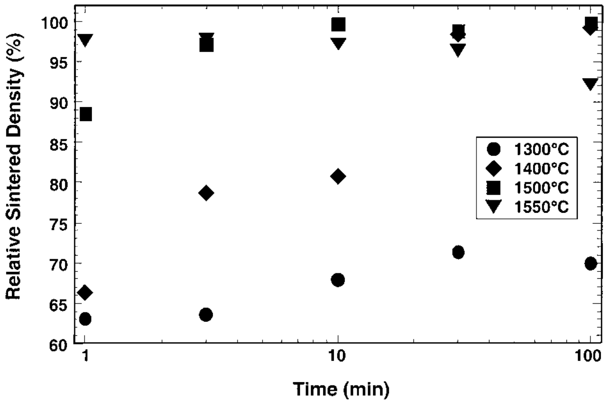
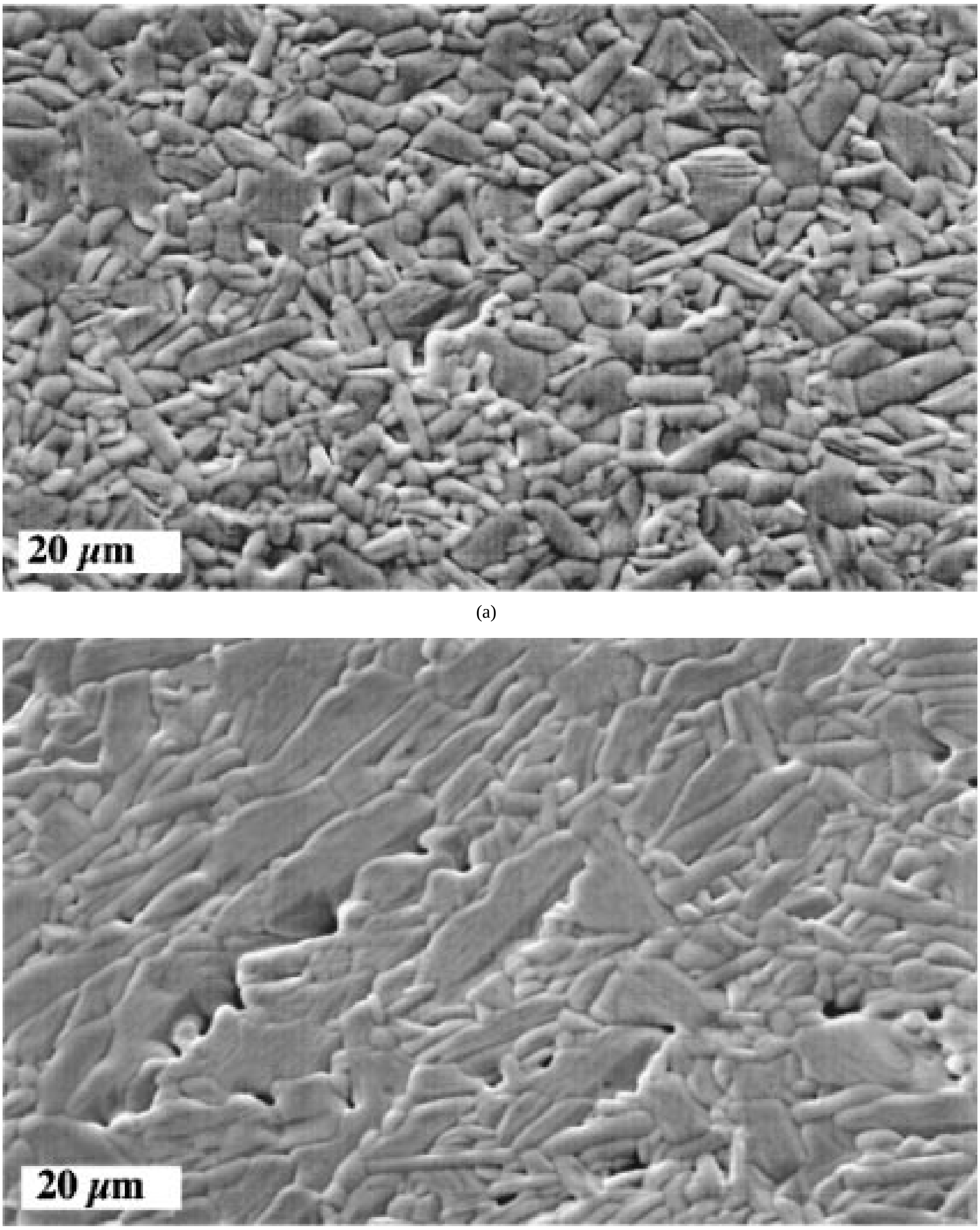


Figure 3 Isothermal sintered density as a function of time at different temperatures for 2 mol% La-doped $Sr_2Nb_2O_7$.

onset of exaggerated grain growth was not satisfied. However, the development of a bimodal grain size distribution from an initial microstructure composed of a narrow grain size distribution has been observed in other systems. Based on our observations, the formation of a liquid at certain grain boundaries causes the appearance of large anisotropic grains at 1400°C in $Sr_2Nb_2O_7$. This observation is consistent with the model proposed by Rios [14] as well as the explanation for exaggerated grain growth in $BaTiO_3$ [11].

3.3. Grain growth in La-doped $Sr_2Nb_2O_7$

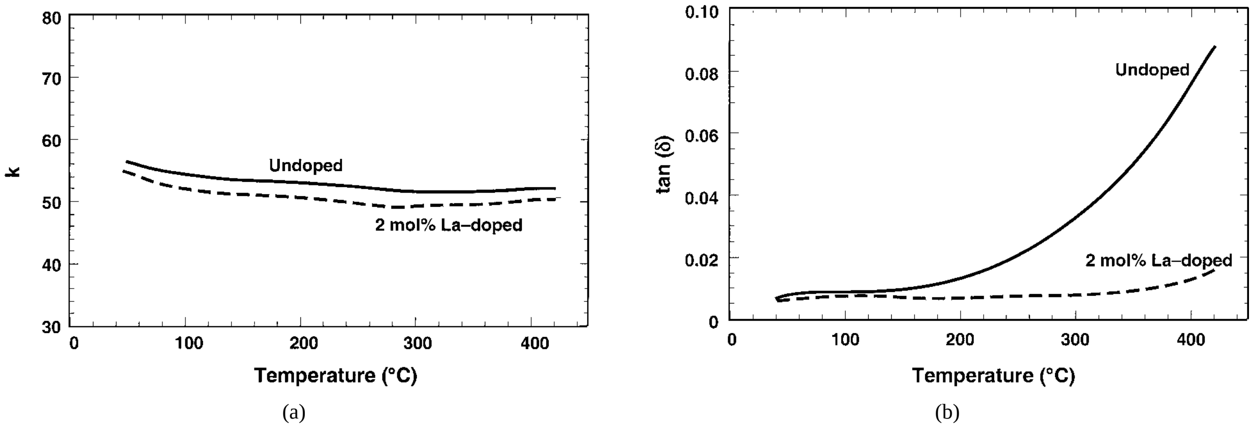
Fig. 7 shows how the grain size distribution changes as a function of major axis length for various hold



(a)

(b)

Figure 4 SEM micrographs of 2 mol% La-doped $Sr_2Nb_2O_7$ sintered at 1550°C for (a) 10 min, (b) 100 min.



(a) (b)

Figure 5 (a) Dielectric constant, *k*, and (b) dielectric loss as a function of temperature for >98% dense undoped and 2 mol% La-doped ceramics.

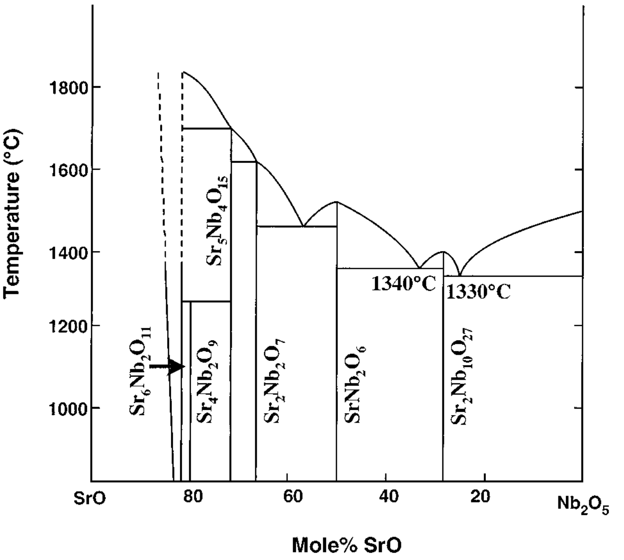


Figure 6 SrO-Nb_2O_5 phase diagram from Leschenko *et al.* [10].

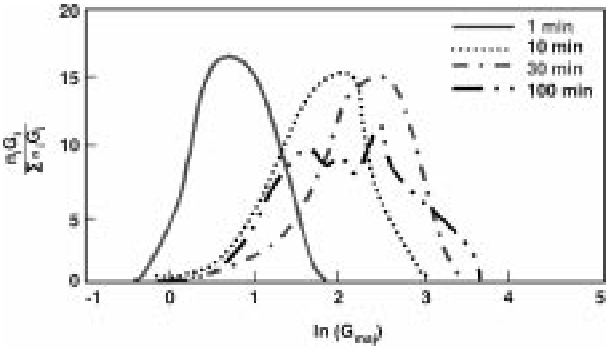


Figure 7 Isothermal grain growth in La-doped $Sr_2Nb_2O_7$ at 1550°C.

times at 1550°C. The distributions are self similar for hold times ranging from 1 minute to 30 minutes. As seen in Fig. 4, some broadening of the distribution, and growth of larger grains was observed for a hold time of 100 minutes. Interestingly, there is less anisotropic grain growth in doped samples relative to undoped $Sr_2Nb_2O_7$. Because the amount of La present in the sample is only 2 mol%, it was not possible to locate La_2O_3 in our samples by SEM or EDS. However, from lattice parameter measurements, La incorporation is incomplete until ∼100 minutes at 1550°C. Therefore, La_2O_3 exists as a separate phase, possibly on the grain boundaries, and thus suppresses anisotropic grain growth by pinning the grain boundaries.

To determine the grain growth mechanism, the average grain size from isothermal sintering experiments was fit to the general grain growth equation,

$$G_{av}(t)^n - G_{av}(0)^n = kt,$$

The best fit to the equation was obtained for $n = 3$ ($R^2 = 0.98$). Lower values of n yielded a R^2 parameter < 0.92. A cubic growth law is predicted for kinetics which are a result of drag-limited growth due to either a liquid or a dispersed phase [15]. We conclude that La-doping suppresses anisotropic grain growth as a result of pinning the grain boundaries. Interestingly, the effect of La_2O_3 pinning is completely offset by using Nb-rich $(Sr_{0.99}La_{0.01})_2Nb_2O_7$ (Fig. 8).

3.4. Templated grain growth

Based on the above observations, anisotropic grain growth can be promoted in electrically insulating $(Sr_{0.99}La_{0.10})_2Nb_2O_7$ by using Nb-rich compositions. 10–15 μm Nb-rich $Sr_2Nb_2O_7$ template particles were coated with Nb-oxalate solution. A coating of hydrated niobium oxide was precipitated on the templates by the addition of a base. The particles were then calcined at 1000°C for 1 h to obtain Nb_2O_5 coated $Sr_2Nb_2O_7$ template particles with a molar ratio of Nb : Sr = 1.05.

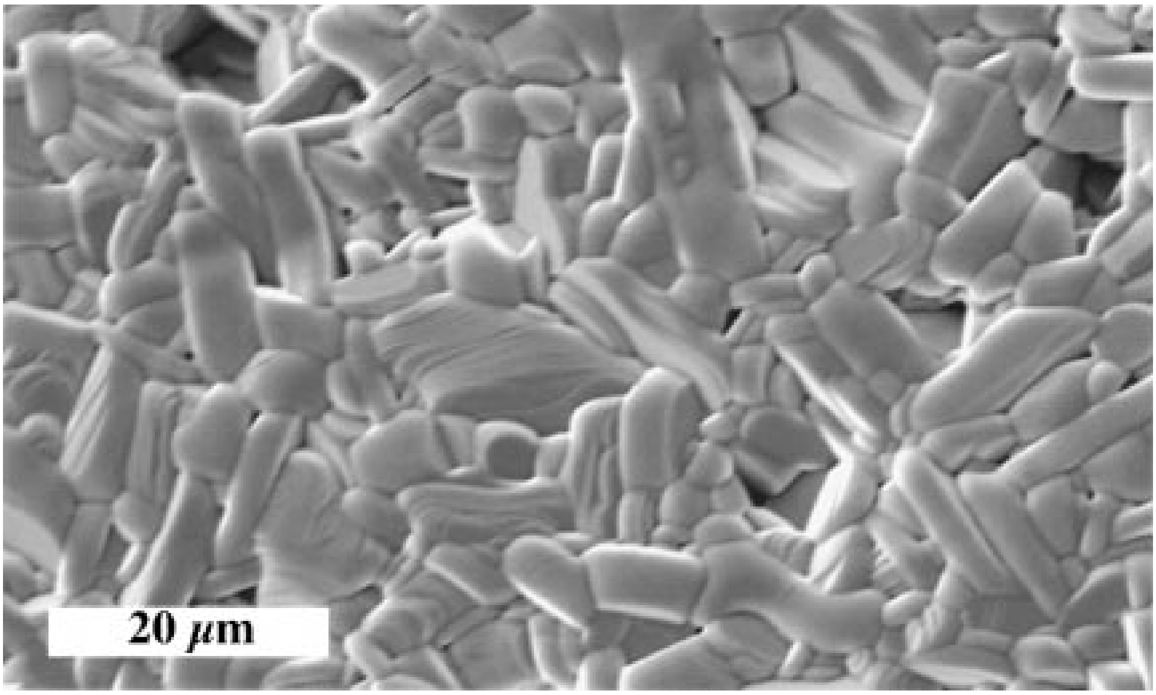
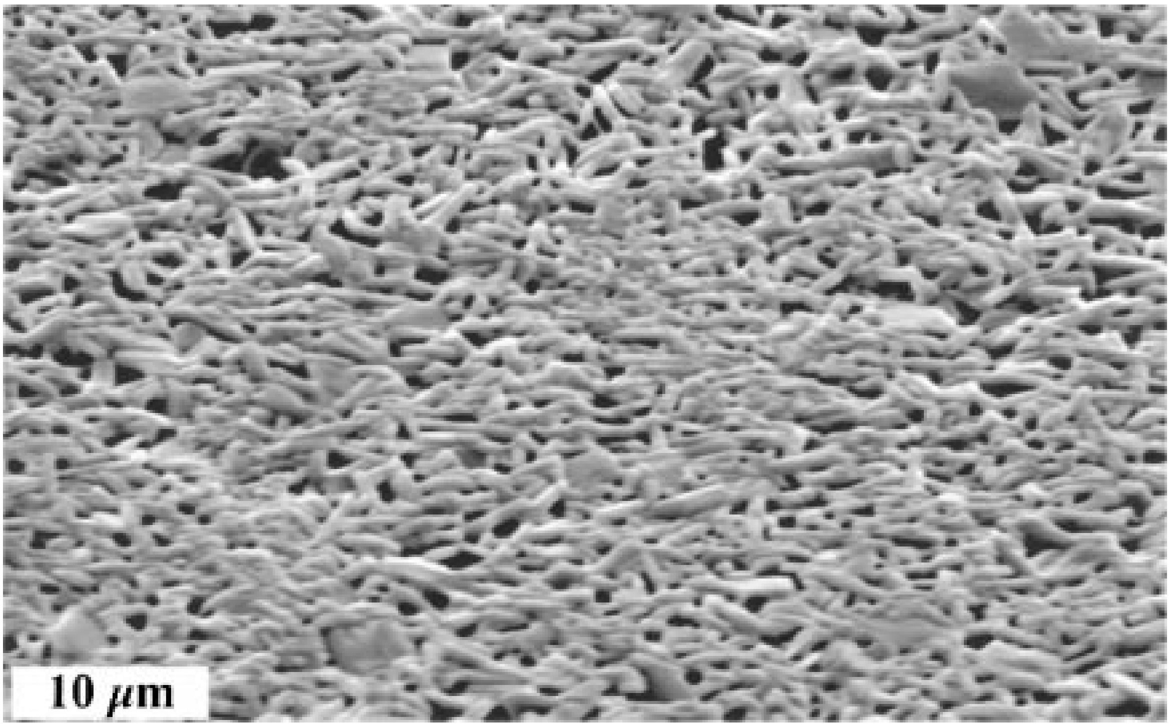
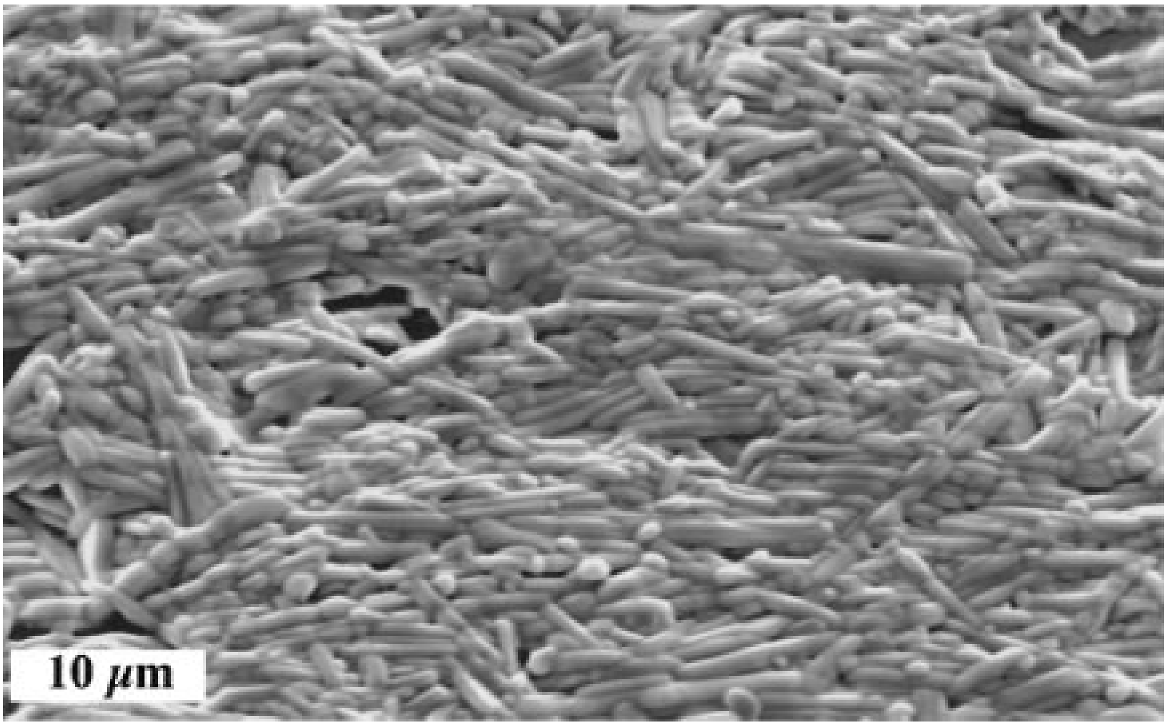


Figure 8 SEM micrograph of 2 mol% La-doped sample with Nb/Sr = 1.1.

Initial template concentrations of 10 vol% and 25 vol% were studied. The growth behavior of templates with Nb : Sr = 1.05 in a La-doped matrix of Nb : Sr = 1 and Nb : Sr = 1.05 is compared in Fig. 9. Nb-rich templates grew to ~10 μm length in 1 h at 1450°C in a stoichiometric matrix. On the other hand, much larger grains in the 20–50 μm length range were observed in the Nb-rich matrix due to the growth of Nb-rich templates. The presence of a liquid in the matrix resulted in denser microstructures with larger grains. As seen from Fig. 9c and d, a higher concentration of templates led to an increase in the number of large anisotropic grains in the templated microstructure. These results indicate that template growth can be enabled in La-doped $Sr_2Nb_2O_7$ by using Nb-coated templates for TGG in a Nb-rich matrix.

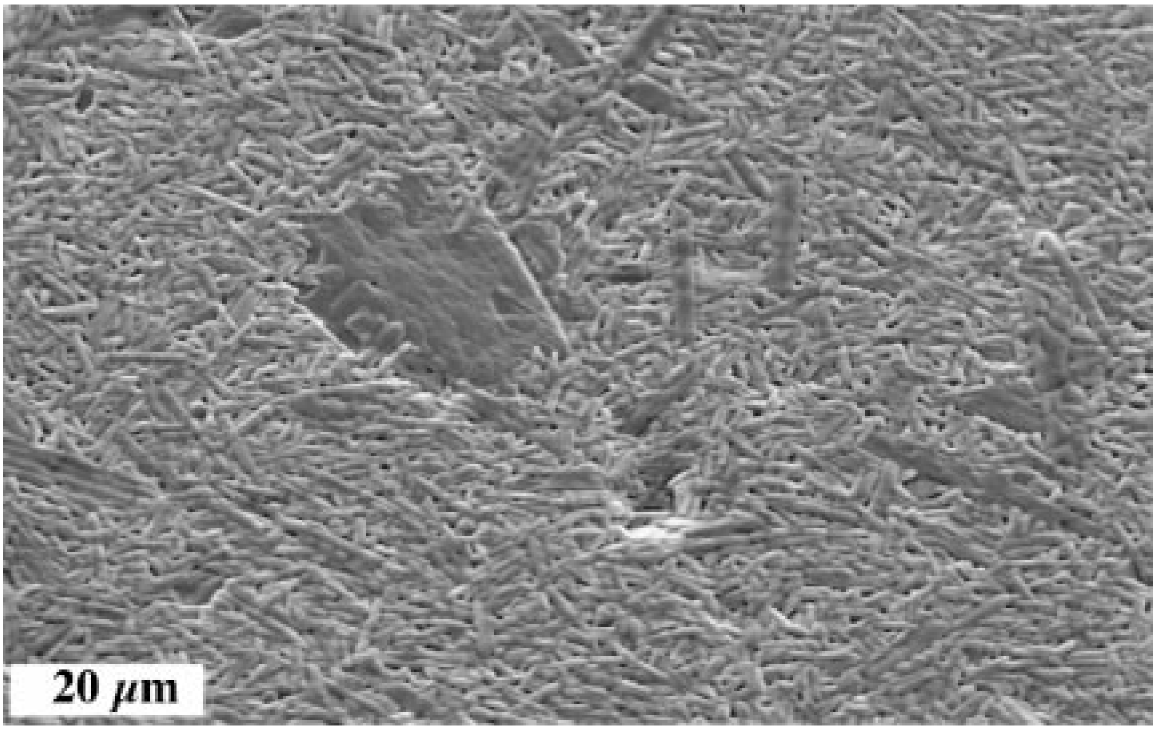


(a)

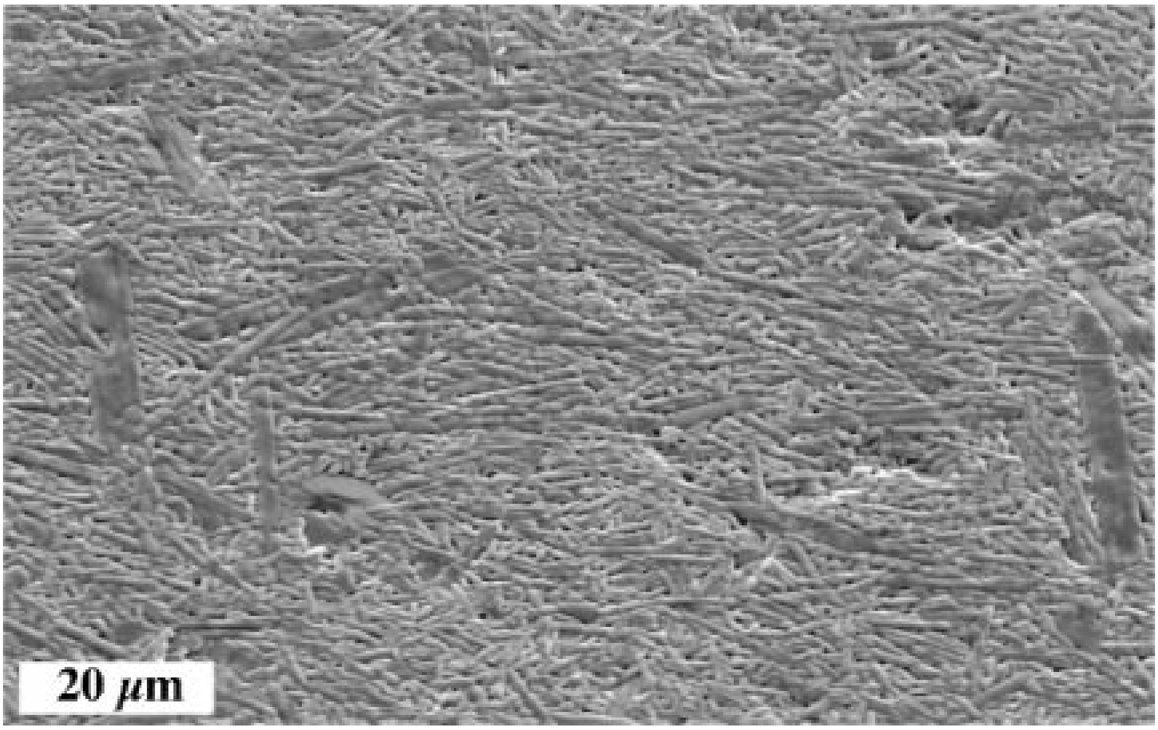


(b)

Figure 9 Growth behavior of templates in La-doped matrix. (a) La-doped matrix + 10 wt% Nb-rich templates, (b) La-doped matrix + 25 wt% Nb-rich templates, (c) Nb-rich, La-doped matrix + 10 wt% Nb-rich templates, (d) Nb-rich, La-doped matrix + 25 wt% Nb-rich templates. Sample a was sintered at 1450°C for 1 min, and sample b, c, and d were sintered at 1450°C for 1 h. (*Continued*)



(c)



(d)

Figure 9 (*Continued*).

4. Conclusions

It was found that in $Sr_2Nb_2O_7$, growth of large, anisotropic grains is due to the heterogeneous formation of a liquid phase at certain Nb-rich grain boundaries. When this liquid phase is not present (as was the case for Nb-poor samples), more equiaxed microstructures are obtained. Careful control over the Sr : Nb ratio allows high density $Sr_2Nb_2O_7$-based ceramics to be fabricated with either fine-grained microstructures or with large, anisotropic grains.

La-doping has previously been shown to improve the dielectric loss of $Sr_2Nb_2O_7$ ceramics. It was found here that $(Sr_{0.99}La_{0.01})_2Nb_2O_7$ samples showed less anisotropic grain growth than undoped ceramics. This is believed to be due to segregation of some of the La to the grain boundaries. The resulting second phase particles act as pinning sites for grain growth. Anisotropic grain growth, could, however, be achieved in this system, if excess Nb was introduced to facilitate development of a liquid phase at the sintering temperature.

It was demonstrated that introduction of template particles into $(Sr_{0.99}La_{0.01})_2Nb_2O_7$ samples promoted microstructures dominated by large, anisotropic grains. As the template concentration increased from 10 to 25 volume percent, a larger fraction of the resulting ceramic was composed of the large grains. The templated grain growth process was facilitated in these samples by introduction of Nb-coatings onto the template particles. Well-oriented ceramics produced by the process are potentially interesting for high temperature piezoelectric applications due to the high Curie temperature of this compound. Based on the conditions determined for anisotropic grain growth we have fabricated highly textured $Sr_2Nb_2O_7$ by templated grain growth [16].

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