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Hot-press sintering $Sr_2Nb_2O_7$ ceramics and their electrical properties

Xin Cai[1] · Yuancheng Teng[1] · Lang Wu[1] · Kuibao Zhang[1]

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Abstract $Sr_2Nb_2O_7$ ceramics with high densities were synthesized by the hot-press sintering process, and the effects of sintering temperature and holding time of phase composition and microstructure were studied. The dielectric, piezoelectric, and ferroelectric properties of $Sr_2Nb_2O_7$ ceramics were also investigated. A relative density of 98% was obtained when the $Sr_2Nb_2O_7$ ceramics were prepared by hot-pressing (30 MPa) at temperature as low as 1200 °C for 2 h. The grain size of $Sr_2Nb_2O_7$ increases gradually with the variation of temperature from 1150 to 1200 °C. The grains are plate-like and the length of grain size is 15 μm when the temperature increased to 1200 °C. In addition, the grain boundary became unclear at 1300 °C for 2 h. The dielectric constant and dielectric loss of the ceramics sintered at 1200 °C for 2 h were 57 and 1.6% at 10 kHz, respectively. The piezoelectric constant reached 2.1 pC/N. The remanent polarization and the coercive field were 0.24 μC/cm^2 and 15.1 kV/cm, respectively.

1 Introduction

High-temperature piezoelectric materials have attracted significant interest because of their applicability in aerospace, automotive, and power generating industries [1, 2]. The commercial piezoelectric sensors used for high temperature application such as tourmaline ($d_{33} \sim 1.8$ pC/N) have lower d_{33} compared to $Pb(Zr_xTi_{1-x})O_3$ (PZT, $d_{33} > 200$ pC/N) [3–5]. Besides, no suitable piezoelectric material can be used for commercial field when the operating temperature is higher than 750 °C. Therefore, seeking the higher temperature lead-free piezoelectric ceramics is necessary for several extreme temperature application. Ferroelectrics with perovskite-like layer structure (PLS), such as strontium niobate ($Sr_2Nb_2O_7$, short for SNO,), as well as $La_2Ti_2O_7$, $Pr_2Ti_2O_7$ and $Nd_2Ti_2O_7$, have attracted much attention as the promising base-materials for lead-free piezoelectrics because of their super high Curie point (>1200 °C) [2, 6–9]. Among of these PLS ferroelectric ceramics, $Sr_2Nb_2O_7$ is a suitable candidate for super high temperature piezoelectric application due to its relatively larger piezoelectric constant ($d_{33} \sim 2.8$ pC/N) and high Curie point (1327 °C) [8].

Single-crystal $Sr_2Nb_2O_7$, which was produced by the floating zone technique, was first reported by Nanamatsu in the 1970s [1]. It has a high Curie point of 1342 °C and the piezoelectric constant (d_{33}) was measured as 2.8 pC/N. In recent years, the synthesis method, dielectric, piezoelectric and ferroelectric properties of SNO ceramics have been extensively researched according to a wide variety of doping [10–13]. These SNO ceramics were generally sintered by the conventional pressureless sintering process, which has relatively high sintering temperature (1350–1450 °C) and long holding time (4–10 h). Fu et al. [10] reported that the SNO ceramics were obtained by conventional sintering at 1350 °C for 4 h and found that the dielectric constant and dielectric loss were 54 and 1.3% at 10 kHz. Furthermore, the d_{33} reached 2.4 pC/N and the remanent polarization P_r of SNO ceramics was 0.022 μC/cm^2. Liou et al. [12] prepared 97.9% dense Ti-doped $Sr_2Nb_2O_7$ ceramic by pressureless reaction-sintering at 1400 °C for 6 h. However, the high sintering temperature

✉ Yuancheng Teng
tyc239@163.com

[1] State Key Laboratory Cultivation Base for Nonmetal Composites and Functional Materials, Southwest University of Science and Technology, Mianyang 621010, People's Republic of China

and long holding time are not conducive to the preparation of Strontium niobate ceramics.

Hot-press sintering (HP) is a useful method to synthesize low-temperature densification ceramics [14–19]. Wang et al. [17] prepared 97.9% dense Nb-doped $SrBi_2Ta_2O_9$ by hot-press sintering at 1000 °C for 2 h. Yu et al. [18] studied the $Ba^{2+}/La^{3+}/Sn^{4+}$ tri-doped $PbZrTiO_3$ antiferroelectric ceramics by hot-press sintering at 1150 °C for 2.5 h and found that dielectric loss was obviously reduced by hot-press sintering. However, there is very limit information on the preparation of Strontium niobate ceramic by the hot-pressing process. In this paper, the SNO ceramics are prepared by the low temperature hot-press sintering method, and their microstructure (density, grain size, phase composition) and electrical properties (dielectric, piezoelectric, ferroelectric) were also investigated.

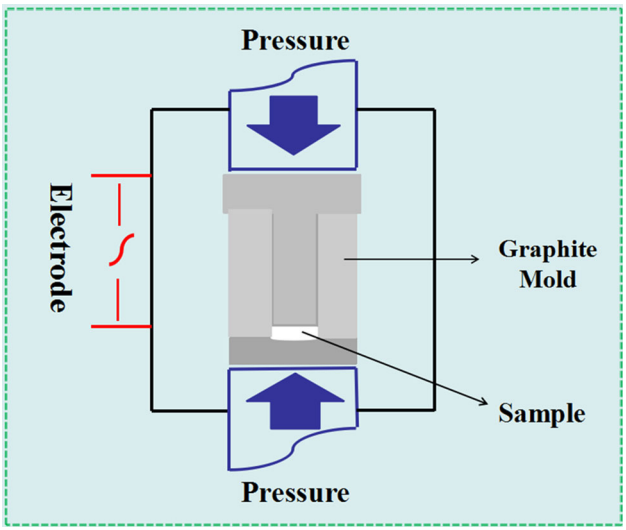

Fig. 1 Schematic diagram of the hot-press sintering system

2 Experimental details

Pure analytically powders of strontium carbonate ($SrCO_3$) and niobium oxide (Nb_2O_5) were used as raw materials. Specimens with composition of $Sr_2Nb_2O_7$ were synthesized as follows:

- The raw materials were mixed by ball-milling at a speed of 350 rpm for 10 h using ethanol as the dispersion agent and then dried at 85 °C for 8 h.
- The ball-milled powders were calcined at 1200 °C for 4 h in air by a muffle furnace (heating rate 5 °C/min), and then the acquired powders were pelleted with the polyvinyl alcohol (PVA, the concentration of 8–10 wt%).
- The obtained particles were pressed in a steel mold with a diameter of 20 mm at 60 MPa pressure, followed by cold isostatic pressing at 200 MPa for 10 min.
- The compacted specimens were subsequently calcined at 750 °C for 6 h for the decomposition of PVA.

The HP process was conducted as illustrated in Fig. 1. Two series specimens were prepared: (1) 1150, 1200, 1250, 1300 °C for 2 h; (2) 1200 °C for 1, 2, 3 and 4 h. The green bodies were sintered by hot-pressing process in a graphite mold (vacuum atmosphere, heating rate 10 °C/min) under 30 MPa pressure. In addition, the SNO specimen was prepared by pressureless sintering at 1400 °C for 4 h to compared its microstructure with SNO ceramics sintered by hot pressing.

Bulk density of sintered SNO ceramics was measured by the Archimedes method. The final relative density was determined by the experimental bulk density divided by theoretical density (5.259 g/cm^3).

Powder X-ray diffraction (XRD) patterns were obtained with X'Pert PRO Roentgen diffractometer system using Cu K_α radiation ($\lambda = 1.5418$ Å) from 10° to 60° (2 θ). The microstructures of polished and fracture surface were examined using a field emission scanning electron microscope (FE-SEM, JEOL JSE-7500F). The specimens for SEM were polished, and then thermally etched at 100 °C below their sintering temperatures for 0.5 h to reveal grain structures.

To measure the electric properties, silver paste was painted on the polished samples as the electrodes and fired at 750 °C for 2 h. The frequency dependence of the capacitance and dielectric loss were determined with an Agilent 4294A LCR. The dielectric constant was calculated from the capacitance using the following equation:

$$\varepsilon = Cd/\varepsilon_0 A$$

where C is the capacitance (F), ε_0 the free space dielectric constant value (8.85×10^{-12} F/m), A the capacitor area (m^2) and d the thickness (m) of the ceramics. Specimens for the piezoelectric constant was measured using a d_{33} m (YE2730A, Institute of acoustics academic sinica, Beijing, China). The ferroelectric hysteresis loops (P–E) were measured with the TF2000E ferroelectric test system (aixACCT Inc., Germany, TF2000).

3 Result and discussion

3.1 XRD analysis

Figure 2a, b show the XRD patterns of the SNO powder sintered under different temperatures (1150, 1200, 1250 and 1300 °C) for 2 h and several holding time (1, 2, 3 and 4 h) at 1200 °C, respectively. According to the XRD patterns, the diffraction peaks of all samples match the

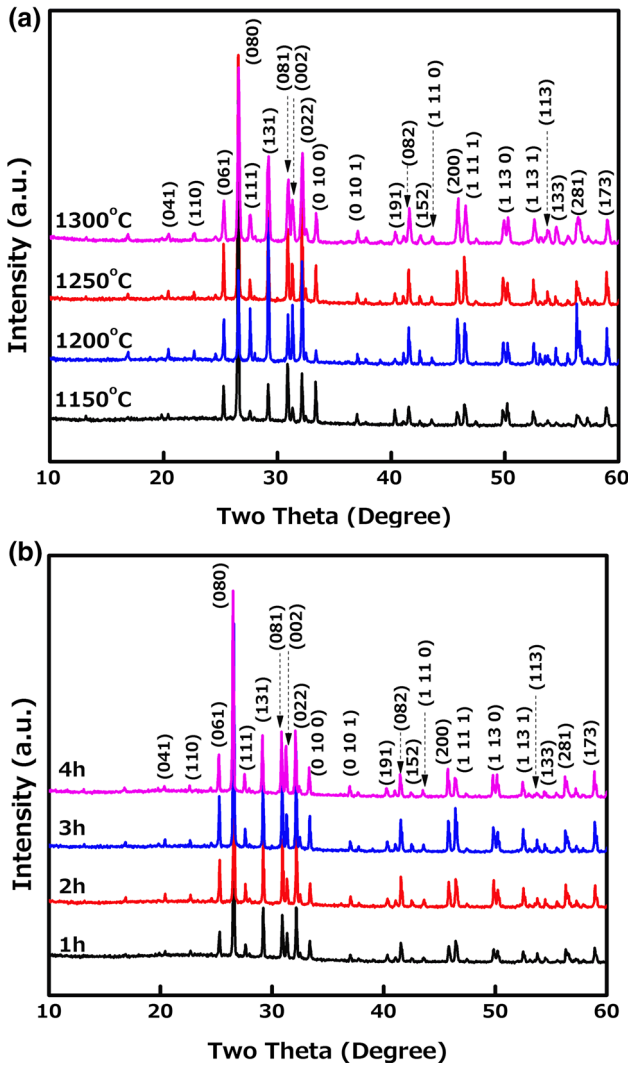

Fig. 2 XRD patterns of the specimens sintered at different temperatures (1150–1300 °C) for 2 h (**a**) and diverse holding times (1–4 h) at 1200 °C (**b**)

indexed peaks for the structure parameters of $Sr_2Nb_2O_7$ (JCPDS file no. 070-0114), which indicates that the ceramics are single phase within the sensitivity of the technique. Moreover, it can be seen in Fig. 2a that the intensities of XRD peaks of $Sr_2Nb_2O_7$ phases increase with increasing temperature from 1150 to 1200 °C and scarcely alter when the temperature reaches to 1300 °C. Meanwhile, the intensities have changed little with extending holding time from 1 to 4 h (Fig. 2b).

3.2 Microstructure analysis

The variation of relative densities for SNO ceramics with different temperature and diverse holding time are shown in Fig. 3. All specimens exhibit high relative densities (96–98%). As seen in Fig. 3, the relative density of the ceramics gradually increases with the increase of sintering

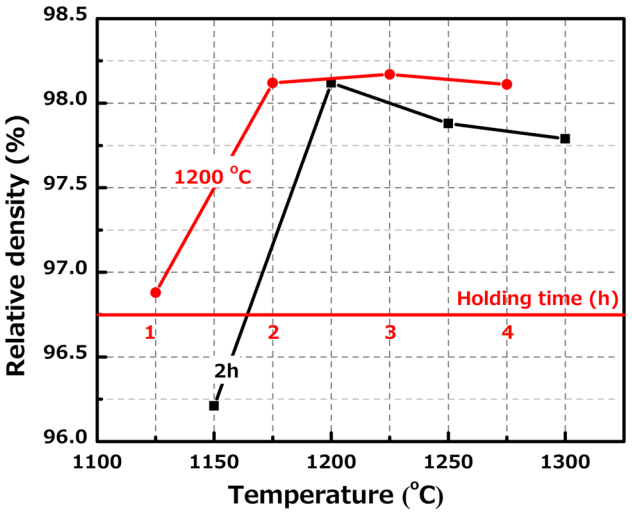

Fig. 3 The variation of the relative densities for the SNO ceramics with different sintered temperatures (1150–1300 °C) for 2 h and several holding times (1–4 h) at 1200 °C

temperature, and then reaches the maximum value of 98.1% when the sintering temperature is 1200 °C. While the relative densities have slightly decreased with further increasing sintering temperatures. In addition, the effect of holding time is also shown in Fig. 3. It can be observed that expending the holding time has slight influence on the relative density of the samples. It is observed that the relative density increases from 96.9 to 98% (2 h) and does not increase obviously with prolonging holding time from 2 to 4 h. This result show that the synthesized SNO ceramics are nearly full dense at a lower sintering temperature.

The changes of relative density can also be confirmed by the evolution microstructure images. The microstructures of polished and fracture surfaces for hot-pressing SNO ceramics at various sintering temperatures (1150, 1200 and 1300 °C) for 2 h are shown in Fig. 4a–f. According to the Fig. 4a–c, their grains are plate-like, which is typical for PLS ceramics [2]. The orientation of plate-like grains are perpendicular to the HP pressing direction. the average grain size of SNO ceramics with sintering at 1150, 1200 and 1300 °C is 5–8, 14–18 and 20–25 μm, respectively. During the HP method, a high uniaxial pressure was applied simultaneously with high temperature. The SNO grains grow preferentially along the direction perpendicular to the pressing direction. Figure 4a, d show that the SNO ceramic, which was prepared at 1150 °C for 2 h, exhibits heterogeneous microstructure and appears coalescent grains. This phenomenon could demonstrate one of the first steps of the SNO grains growth. In addition, a small number of intergranular and intragranular pores are also observed on the fracture and polished surface of the specimens, indicating that the relative density of the specimen at 1150 °C is relatively lower, namely, the grain

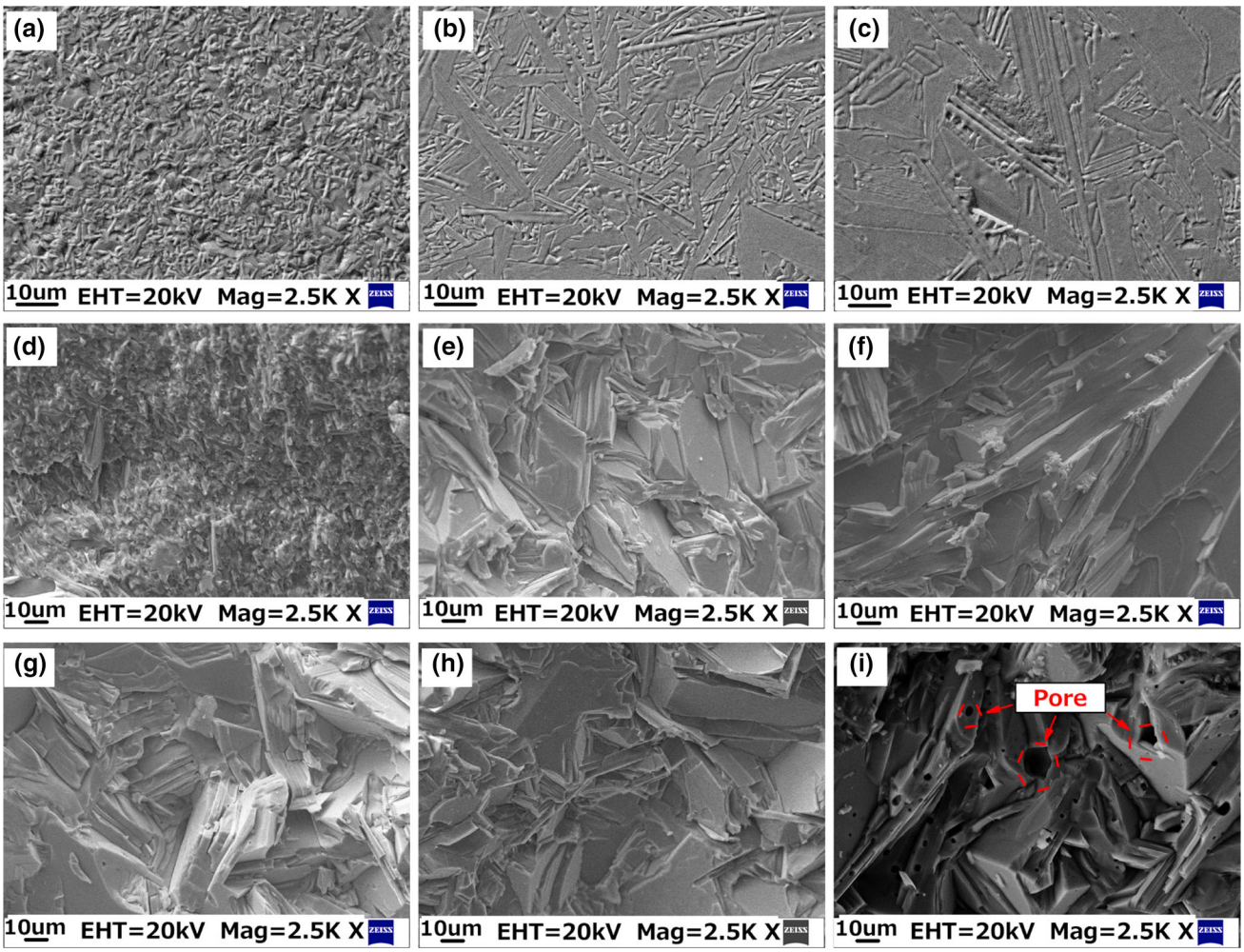

Fig. 4 SEM images of the polished surfaces of SNO ceramics hot-press sintered at **a** 1150 °C, **b** 1200 °C and **c** 1300 °C for 2 h, and the fracture surfaces of specimens sintered at **d** 1150 °C for 2 h, **e** 1200 °C for 2 h, **f** 1300 °C for 2 h, **g** 1200 °C for 1 h and **h** 1200 °C for 4 h. **i** The fracture surface of specimen sintered by pressureless process at 1400 °C for 4 h

growth may be happening but not yet completed. When the sintering temperature increases to 1200 °C, the plate-like SNO grain sizes rapidly increase with average size of about 2.5 μm in thickness and about 14–18 μm in the other dimensions, which might be caused by the rapid grain boundary diffusion under hot-press sintering [20]. As can be seen in Fig. 4b, e, the grain boundaries of this specimen are well-defined, in which almost no pores can be observed, indicating that the sample at 1200 °C are well sintered with high density. It could be explained by the prominent plastic deformation behavior of particles under hot-pressing process at 1200 °C, which was conducive to decrease the deformation resistance and improve the densification of the specimen [21]. However, it can be observed that the grain boundary becomes unclear when the SNO ceramic was sintered at 1300 °C for 2 h, which probably resulted from the oversintering (Fig. 4c, f).

The cross-sectional view of hot-pressing SNO ceramics sintered at several holding times were illustrated in Fig. 4: g 1200 °C-1 h, e 1200 °C-2 h and h 1200 °C-4 h. It could be seen that SNO grains are in tight compaction, and pores are seldom observed. All the ceramics with diverse holding time showed similar microstructure, suggesting that the evolution of the holding time almost has no influence on the microstructure of the SNO ceramics. On the other hand, Fig. 4i shows the microstructure of fracture surface for pressureless SNO ceramic sintered at 1400 °C for 4 h and a number of intragranular pores are observed. All the above-mentioned results demonstrate that the hot-press sintering is an effective method to synthesis SNO ceramics with high density and ideal microstructure at relatively low temperature than the pressureless sintering method.

3.3 Electrical properties

Figure 5 illustrates the temperature and frequency dependence of dielectric constant and loss of SNO ceramic measured at room temperature. For SNO specimens which

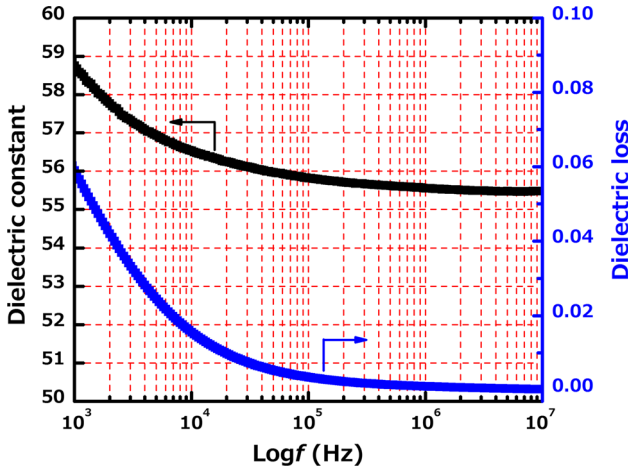

Fig. 5 Frequency dependence of dielectric constant and loss of SNO ceramics sintered at 1200 °C for 2 h (30 Mpa)

is hot-pressed at 1200 °C for 2 h, the dielectric loss of SNO specimen is low in the whole frequency range. Both the dielectric loss and dielectric constant decrease with increasing frequency from 1 kHz to 10 MHz. At 10 kHz, the dielectric constant and dielectric loss are 57 and 1.6%, respectively. Comparing with pressureless sintering [10], the dielectric constant is higher and the dielectric loss is almost equivalent. Furthermore, the dielectric constant and loss of SNO are stable for the range of frequencies from 10 kHz to10 MHz.

The SNO specimens sintered at 1200 °C for 2 h were poled in silicone oil at 200 °C under DC electric field of 10 kV/mm (maximum electric field of the polarization devices). However, the specimens could not be poled completely under these conditions. The measured piezoelectric constant d_{33} is 2.1 pC/N, which is slightly lower than the value of SPS samples (2.8 pC/N). Figure 6 shows

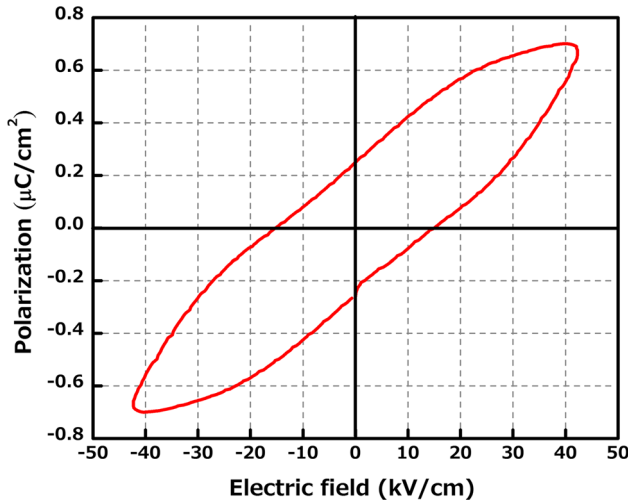

Fig. 6 The polarization–electric field (*P–E*) hysteresis loop for specimens sintered at 1200 °C for 2 h (30 Mpa)

the polarization–electric field (*P–E*) hysteresis loops of the same SNO ceramics, which was measured in silicone oil at 20 °C and 1 kHz. According to the *P–E* curves, the hysteresis loops are well-behaved. It is demonstrated that the crystal structures are ferroelectric phase. Furthermore, the remanent polarization P_r and coercive field E_c of hot-pressing SNO ceramics are 0.24 μC/cm^2 and 15.1 kV/cm, respectively. These values are higher than the pressureless specimens reported by Fu [10].

4 Conclusions

Single-phase $Sr_2Nb_2O_7$ ceramics were fabricated by hot-press sintering method using $SrCO_3$ and Nb_2O_5 as raw materials. The optimal sintering temperature and holding time at 30 MPa were 1200 °C and 2 h, respectively, making the relative densities of SNO ceramic reach 98%. The microstructure of the SNO ceramic became more regular and the grain sizes obviously increased with the increasing of sintering temperature from 1150 to 1200 °C. However, the grain boundary became unclear from 1200 to 1300 °C, which probably resulted from oversintering. Besides, the grain sizes have no significant changes with the variation of holding time. These results indicated that hot-press sintering is a low temperature and rapid densification technique. In addition, the dielectric constant and loss of SNO specimen sintered at 1200 °C for 2 h were 57 and 1.6% at 10 kHz, respectively. The piezoelectric constant d_{33} reached 2.1 pC/N. According to the hysteresis loops, the remnant polarization $P_r \sim 0.24$ μC/cm^2 and coercive electric field $E_c \sim 15.1$ kV/cm were observed for SNO ceramics sintered at 1200 °C for 2 h.

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References

1. S. Nanamatsu, M. Kimura, K. Doi et al., Ferroelectric properties of $Sr_2Nb_2o_7$ single crystal. J. Phys. Soc. Jpn. **30**(1), 300–301 (1971)
2. H. Yan, H. Ning, Y. Kan et al., Piezoelectric ceramics with super-high curie points. J. Am. Ceram. Soc. **92**(10), 2270–2275 (2009)
3. Y. Saito, H. Takao, T. Tani et al., Lead-free piezoceramics. Nature **432**(7013), 84–87 (2004)
4. S. Zhang, F. Yu, Piezoelectric materials for high temperature sensors. J. Am. Ceram. Soc. **94**(10), 3153–3170 (2011)
5. Z. Gao, H. Ning, C. Chen et al., The effect of barium substitution on the ferroelectric properties of $Sr_2Nb_2O_7$ ceramics. J. Am. Ceram. Soc. **96**(4), 1163–1170 (2013)

6. M. Kimura, S. Nanamatsu, T. Kawamura et al., Ferroelectric, electrooptic and piezoelectric properties of $Nd_2Ti_2O_7$ single crystal. Jpn. J. Appl. Phys. **13**(9), 1473 (1974)
7. Z. Gao, H. Yan, H. Ning et al., Piezoelectric and dielectric properties of Ce substituted $La_2Ti_2O_7$ ceramics. J. Eur. Ceram. Soc. **33**(5), 1001–1008 (2013)
8. H. Ning, H. Yan, M.J. Reece, Piezoelectric strontium niobate and calcium niobate ceramics with super-high curie points. J. Am. Ceram. Soc. **93**(5), 1409–1413 (2010)
9. S. Nanamatsu, M. Kimura, K. Doi et al., A new ferroelectric: $La_2Ti_2O_7$. Ferroelectrics **8**(1), 511–513 (1974)
10. C. Fu, H. Liu, G. Chen et al., Microstructure and electric properties of strontium niobate ceramics. Ceram. Int. **38**(3), 2601–2603 (2012)
11. L. Xiang, G. Chen, C. Fu et al., Effect of Ta doping on the microstructure, dielectric and ferroelectric properties of $Sr_2Nb_2O_7$ ceramics. Ferroelectrics **467**(1), 165–172 (2014)
12. Y. Liou, W. Tsai, J. Yu et al., Effects of Ti addition on properties of $Sr_2Nb_2O_7$ thermoelectric ceramics. Ceram. Int. **41**(5), 7036–7041 (2015)
13. Y. Liou, W. Tsai, J. Yu, Effects of La addition on properties of $Sr_2Nb_2O_7$ thermoelectric ceramics. Ceram. Int. **44**(12), 4857–4863 (2015)
14. G.H. Haertling, Properties of hot-pressed ferroelectric alkali niobate ceramics. J. Am. Ceram. Soc. **50**(6), 329–330 (1967)
15. X. Wang, K. Murakami, O. Sugiyama et al., Piezoelectric properties, densification behavior and microstructural evolution of low temperature sintered PZT ceramics with sintering aids. J. Eur. Ceram. Soc. **21**(10), 1367–1370 (2001)
16. W. Wang, Z. Fu, H. Wang et al., Influence of hot pressing sintering temperature and time on microstructure and mechanical properties of TiB_2 ceramics. J. Eur. Ceram. Soc. **22**(7), 1045–1049 (2002)
17. W. Wang, J. Rao, H. Ke et al., Domain structures in hot-press sintered $SrBi_2Ta_{1.6}Nb_{0.4}O_9$ and $SrBi_2Ta_2O_9$ ferroelectric ceramics. Ceram. Int. **38**(5), 3963–3967 (2012)
18. G. Zhang, S. Liu, Y. Yu et al., Microstructure and electrical properties of $(Pb_{0.87}Ba_{0.1}La_{0.02})(Zr_{0.68}Sn_{0.24}Ti_{0.08})O_3$ anti-ferroelectric ceramics fabricated by the hot-press sintering method. J. Eur. Ceram. Soc. **33**(1), 113–121 (2013)
19. Y. Teng, S. Wang, Y. Huang et al., Low-temperature reactive hot-pressing of cerium-doped titanate composite ceramics and their aqueous stability. J. Eur. Ceram. Soc. **34**(4), 985–990 (2014)
20. Y. Teng, X. Wang, Y. Huang et al., Hot-pressure sintering, microstructure and chemical durability of $Ce_{0.5}Eu_{0.5}PO_4$ monazite ceramics. Ceram. Int. **41**(8), 10057–10062 (2015)
21. Y. Teng, P. Zeng, Y. Huang et al., Hot-pressing of monazite $Ce_{0.5}Pr_{0.5}PO_4$ ceramic and its chemical durability. J. Nucl. Mater. **465**, 482–487 (2015)

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