

The sintering behavior of CeO₂-doped strontium barium niobate ceramics

Jyh-Tzong Shiue, Tsang-Tse Fang*

Department of Materials Science and Engineering, National Cheng Kung University, Tainan 701, Taiwan

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Abstract

In this study, the isothermal sintering behaviors of pure and CeO₂-doped Sr_{0.5}Ba_{0.5}Nb₂O₆ ceramics were evaluated. It was found that the cerium dopant would increase the sintering temperature and the activation energy of the SBN ceramics sintered in air. The defects for the charge compensation were studied and discussed. It is suggested that the excessive oxygen ion occupying the O(4) site be the defect for charge compensation. © 2002 Published by Elsevier Science Ltd. All rights reserved.

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1. Introduction

Strontium barium niobate, Sr_xBa_{1-x}Nb₂O₆ (SBN) (0.25 ≤ *x* ≤ 0.75), possesses excellent pyroelectric^{1–3} and linear electro-optic coefficients^{4,5} and a strong photo-refractive effect,^{6,7} so it has been of interest for many optical applications, e.g. volume holographic storage,⁸ self-pumped phase conjugation,⁹ photoassisted switching of ferroelectric domains,¹⁰ and fast recording with enhanced sensitivity at high light intensities.¹¹ Although SBN single crystals could be used in wide applications, high cost and difficult fabrication have limited its practical use. Ceramic SBN, which has advantages of low cost, easy fabrication, and large size, would be promising in those applications. For optical applications, a ceramic with almost full density and a uniform microstructure is greatly desired.^{13–15} Lee and Fang^{16–18} have done a systematic study in sintering undoped SBN and proposed a possible mechanism of abnormal grain growth of SBN.¹⁹ It was reported that Ce ion could improve the optical properties of SBN,¹² but, so far, there are a limited number of studies dealing with the effect of the CeO₂ dopant on the defect structures and sintering behavior of SBN ceramics. The purpose of this investigation is to study the effect of the CeO₂ dopant

on the defect structure and sintering behavior of SBN ceramics.

2. Experimental procedure

High-purity powders of BaCO₃ (99.99%), SrCO₃ (99.995%) (Aldrich-APL), CeO₂ (99.99%) (Johnson-Matthey), and Nb₂O₅ (99.998%) (CERAC) were wet-mixed with ethyl alcohol for 24 h according to the formula Sr_{0.5}Ba_{0.5}Ce_xNb₂O_{6+δ} (*x* = 0, 0.01, 0.02, 0.04, and 0.06, represented by S50, 1CeS50, 2CeS50, 4CeS50, and 6CeS50, respectively). The mixed powders were microwave-dried to reduce the precipitation, ground in a mortar, and calcined at 1250 °C for 4 h. The calcined powders were wet-ball-milled in ethyl alcohol for 24 h and dried. The single-phase powders of all compositions were deagglomerated and then uniaxially compacted in a 12 mm die at 30 MPa, and thereafter, cold isostatically pressed at 200 MPa to form pellets with a green density of 60% of the theoretical density (*D*_{th}). The particle size distribution of each powder was determined by the sedimentation method (SediGraph 5100, Micromeritics Instrument Group, Norcross, GA). The average particle sizes of S50, 1CeS50, 2CeS50 and 4CeS50 were 1, 1.1, 1.2, and 1.2 μm, respectively. The isothermal sintering behaviors of green compacts (S50, 1CeS50, 2CeS50, and 4CeS50) were performed in a dilatometer at different temperatures using a heating rate of 20 °C/min to reach

* Corresponding author. Tel.: +886-6-275-7575; fax: +886-6-234-6290.

E-mail address: ttfang@mail.ncku.edu.tw (T.-T. Fang).

the desired temperature. The morphological kinetic equation²⁵ was used to evaluate the activation energy of the single-phase SBN doped with different molar ratios of the cerium ions. It can be expressed as

$$\ln(\dot{\varepsilon}T) = \ln \left[\left(\frac{\gamma}{k} \right) D^* A_i F_i(\gamma, z) \left(\frac{p}{p_0} \right)^{m_i} \right] + \left[\left(\frac{-Q}{R} \right) \left(\frac{1}{T} \right) \right] \quad (1)$$

where $\dot{\varepsilon}$ is the densification rate, D^* the diffusion constant, γ the surface energy, Q the activation energy, and R the Boltzmann's constant; p and p_0 represent the porosity and the onset porosity, respectively. The intercept parameter, A , is a function of the initial condition for each stage, and the morphological terms, m and γ , are related to the pore-size distributions. Z represents the fraction of shrinking pores. The subscript i represents the intermediate ($i=1$) and final ($i=2$) stages of sintering. In this investigation, the difference of the morphological parameters (γ , z , and m) in the pre-exponential term on the right-hand side of Eq. (1) is assumed to be small at the same density level for different sintering temperatures; thus, the parameters can be assumed to be constant, especially on a logarithmic scale. The field emission transmission electron microscope (FE-2000, Hitachi, Tokyo, Japan) equipped with EDS (Voyager 1100, Noran Instrument, Middleton, WI) was employed to examine the existence of the second phase.

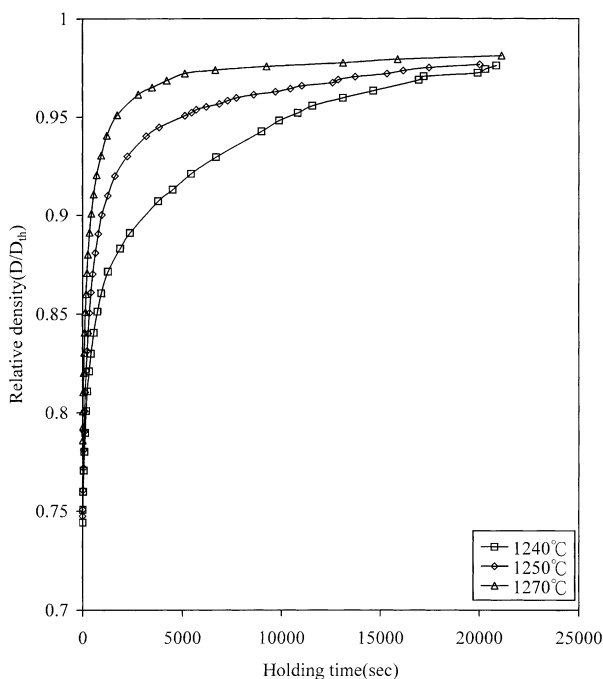


Fig. 1. The densification behaviour of the powder compacts of S50 isothermally sintered at 1240, 1250 and 1270 °C in air.

3. Results

Figs. 1–4 show the isothermal sintering behavior of the compacts with different compositions. It shows that the sintering temperatures increased with the cerium oxide content, which implies that the densification rate decreased with increasing the cerium oxide dopant, shown in Fig. 5. Based on Eq. (1) and data of Figs. 1–4, the activation energy could be evaluated by the plot of $\ln(\dot{\varepsilon}T)$ v.s. $(1/T)$ at each density level. The evaluated values of the activation energy, shown in Fig. 6 are 825, 989, 1049, and 1356 kJ/mol for S50, 1CeS50, 2CeS50, and 4CeS50, respectively. Fig. 7 shows the microstructures of 4CeS50, 5CeS50, and 6CeS50 characterized by the HRTEM, in which no second phase was observed. Fig. 8 shows the change of the lattice parameters of S50 doped with different amount of CeO_2 . It shows that the lattice parameter of a -axis increased but that of c -axis decreased when the cerium oxide dopant increased.

4. Discussion

In sintering polycrystalline ceramics, diffusion path of the rate-limiting species related to densification was usually considered as one of two limiting cases, i.e. grain boundary and lattice. However, it is common that both grain boundary and lattice diffusion can contribute to mass transport in the system. Therefore, the activation energy of sintering should be proper to assume as that of the apparent diffusion coefficient of the rate-limiting

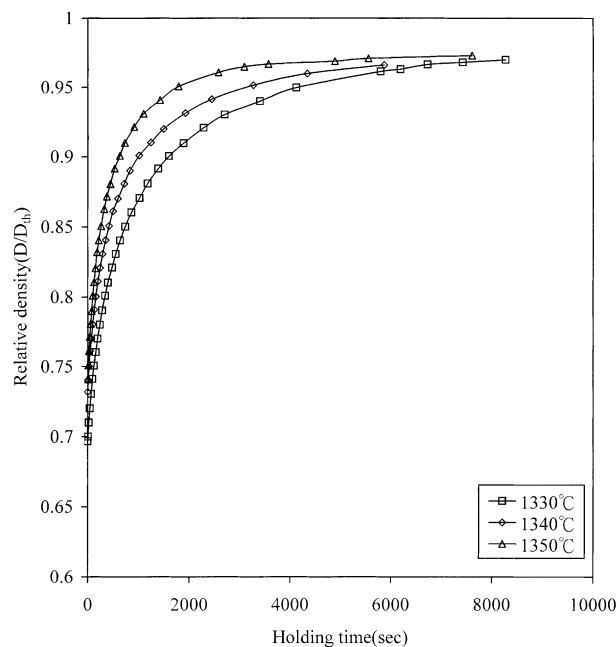


Fig. 2. The densification behaviour of the powder compacts of 1CeS50 isothermally sintered at 1330, 1340 and 1350 °C in air.

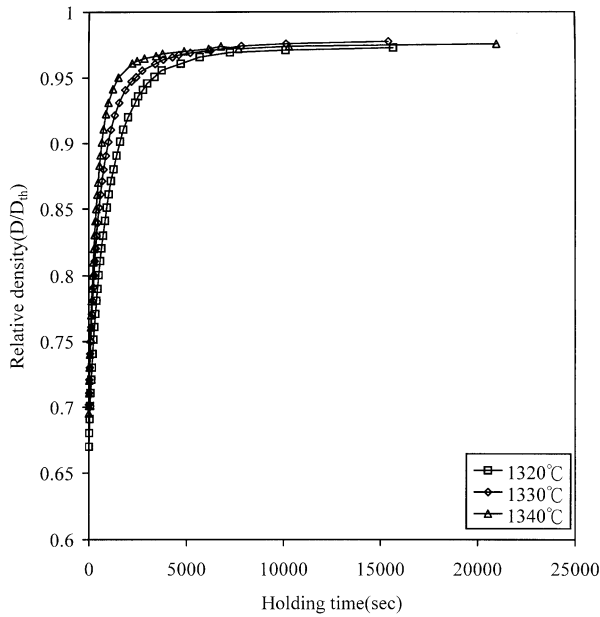


Fig. 3. The densification behaviour of the powder compacts of 2CeS50 isothermally sintered at 1320, 1330 and 1340 °C in air.

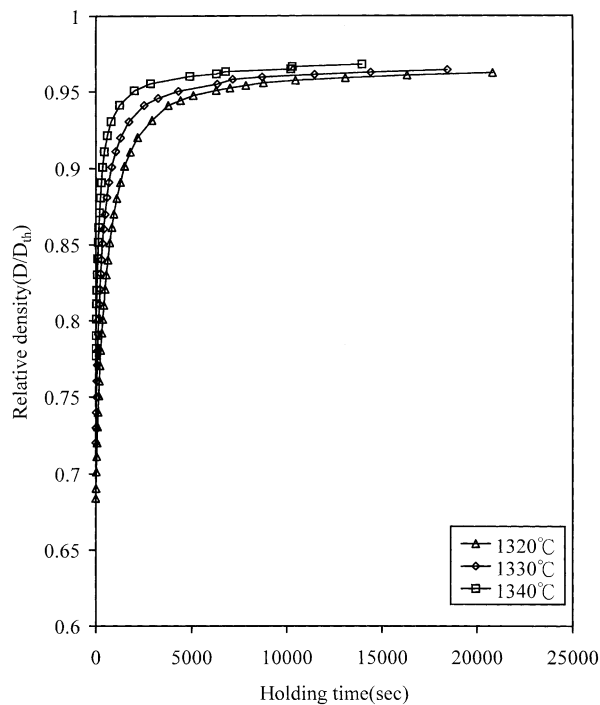


Fig. 4. The densification behaviour of the powder compacts of 4CeS50 isothermally sintered at 1320, 1330 and 1340 °C in air.

species of sintering. The rate-limiting species in sintering SBN ceramics was suggested as the niobium ion,¹⁶ so the apparent diffusion coefficient could be simplified as:²⁰ $D_{app} = \frac{1}{\alpha} \left(D_{Nb}^l + \frac{\pi \delta D_{Nb}^b}{d} \right)$, where $\alpha = 2$, δ is the grain boundary width, and d is the grain size. Therefore, if grain size is fine and the temperature is not high, D_{app} is

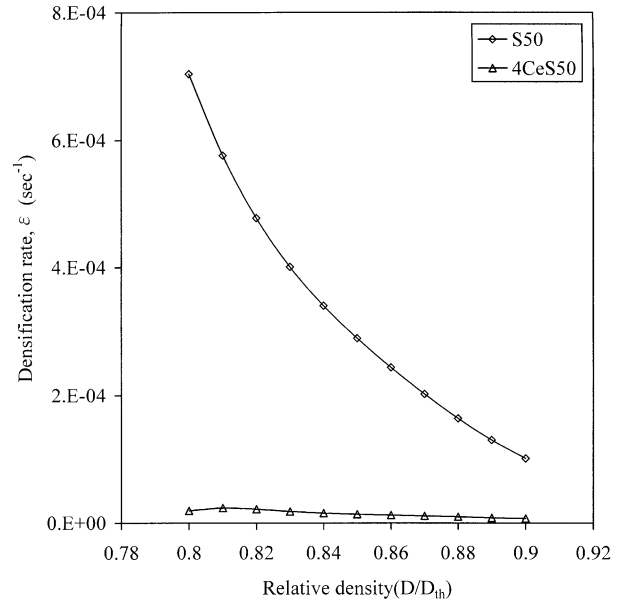


Fig. 5. Densification rate as a function of the relative density at 1270 °C in air for S50 and 4CeS50.

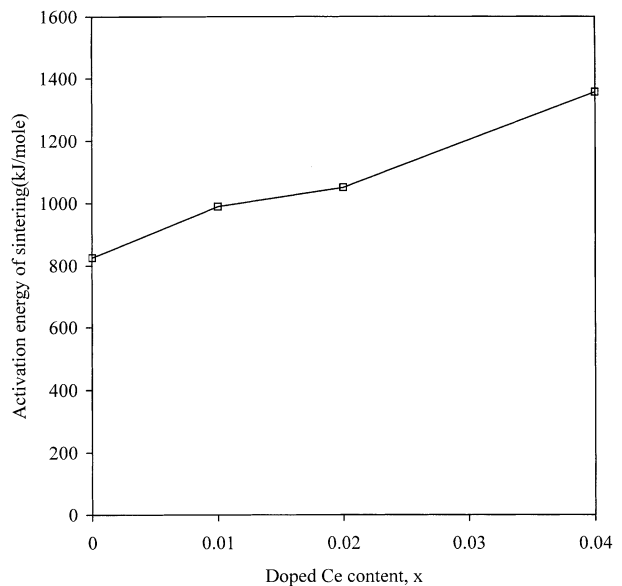


Fig. 6. Variation of the activation energy of the isothermal sintering as a function of the doped Ce content for S50, 1CeS50, 2CeS50, and 4CeS50.

determined by D_{Nb}^b . However, if temperature is high enough to have a significant contribution of lattice diffusion, both D_{Nb}^l and D_{Nb}^b would contribute to D_{app} . Some reports^{27–29} have suggested that the change of the relative contribution of D_l and D_b (D_l is the lattice diffusion coefficient and D_b is the grain boundary one) due to the difference of the impurity level or grain size could affect not only the pre-exponential factor in Eq. (1) but also the activation energy of the apparent diffusion coefficient in Eq. (1). In this investigation, grains were

fine and the sintering temperature was quite high, so both D_{Nb}^{l} and D_{Nb}^{b} would contribute to D_{appr} . However, the Ce ion did not segregate to grain boundary, so it would be assumed that the Ce ion would have more significant influence on the D_{Nb}^{l} value. Thus, the change of D_{appr} would mostly be arisen from D_{Nb}^{l} when the Ce ion was added.

In considering lattice diffusion, it is well known that the defects created by dopants would have a great influence on it. Several reports^{20–22,24} have suggested that the valence state of the Ce ion in SBN be +3, and it preferred to occupy Sr or Ba site. Although Baetzold²³ has proposed that a self-compensation reaction is

a preferred incorporation for Ce dopant to substitute Nb and Ba/Sr ions, the substitution of Nb ion is excluded because Ce dopant has been identified as Ce^{3+} and its radius (0.115 nm) is much larger than that of Nb^{5+} ion (0.078 nm). For the substitution of Ba or Sr, the possible charge compensation would be either cation vacancies (V_{Ba}'' , V_{Sr}'' , and V_{Nb}'''') or excessive oxygen ions. If the cation vacancies were created, cation ions might segregate to the grain boundary to form a second phase as reported in BaTiO_3 .²⁶ However, the second phases were not detected, even when the amount of CeO_2 dopant reached 6%, shown in Fig. 7. Moreover, because Nb ion has been suggested as a rate-limiting species during sintering of SBN ceramics,¹⁶ the creation of Nb vacancies would lead to the increase of the densification rate, which, however, is contradicted to the densification behavior shown in Fig. 5. Therefore, the creation of Nb vacancy should be excluded. Furthermore, if the vacancies of strontium ion (V_{Sr}'') and barium ion (V_{Ba}'') were created, it would contract the A site space, which in turn would enlarge the neighboring NbO_6 octahedral unit; i.e. the Nb–O bond would be lengthened, and thus, Nb–O bond strength would decrease. Therefore, the diffusion of the niobium ion would become easier in the structure; i.e., the activation energy of diffusion would be reduced, which, however, contradicted the result that CeO_2 dopant increased the activation energy of sintering of SBN. Based on the above discussion, the creation of Sr or Ba vacancy is also impossible.

It has been reported that only 50% of the O(4) sites of the B1 framework in the SBN structure were occupied.¹ Therefore, if the oxygen ion derived from oxygen gas of atmosphere is the charge compensation when SBN was

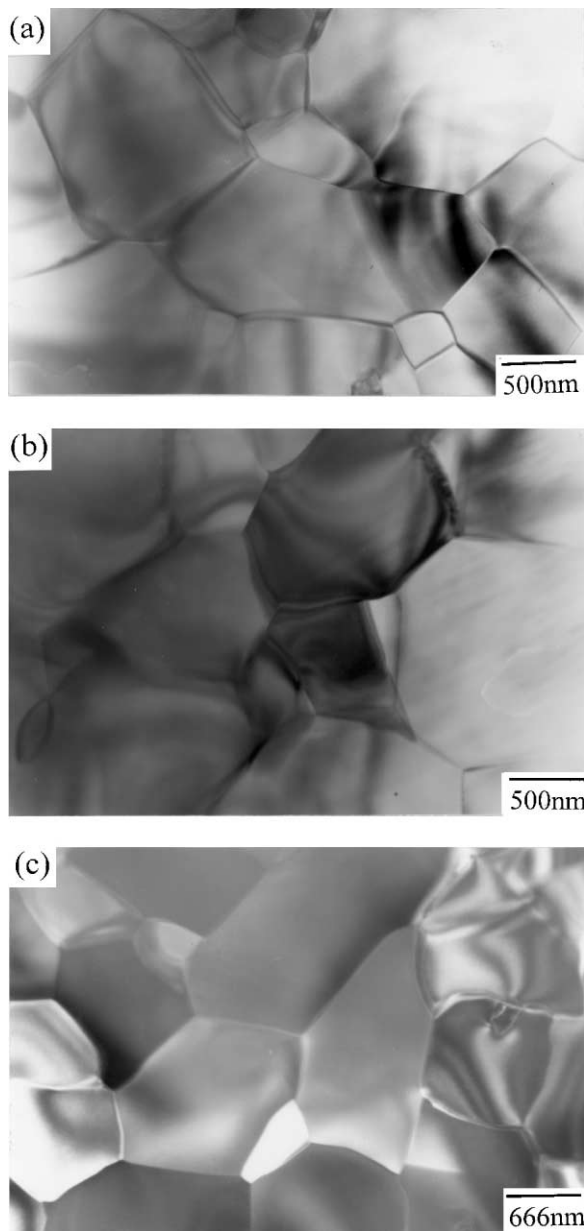


Fig. 7. The microstructure observed by the HRTEM with compositions (a) 4CeS50, (b) 5CeS50, and (c) 6CeS50 sintered at 1350 °C, 1 h with the heating rate of 10 °C/min in air.

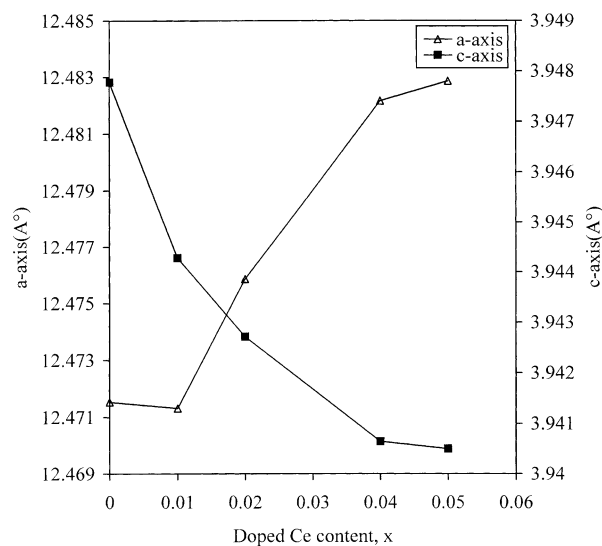


Fig. 8. The change of the lattice parameters for S50 doped with different amount of CeO_2 sintered at 1350 °C, 1 h using a heating rate of 10 °C/min in air.

doped with cerium ions, these oxygen ions would more probably occupy O(4) sites. If so, the Nb–O bond strength in the octahedral unit of NbO₆ would increase, which in turn would reduce the diffusivity of the niobium ion and increase the activation energy in sintering SBN ceramics. Besides, based on SBN structure, when more oxygen ions occupy the O(4) sites, it will decrease c-axis but increase a-axis because of the coulomb attraction between the oxygen ion in O(4) sites and niobium ion and repulsion of oxygen ion between O(4) and O(1). This viewpoint has been evidenced in Fig. 8, in which the c-axis was shortened and the a-axis was lengthened. Therefore, it is concluded that the charge compensation could be excessive oxygen ion occupying O(4) site when SBN was doped with CeO₂.

5. Conclusion

The sintering temperature of SBN increases with the increase of the CeO₂ dopant. The activation energies of the isothermal sintering for pure and CeO₂-doped SBN50 ceramics have been evaluated, in which the values are 825, 989, 1049, and 1356 kJ/mol for S50, 1CeS50, 2CeS50, and 4CeS50, respectively. It is suggested that the charge compensation of the cerium ion dopants be the excessive oxygen ion occupying the O(4) sites.

Acknowledgements

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