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On the discontinuous grain growth of $Sr_xBa_{1-x}Nb_2O_6$ ceramics

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Abstract

Strontium barium niobate powders with various compositions have been milled and annealed at a low temperature, 1000°C. It was found that powders of $Sr_xBa_{1-x}Nb_20_6$ with $x>40$ were partially decomposed and the higher the Sr/Ba ratio, the more they decomposed. It was also found that pre-treatment at or higher than complete formation temperature could prevent discontinuous grain growth by evading the development of liquid phase. The possible reasons for the development of liquid phase and discontinuous grain growth are proposed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Grain growth; Microstructure-final; Milling; Strontium barium niobate

1. Introduction

Strontium barium niobate (SBN) ceramics of the formula $Sr_xBa_{1-x}Nb_2O_6$ ($0.25 \leqslant x \leqslant 0.75$) have drawn considerable attention because of their potential applications for electro-optic,[1] pyroelectric,[2] piezoelectric,[3] and photorefractive devices.[4] Although single -crystal SBN has made good progress, in regard to its quality, and has been demonstrated to be useful for optical phase conjugation,[5,6] high cost and difficult fabrication have limited its applications. Ceramic SBN, which has the advantages of low cost, easy fabrication, and large size, has potential for such applications.

For optical applications, a ceramic with almost full density and a uniform microstructure is greatly desired. However, SBN has been found to be difficult to sinter to a high density via pressureless sintering because of abnormal grain growth.[7] Efforts have been made to obtain high-density products using hot pressing,[8] double-stage sintering,[7] or the additives in the sintering,[9] but the reason for the development of discontinuous grain growth is still ambiguous. Lee and Freer[10] have proposed that liquid phase resulting from locally inhomogeneous compositions due to partially uncomplete calcination would be the possible mechanism for the discontinuous grain growth. In this investigation, we further prove that the local inhomogeneous compositions could be partially-decomposed SBN due to the ball milling.

2. Experimental procedure

High purity powders of $BaCO_3$ (99.99%), $SrCO_3$ (99.995%) and Nb_2O_5 (99.999%) (APL, Engineered Materials, Inc., USA) were mixed with different ratios of Sr/Ba for $Sr_xBa_{1-x}Nb_2O_6$ ($x=0.2$ to 0.7) by wet ball-milling for 24 h. The mixed powders of different ratios of Sr/Ba were dried and calcined at each formation temperature summarized in Table 1, and then wet ball-milled for 24 h. The milled powers were further annealed at 1000°C for 0.2 h and 12 h.

The calcined powder of SBN60 was selected for the study of the effect of the pre-treatment, which was uniaxially pressed in a 12 mm die at a pressure of 30 MPa and then was further pressed by the cold isostatic pressing at 200 MPa to form a compact with a green density of 60% theoretical density. The green compacts were sintered in air using conventional and pre-treated profiles at a heating rate of 10°C/min. The conventional heating profile was to sinter specimens at 1300°C for 1 h; the pre-treated one was to sinter specimens at 1225°C for 6 h and then sinter at 1300°C for 1 h.

XRD (D/MAX III.V XRD, Rigaku, Tokyo, Japan) was employed to analyze the phases of the powders. The microstructures of the sintered samples were examined

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Table 1
The formation temperatures of SBN with different compositions

Composition	Formation temperature (°C)
SBN30	1100
SBN40	1125
SBN50	1150
SBN60	1225
SBN70	1375

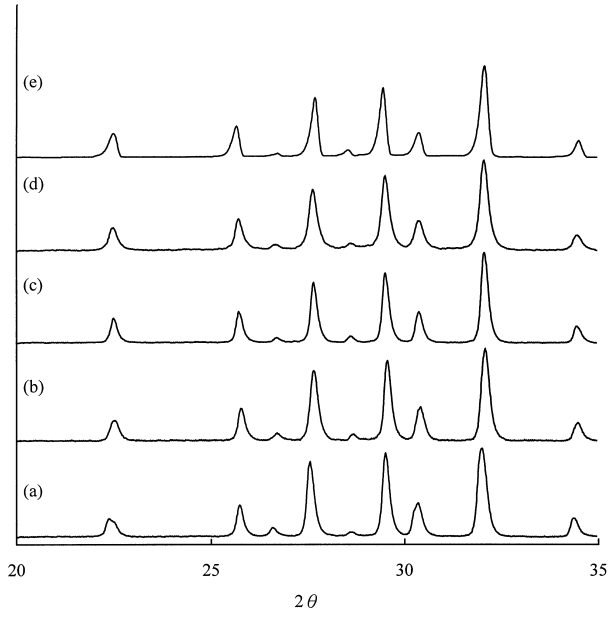

Fig. 1. X-ray diffraction patterns of calcined $Sr_xBa_{1-x}Nb_2O_6$ after ball milling: (a) $x=0.3$, (b) $x=0.4$, (c) $x=0.5$, (d) $x=0.6$ and (e) $x=0.7$, showing that the SBN phase did not decompose.

by scanning electron microscopy (SEM, S-4200 Field Emission SEM, Hitachi, Japan) and transmission electron microscopy (TEM, H-700H, Hitachi, Japan).

3. Results and discussion

3.1. Effect of ball milling on the decomposition of SBN

The calcined SBN was completely formed a single phase. The calcination temperatures for each composition are summarized in Table 1. Fig. 1 shows the X-ray patterns of a series of SBN powders after ball milling, in which these powders did not decompose. However, Fig. 2 shows that when the milled SBN powders were heated at 1000°C for 0.2 h, they have partially decomposed except SBN 30 and 40. It was also observed that the higher the ratio of Sr/Ba, the more it decomposes. Furthermore, Fig. 3 shows that if the milled SBN powders were heated at 1000°C for 12 h, the powders were further decomposed. Based on the results of Figs. 1–3, it is

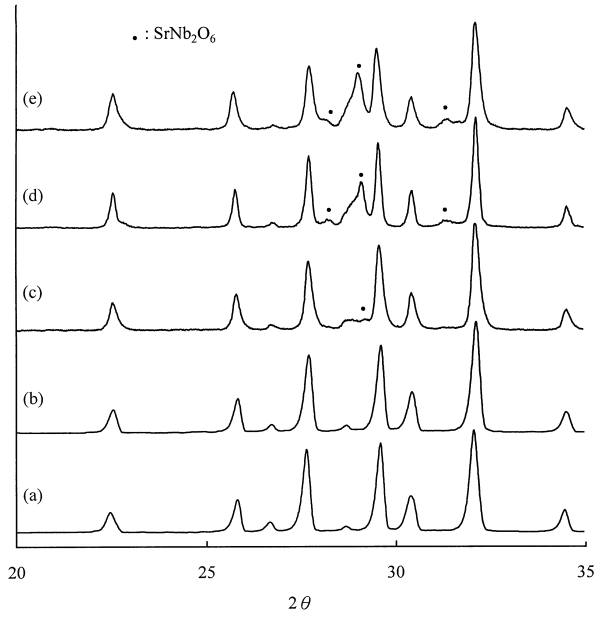

Fig. 2. X-ray diffraction patterns of milled $Sr_xBa_{1-x}Nb_2O_6$ heated at 1000°C for 0.2 h: (a) $x=0.3$, (b) $x=0.4$, (c) $x=0.5$, (d) $x=0.6$ and (e) $x=0.7$, showing that specimens with $x>40$ have partially decomposed.

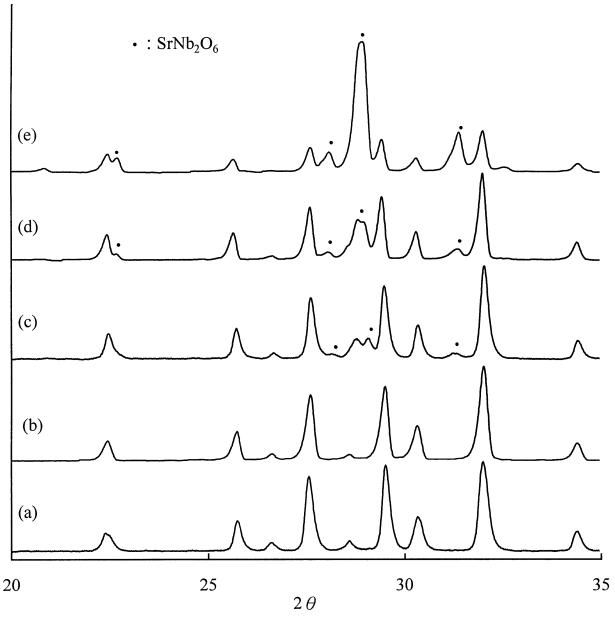

Fig. 3. X-ray diffraction patterns of milled $Sr_xBa_{1-x}Nb_2O_6$ heated at 1000°C for 12 h: (a) $x=0.3$, (b) $x=0.4$, (c) $x=0.5$, (d) $x=0.6$ and (e) $x=0.7$, showing that specimens with $x>40$ have partially decomposed.

apparent that the incompletely formed phases shown in the X-ray patterns were not related to the partially incomplete calcination. Actually, partial decomposition promoted by the ball-mill has been observed in magnetic ferrites,[11] in which the strain energy introduced by the ball milling was considered to be the major cause for the decomposition of milled ferrite powders. Therefore,

it was inferred that the decomposition of milled SBN powders might also be attributed to the strain energy introduced by the ball milling. If so, it could explain why powders of SBN 30 and 40 did not decompose and the extent of the decomposition increases with the increase of the ratio of Sr/Ba. In the previous work,[12] it was found that lattice distortion was increased with increasing the ratio of Sr/Ba. Thus, it is argued that the total energy, i.e. the lattice distortion energy and the strain energy introduced by ball milling, might increase with the increase of the ratio of Sr/Ba. Moreover, it was reported[3] that SBN33 possesses the lowest free energy. Therefore, the total energy might not be sufficient to make $Sr_xBa_{1-x}Nb_2O_6$ with $x<40$ partially decompose but to do so for $x>40$, in which the decomposed amount would increase with the increase of the ratio of Sr/Ba.

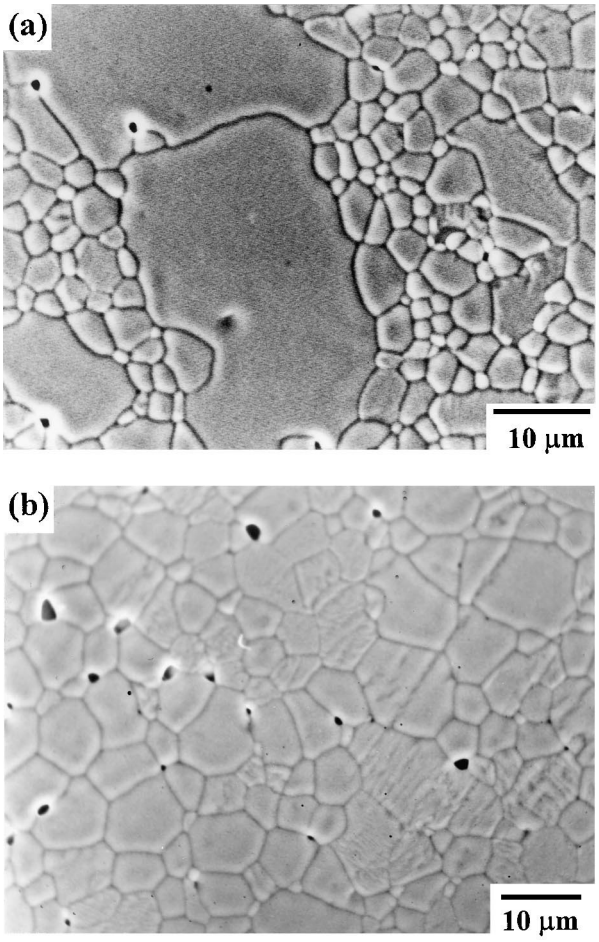

Fig. 4. Comparison of the microstructures of SBN60 sintered at 1300°C for 1 h (a) without pre-treatment and (b) with pre-treatment at 1225°C for 6 h.

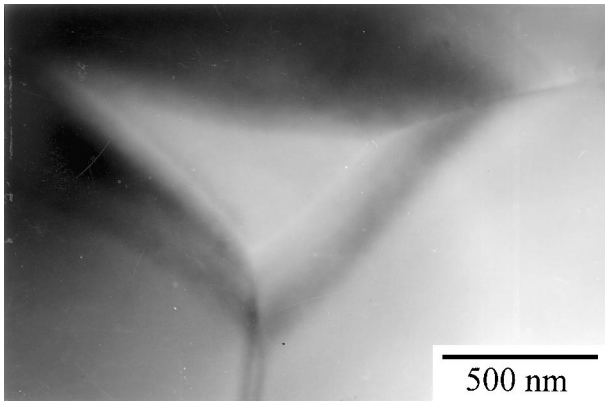

Fig. 5. Microstructural observation of TEM showing the possible existence of a liquid phase in a triple-point pocket.

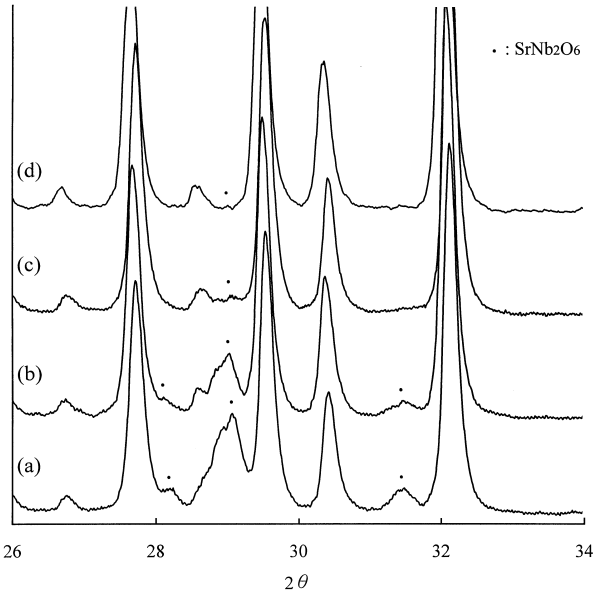

Fig. 6. X-ray diffraction patterns of SBN60 sintered without holding at (a) 1225°C, (b) 1250°C, (c) 1275°C and (d) 1300°C, showing that the decomposed phase is still retained.

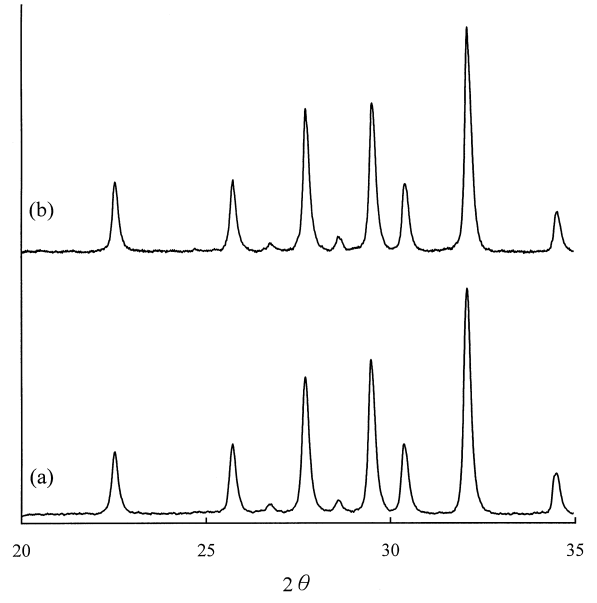

Fig. 7. X-ray diffraction patterns of sintered SBN60 with pre-treatment at (a) 1225°C for 6 h and (b) 1250°C for 0.5 h, showing the disappearance of the decomposed phase.

3.2. Effect of pre-treatment on the microstructural development of SBN

Fig. 4 shows comparisons of the sintered microstructures of samples with and without pre-treatment after ball milling. Discontinuous grain growth occurred in the samples without pre-treatment but did not in the pre-treated samples. Fig. 5 shows a possible liquid phase existing in the triple-point pocket indicating that liquid phase might develop during sintering. However, more work should be done to verify it. While it has been reported[10] that liquid phase might induce the discontinuous grain growth, the cause for developing the liquid phase is ambiguous. In order to realize this reason, milled SBN 60 powder was selected for further study. At first, we simulate the heating schedule of sintering, i.e. heat at 10°C/min to the desired temperature without holding. It is clearly shown in Fig. 6 that the decomposed phases decreased with increasing temperature and are retained till 1300°C. This would provide opportunity for the development of liquid phase according to the results of Lee and Freer,[10] that the liquid phase formed between 1250 and 1300°C. However, it is shown in Fig. 7 that the decomposed phase would disappear when the milled powder was heated at or higher than the temperature of the complete formation temperature,[13] i.e. 1225°C for SBN60 for a reasonable time. Thus, this explains why dual-stage sintering would effectively prevent discontinuous grain growth.[10]

As mentioned above, it is suggested that the development of the liquid phase might be attributed to the nonstoichiometric decomposed phase due to the effect of ball milling rather than the partially incomplete calcination. Finally, it should be noted that while the pre-treatment could prevent the occurrence of the discontinuous grain growth during sintering around 1300°C, at higher temperatures >1300°C, duplex structure was still observed, which might be due to the anisotropic grain growth.[14]

4. Conclusions

1. SBN partially decomposed when it was heated at 1000°C for 0.2 h after ball milling. This was related to the lattice distortion introduced by ball milling. Moreover, the higher the ratio of Sr/Ba, the more the phase decomposed.
2. The development of the liquid phase might be due to the nonstoichiometric decomposed phase. Pre-treatment at or higher than the complete formation temperature of SBN could make the decomposed phase disappear, which in turn could prevent the occurrence of the discontinuous grain growth.

Acknowledgements

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