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Investigation of the origin of abnormal grain growth in the sintering process of Sr_{0.5}Ba_{0.5}Nb₂O₆ ceramics without eutectic liquid-phase

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Abnormal grain growth in the traditional sintering process of $(Sr_xBa_{x-1})Nb_2O_6$ limites its application and the localized liquidphase exsisting is regarded the main reason for the presence of abnormal grain growth. To prevent the presence of a localized liquid-phase, the sol-gel method was employed to synthesize nano-sized powders of $Sr_{0.5}Ba_{0.5}Nb_2O_6$, which was followed by a pure solid-phase sintering process of nano-sized powders to observe the evolution of the grain morphology. SEM observation revealed that the abnormal and preferential rod-like grain growth along the c-axis existed in the pure state-phase sintering for the $Sr_{0.5}Ba_{0.5}Nb_2O_6$ material companied with some of the smaller grains being diminished or consumed. This behavior would exist in the traditional solid-phase sintering with or without the localized liquid-phase. This would be another important factor to aid the abnormal grain growth and should be prevented in the manufacturing process. The effects of grain sizes on the dielectric constant, Tc and diffuse phase transion (DPT) were observed in the $Sr_{0.5}Ba_{0.5}Nb_2O_6$ ceramics.

Key words: Niobates, Sintering, Microstructure-final, Sol-gel processes, Dielectric properties.

Introduction

Strontium barium niobates, $Sr_xBa_{1-x}Nb_2O_6$ (0.25 $\geq x \leq$ 0.75, SBN), have received much attention for several decades not only because their promise as lead-free functional materials for optical and electrical applications [1, 2, 3], but also they have modified physical properties with varying composition [2, 4, 5] and various dopants [6, 7, 8, 9, 10]. In recent years, many studies have been focused on the preparation and properties of ceramic SBN due to the advantages of easy fabrication and low cost. Although much progress on the methods of synthesis and preparation, such as a solid-state reaction method [11], a sol-gel method [12], a co-precipitation method or a partial co-precipitation method [13, 14], have been made, the final microstructure of the ceramics SBN fabricated by pressureless sintering shows a tendency for abnormal grain growth, which limits its physical, electrical properties and applications [2, 11, 14]. Therefore, efforts have been devoted to explore the origination of the abnormal grain growth in conventional sintering processes and pursue a dense microstructure with uniforme morphology of grains.

Lee and Feer [15, 16] suggested that the localized liquid phase caused by a Nb-rich, Ba-poor phase at grain boundaries, which was induced due to a partially uncompleted calcination process, resulted in abnormal grain growth. The Nb-rich, Ba-poor phase has a lower melting temperature than the normal sintering temperature, Then, a dualstage sintering and fast sintering process was put forward to inhibit abnormal grain growth. Fang et al. [17] believed that the partially decomposed phase of SBN by the effect of ball milling was the main reason for the development of a localized liquid phase, and a pre-treatment process at or higher than the complete formation temperature of SBN was also used to prevent the occurrence of the discontinuous grain growth. Based on the above views, it is critical to eliminate the eutectic phase with inhomogeneous compositions in localized areas whether it is caused by the partially uncomplete calcination process or by the effect of ball milling. There would be two ways of achieving this. One is to provide sufficient liquid phase, which can wet well on the surface of all the grains to eliminate the local eutectic phase. Another is to eliminate any eutectic phase around all grains by a suitable fabrication process. So, amorphous SiO₂ with a lower melting temperature was introduced as a sintering additive [18] to promote the uniforme distribution of the eutectic phase around the primary grains as well as to improve the evolution of the microstructure of SBN ceramic. It was found that the sintering additive of SiO₂ (1.0-1.5 wt%) can effectively eliminate the presence of the local liquid phase and inhibit the discontinuous grain growth. In this study, we prepare pure and nano-sized powders of Sr_{0.5}Ba_{0.5}Nb₂O₆ by a sol-gel chemical method and no ball-milling mixture process was used in the following preparation steps, which could prevent the presence of any possible localized liquidphase. Then a sintering stage was followed to investigate the microstructural evolution of Sr_{0.5}Ba_{0.5}Nb₂O₆ ceramics. The aim of this study is to explore if other mechanisms related with the phenomenon of abnormal grain growth existe in the sintering process.

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Experimental Procedure

A sol-gel technical method was employed to fabricate nano-sized $Sr_{0.5}Ba_{0.5}Nb_2O_6$ powders. The starting materials used were Nb_2O_5 , $BaCO_3$, $SrCO_3$, and citric acid and ammonia solution all in chemically pure grades. For the preparation of the Nb-citrate acid solution, Nb_2O_5 was added to sulfuric acid with a ratio of 1:30 (g/ml) and it was heated to form a uniform solution. The solution was dropped into deionized water with stirring and then aqueous ammonia solution in excess was dropped slowly into the diluted Nb-sulfuric acid solution, after which the complex-solution of precipitates was filtered and washed with deionized water to remove the sulfur. Finally, the precipitate obtained was added to a citrate acid solution with stirring at 80 °C for 8 hours to form a Nb-citrate acid solution.

According to the chemical formula $Sr_{0.5}Ba_{0.5}Nb_2O_6$, the starting materials were taken as the mole ratios of Sr : Ba : Nb is 1 : 1 : 4 for the preparation of pure and nano-sized $Sr_{0.5}Ba_{0.5}Nb_2O_6$ powders. First, the amount of $SrCO_3$ was added to the amount of Nb-citrate acid solution with stirring to form a transparent solution and its PH value adjusted to 3 by adding aqueous ammonia drop by drop. Subsequently, BaCO₃ was added into the solution with stirring, and then the PH value of the solution was adjusted to 8 by dropping aqueous ammonia continuously to form a sol with a yellow color. Next the sol was dried at 80 °C until it was transformed to a dried gel precursor. Finally, the dried gel was calcined at three different temperatures (600, 700 and 800 °C) in air for 2 hours and the powders obtained were used for the analysis by XRD and observation by TEM.

Based on the results of XRD analysis, the powders calcined at 800 °C were used for the preparation of $Sr_{0.5}Ba_{0.5}Nb_2O_6$ ceramics. The nano-sized powder was axially pressed in a die of 12 mm diameter at a pressure of 200 MPa to form green compacts. Next the green compacts were dried in air at 80 °C. After that the compacts were sintered in air at 1000, 1050, 1100 and 1150°C for 2 h. The heating rate was kept at 2.5 K minute⁻¹.

X-ray diffraction analysis (D8ADVANCE, German Bruker, and Karlsruhe, Germany) was employed to analyze the crystallization process of the SBN gel powders with a scan rate of 5°/minute. The morphology of the calcined powders was observed with a Transmission Electron Microscope (JSM-1200EX, JEOL, Japan). The microstructure of the ceramics was investigated with a scanning electron microscopy (JSM-6390LV, JEOL, Japan). The samples were well polished and sputtered with gold. An LCR meter (TH2819-GDS-100, China) was employed to measure the dielectric properties from –70 °C to 100 °C at 10 KHz frequency.

Results and Discussion

In the traditional technology of the solid-phase synthesis for SBN ceramics, there are two synthetic mechanisms to affect the structural evolution of single-phase SBN grains; one is that the intermediate phases, Ba₅Nb₄O₁₅, Sr₅Nb₄O₁₅, BaNb₂O₆ and SrNb₂O₆, would be existed in the solid-phase process of SBN [19]. This means that some intermediate reactions must accur and a higher sintering temperature is needed for the synthesis of pure SBN, and these reactions will disturb the normal evolution of SBN grains. So the phenomenon of the formation of intermediate phases should be avoided in this investigation. Another is that a single phase tetragonal tungsten bronze (TTB) SBN ceramic could be easier to obtain when the x values equals 0.5, otherwise some intermediate phases, such as the orthorhombic phase BaNb₂O₆ or SrNb₂O₆ for x < or > 0.5, easily appeare before a completed TTB SBN ceramic is formed at a higher synthetic temperature [5]. These intermediate reactions would also disturb the evolution of SBN grains. But when the x equals 0.5, a pure single tetragonal tungsten bronze phase Sr_{0.5}Ba_{0.5}Nb₂O₆, can be obtained at a lower synthesis temperature and no intermediate reactions existe [5]. Therefore, the composition $Sr_{0.5}Ba_{0.5}Nb_2O_6$ (x = 0.5) was chosen as the target material of this study and the solgel method was used to prepare the precursor and nanosized powders of Sr_{0.5}Ba_{0.5}Nb₂O_{6 to} prevent the presence of intermediate phases. Furthermore, no ball milling steps were used in the preparation process of the $Sr_{0.5}Ba_{0.5}Nb_2O_6$ powder and ceramics, so no localized liquid phases and no impurities could be induced in the evolution of the grain growth.

Characterization for phase composition

Fig. 1 shows the XRD patterns for $Sr_{0.5}Ba_{0.5}Nb_2O_6$ powders calcined at 600 °C, 700 °C and 800 °C for 2 h. According to the figure, a single tetragonal tungsten bronze (TTB) phase $Sr_{0.5}Ba_{0.5}Nb_2O_6$ powder with well-crystallized



Fig. 1. XRD patterns of dried gel calcined at different temperatures for 2 h.



Fig. 2. XRD pattern of sample sintered at 1000 °C for 2 h.

grains could be obtained at a calcination temperature of 800 °C, but under the temperature of 800 °C the crystallization of the powders was not completely accomplished. Compared to Fig. 2, which gives the pattern of XRD phase analysis for the sample sintered at 1000 °C for 2 h, it could be found that the two patterns (800 °C and 1000 °C) have the same phase construction and phase composition (TTB, Sr_{0.5}Ba_{0.5}Nb₂O₆). The X-ray diffraction analysis verifies that the single phase of TTB type structure is preserved in the calcined powders and the sintered samples. This illustrates that the history of the sintering process from the powders to the ceramics is only a stage of grain



Fig. 3. TEM image of Sr_{0.5}Ba_{0.5}Nb₂O₆ powder calcined at 800 °C.

growth, and no chemical reaction and intermediate phases existed in this process. It is expected that this procedures can prevent any disturbed steps of intermediate reactions in the sintering process.

Evolution of grain morphology

TEM analysis was used to observe the particle size and morphology for the powders calcined for 2 h at 800 °C (Fig. 3). This clearly shows that a uniform-sized and weaklyagglomerated $Sr_{0.5}Ba_{0.5}Nb_2O_6$ powders having the sizes of about 10-30 nm were obtained in this process. These nanosized powders were directly pressed and shaped into disk pellets which were followed by a sintering process. Therefore, no impurities could be involved because no ball-milling mixture process was used in this manufacturing process.

Fig. 4(a, b, c, d) shows the microstructures of the grains for the samples sintered at different temperatures



Fig. 4. SEM images of samples sintered for 2 h at 1000 °C (a, b), 1100 °C (c) and 1150 °C (d).

of 1000, 1100 and 1150 °C for 2 hours. This sintering process is believed to be a pure solid-phase sintering stage. Fig. 4(a, b) show the microstructure of the sample sintered at 1000 °C, in which extensive porosity and similar aggregates particles are observed. The shape of the grains is nearly spherical and the grain sizes range between 100 and 400 nm. Compared with the shapes and sizes of the grains in the powder calcined at 800 °C (Fig. 4), the grains have only an initial growth in size. This illustrates that a sintering temperature of 1000 °C is not sufficient to gaine active energy of dense sintering and it would only give an initial stage of solid-state sintering.

Fig. 4(c) gives the microstructure of the sample sintered at 1100; it presents a microstructure of well-packed grains, a few pores and a high density. In particular it shows that the shape of most of the grains changed from sphere-like to short rod-like. Namely, as the sintering temperature increased, a preferential growth along the c axis direction happened for some grains. The final sizes of the rod-like grains increased to about 200 nm in diameter and about 500 nm in length. A narrower grain size distribution could also be observed in this image, but a few smaller grains with the sphere-like shape still existed. This indicates that the grains were in a normal growth stage with the movement of grain boundaries in this sintering stage, in which some small grains were gradually diminished in size. This stage can fall into the phase of medium-last or dense sintering.

From Fig. 4(d) it can be seen that the sample sintered at 1150 °C presents the features of a duplex structure comprising two types of primary grains, in which one is rod-like grains with a large aspect ratio of 5-7, whose sizes are 0.4-0.6 µm in diameter and 2-3 µm in length, and another is short rod-like grains with small aspect ratio of about 2, whose size is about 0.4 µm indiameter, and a few spherical grains with a size of about 200 nm also existe. Inparticular, it can be observed that some bigger pores were regenerated around the rod-like grains with a large aspect ratio. The grains which are rod-like with a large aspect ratio were formed indicating that the abnormal and preferential grain growth along the c-axis occurred for some grains in the last stage of the sintering process. And it can also illustrate that the preferential rod-like grain growth was companied with some of the smaller grains being diminished or consumed.

Because the sol-gel technical route was used and no ball-milling process was involved in the preparation process of these $Sr_{0.5}Ba_{0.5}Nb_2O_6$ ceramics, we can insure that any eutectic liquid phases or any local liquid-phase, which are regarded as key factors for the drawback of abnormal grain growth, can not be generated in this sintering process, so the phenomenon of abnormal and preferential growth of rod-like grains along the c-axis could happen not only in the pure solid-phase sintering but also in the sintering process of a traditional solid-phase with or without local liquidphases. Namely when local liquid-phases are introduced by the effect of ball milling or an Nb-rich, Ba-poor phase at grain boundaries in the traditional sintering process, the phenomenon of abnormal grain growth could in part resulte from the abnormal and preferential growth of rod-like grains along the c-axis in the regions without local liquid-phases and it would be another important factor to aid the abnormal grain growth or discontinuous grain growth except for the reasons known before [15-17]. So, it would not be an effective method to eliminate the influence of local eutectic liquid phases to prevent the problem of the abnormal grain growth.

Based on the discussion above, the images (Fig. 4) describe typically the evolution of the grain growth in the pure state sintering process. In the initial sintering stage, the nano-sized grains grow only in size and sintering may occur preferentially in the aggregate particles, which may give a resistance to the sintering process. In this stage, the microstructure of the sample exhibits a loose construction and the grain sizes are in widely distributed. In the stage of medium-last sintering, the shapes of most grains change from sphere-like to short rod-like with the development of the preferential growth of rod-like grains along the c-axis and the densification of the sintering, the abnormal and preferential rod-like grain growth occurs companied by some of the smaller grains becoming diminished or consumed



Fig. 5. Temperature dependence of the dielectric constant for samples sintered at deferent temperatures.



Fig. 6. Temperature dependence of the dielectric loss for samples sintered at deferent temperatures.

and the porosity of the sample becomes bigger again. The result also suggests that reducing the structure of aggregates, using powders with a narrow size distribution and lower the sintering temperature would be effective methods to decrease the abnormal grain growth in the sintering of SBN ceramics.

Dielectric properties

Figs. 5 and 6 show the temperature dependence of the dielectric properties for the samples sintered at different temperatures. According to Fig. 5, the sample sintered at the lower temperature of 1000 °C, which has a microstructure with extensive porosity and nearly sphere-like grains, shows no obvious Curie peak and very low values of the dielectric constant. As the sintering temperature increased, the sample sintered at temperature of 1100 °C, which has a microstructure of dense and short rod-like grains with a well grown morphology, shows enhanced dielectric constants and a typical diffuse phase transition (DPT, a broad Curie peak in the phase transition range) phenomena. When the temperature of sintering was increased to 1150 °C, the DPT of the sample become weaker and the dielectric constants are sharply raised. It should be noticed that the Curie temperature (Tc) was shifted towards a higher temperature as the sintering temperature was increased. Based on this observation we know that the grain sizes of the samples have a direct relation with the sintered temperature, so this also means that the effect of grain size [20] [21] on the dielectric constants, the Tc and the DPT in the Sr_{0.5}Ba_{0.5}Nb₂O₆ ceramics was observed.

As seen from Fig. 6, the dielectric losses of the samples sintered at different temperature increase as the sintering temperature is raised, but it had a sharp decrease when the measured temperature was increased and became very low (under 0.1) after the measured temperature was more than 100 $^{\circ}$ C.

Conclusions

Nano-sized powders of Sr_{0.5}Ba_{0.5}Nb₂O₆ were synthesized by sol-gel method and a pure solid-phase sintering was conducted at different temperatures without any localized liquid-phase and any intermediate chemical reaction or intermediate phases. Based on the SEM observations, the evolution of the grain growth from nano-sized grains to rod-like grains in the pure state sintering process was described.

We report that a phenomenon of abnormal and preferential rod-like grain growth along the c-axis was existed in the post phase of the pure state-phase sintering process for nano-sized Sr_{0.5}Ba_{0.5}Nb₂O₆ powders. This type of abnormal grain growth happened accompanied by some of the smaller grains becoming diminished or consumed. This would be another important factor to aid the abnormal grain growth or discontinuous grain growth in the state-phase sintering with or without a localized liquid-phase. The results also suggest that it would not be an effective method to eliminate the influence of local eutectic liquid phases to prevent the problem of the abnormal grain growth.

An effect of the grain size on the dielectric properties was observed in this material. The Tc was shifted towards a higher temperature and the DPT phenomena of the sample became weaker as the grain size increased.

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