Influence of Sintering Atmosphere on Abnormal Grain Growth Behaviour in Potassium Sodium Niobate Ceramics Sintered at Low Temperature

John G. Fisher^{*,**}, Si-Young Choi^{***}, and Suk-Joong L. Kang^{*,†}

^{*}Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea

^{**}School of Materials Science and Engineering, Chonnam National University, Gwangju 500-757, Korea

^{***}Korea Institute of Materials Science, Changwon 642-831, Korea

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ABSTRACT

The present study aims to identify the effect of sintering atmosphere [O_2 , 75 N_2 -25 H_2 (mol%) and H_2] on microstructural evolution at the relatively low sintering temperature of 1040°C. Samples sintered in O_2 showed a bimodal microstructure consisting of fine matrix grains and large abnormal grains. Sintering in 75 N_2 - 25 H_2 (mol %) and H_2 caused the extent of abnormal grain growth to increase. These changes in grain growth behaviour are explained by the effect of the change in step free energy with sintering atmosphere on the critical driving force necessary for rapid grain growth. The results show the possibility of fabricating $(K_{0.5}Na_{0.5})NbO_3$ at low temperature with various microstructures via proper control of sintering atmosphere.

Key words : Lead-free piezoelectric, Grain growth, Grain boundaries, Sintering atmosphere, Niobates

1. Introduction

In recent years, a great deal of effort has gone into finding lead-free replacements for $Pb(Zr,Ti)O_3$ piezoceramics. One promising family of ceramics is based on solid solutions in the $KNbO_3$ - $NaNbO_3$ pseudo-binary system.¹⁾ Ceramics of the composition $(K_{0.5}Na_{0.5})NbO_3$ have moderate piezoelectric properties ($d_{33} = 70$ -90 pC/N, $k_p = 0.36$ -0.39, $k_t = 0.4$)^{2,3)} that can be improved by addition of compounds which form solid solutions with $(K_{0.5}Na_{0.5})NbO_3$ ^{4,5)} or by producing grain-oriented ceramics.^{6,7)}

It has been noted in the literature that $(K_{0.5}Na_{0.5})NbO_3$ displays abnormal grain growth, with the microstructure consisting of large abnormal grains surrounded by fine matrix grains.⁸⁻¹¹⁾ Abnormal grain growth is generally undesirable as it can inhibit densification^{12,13)} and may also lead to unfavourable dielectric and mechanical properties.^{10,11)} Although many studies have been carried out on improving the sinterability of $(K_{0.5}Na_{0.5})NbO_3$, few detailed studies exist concerning microstructural development. Recent experiments have shown that sintering $(K_{0.5}Na_{0.5})NbO_3$ in reducing atmospheres can reduce abnormal grain growth.^{14,15)} Samples sintered in O_2 or N_2 had very coarse microstructures with grains up to 50 μm in diameter but in samples sintered in 75 N_2 -25 H_2 (mol %) or H_2 , the amount of abnormal grain growth could be reduced or entirely suppressed. This change in microstructure was caused by an increase in the concen-

tration of oxygen vacancies in the samples sintered in reducing atmospheres.^{15,16)} This reduced the critical driving force necessary for grain growth, causing a transition from abnormal to pseudo-normal grain growth.¹⁷⁾ In the previous work, samples were sintered at 1100°C. Changes in sintering temperature can also have an effect on abnormal grain growth behaviour as the critical driving force for grain growth is also dependant on temperature.¹⁷⁾ In the present work the effect of sintering at a lower temperature in various atmospheres will be studied.

2. Experimental

The mixed oxide method was used to prepare powders of $(K_{0.5}Na_{0.5})NbO_3$. K_2CO_3 (99.5%, Junsei), Na_2CO_3 (99.8%, Acros) and Nb_2O_5 (99.9%, Grand Chemical & Material) were mixed in appropriate amounts and ball milled in ethanol for 24 h, using ZrO_2 milling media and polypropylene jars. In order to remove any adsorbed water, the K_2CO_3 and Na_2CO_3 powders were dried at 250°C overnight and the Nb_2O_5 powder was dried at 80°C overnight before weighing. After ball milling, the ethanol was evaporated using a hot plate and magnetic stirrer. The resulting powder was ground with an agate mortar and pestle and passed through a 180 μm sieve. The powder was loaded into an alumina crucible with a lid and calcined at 750°C for 5 h. The calcined powder was examined by X-ray diffraction (Rigaku D/MAX-IIIC, Tokyo, Japan) and found to be single phase perovskite. The calcined powder was ball milled and sieved as before to break up any agglomerates. The particle size distribution after ball-milling was measured using a laser particle size analyser (Photal Otsuka Electronics ELS-Z2, Hirakata, Japan). The particle size distribution of

[†]Corresponding author : Suk-Joong L. Kang
E-mail : sjkang@kaist.ac.kr
Tel : +82-42-350-4113 Fax : +82-42-350-3310

the starting powder was asymmetric, with a peak at 205 nm and a tail out to 310 nm. The mean and standard deviation of the particle radius were 217 nm and 25 nm respectively.

Samples were made by compressing by hand 0.5 g of powder in a steel die 10 mm in diameter. Samples were then removed from the die and cold isostatically pressed at 200 MPa.

Samples were sintered in a closed-end alumina tube in a vertical tube furnace in atmospheres of flowing O_2 , 75 N_2 -25 H_2 (mol%) or H_2 (flow rate $\approx 150 \text{ cm}^3 \cdot \text{min}^{-1}$) at 1040°C for 0.5-10 h. The heating and cooling rates were $5^\circ\text{C} \cdot \text{min}^{-1}$. Samples were placed in an alumina crucible without a lid. The crucible was lined with square spacers made from sintered $(K_{0.5}Na_{0.5})NbO_3$ to prevent the samples from touching the crucible walls. To prevent the samples from sintering to each other, a small amount of $(K_{0.5}Na_{0.5})NbO_3$ powder was placed between samples.

The density of the sintered samples was measured by Archimedes' method in distilled water. For each sintering experiment, three samples were measured three times each, and the mean and standard deviation taken. For microscopy, samples were sectioned and polished to a $0.25 \mu\text{m}$ finish. Scanning electron microscopy (SEM) was carried out using a Phillips XL30 SEM (Phillips, Eindhoven, Netherlands). To observe the microstructure, polished samples were thermally etched at temperatures between 990 - 1035°C for 60 min in air. All samples were Pt coated. Grain size distributions were measured using the same method as in our previous work.¹⁴⁾ Microscopy was also carried out on polished but unetched samples.

For Transmission Electron Microscopy (TEM), samples were prepared by the normal methods of dimpling and ion beam milling. Conventional TEM micrographs were taken using a JEOL 3010 and a JEOL JEM-2100F TEM (JEOL, Tokyo, Japan). Electron Energy Loss Spectroscopy (EELS) was carried out in the JEOL JEM-2100F across grain boundaries in the samples sintered for 2 h in O_2 and H_2 . The O/K ratios were measured at $\sim 30 \text{ nm}$ intervals crossing the grain boundary. The probe size was $\sim 3 \text{ nm}$.

X-ray diffraction (XRD) of samples sintered for 10 h was carried out on a Rigaku D/MAX-2500 diffractometer (Rigaku, Tokyo, Japan). Scans were carried out using a 2θ scan range of 20 - 60° , a scan speed of $1^\circ \cdot \text{min}^{-1}$ and a step size of 0.01° . The unit cell parameters and volume of the samples were determined by Rietveld refinement.

3. Results

The density of the samples is shown in Fig. 1. The theoretical density of $(K_{0.5}Na_{0.5})NbO_3$ is $4.51 \text{ g} \cdot \text{cm}^{-3}$. In the samples sintered in O_2 , the density increases with sintering time up to 2 h and then the rate of densification decreases. The density of the samples sintered in 75 N_2 -25 H_2 (mol %) is noticeably higher than that of the O_2 -sintered samples, even after only 0.5 h. Density increases with sintering time up to 2 h, and then decreases. Sample density increases further as the sintering atmosphere changes from 75 N_2 -25 H_2 (mol %) to H_2 .

Fig. 1. Density of $(K_{0.5}Na_{0.5})NbO_3$ samples sintered in different atmospheres at 1040°C for different times.

For the samples sintered in H_2 , density increases with sintering time up to 2 h, and then levels off.

SEM secondary electron images of samples sintered for 2 h are shown in Fig. 2 (a)-(d). The sample sintered in O_2 has a bimodal microstructure consisting of matrix grains between 1 - $3 \mu\text{m}$ in diameter and abnormal grains up to $70 \mu\text{m}$ in diameter [Fig. 2 (a)]. Both the matrix and the abnormal grains are cuboid in shape with faceted edges. The abnormal grains contain many trapped pores. There is also intergranular porosity between the matrix grains. The sample sintered in 75 N_2 -25 H_2 (mol%) has an extremely coarse microstructure, with grains up to $140 \mu\text{m}$ in diameter [Fig. 2 (b)]. Large pores are visible at the grain boundaries and triple junctions, and many pores are trapped within the grains. Some of the grains lose their cubic shape and appear to have curved grain boundaries. However, at higher magnification the boundaries show micro-faceting, indicating that they are still faceted [Fig. 2 (c), marked with arrows]. The sample sintered in H_2 has a similar microstructure, but with smaller grains (maximum grain diameter of $\sim 120 \mu\text{m}$) [Fig. 2 (d)]. The number of pores trapped within the grains also appears to decrease. Fig. 2 (e) and (f) show backscattered electron images of polished samples sintered in O_2 and 75 N_2 -25 H_2 (mol %) for 2 h. No secondary phases are visible. No secondary phases were also visible on backscattered electron images of a polished sample sintered in H_2 .

Grain size distributions of the samples are shown in Fig. 3. In the samples sintered in O_2 , abnormal grain growth has already taken place after sintering for 0.5 h [Fig. 3 (a)]. The grain size distribution is bimodal; the majority of grains are micron-sized, but abnormal grains up to $50 \mu\text{m}$ in diameter are also present. As sintering proceeds, the grain size distribution becomes broader as the number and size of abnormal grains increase. The samples sintered in 75 N_2 -25 H_2 (mol%) have a much broader grain size distribution than the samples sintered in O_2 . Abnormal grain growth is essentially complete after only 0.5 h of sintering, with grains up to $60 \mu\text{m}$ in

Fig. 2. (a)-(d): SEM secondary electron micrographs of $(K_{0.5}Na_{0.5})NbO_3$ ceramics sintered at 1040°C for 2 h in: (a) O_2 , (b) and (c) $75 N_2$ - $25 H_2$ (mol%), (d) H_2 . White arrows in (c) show microfaceting. (e)-(f): SEM backscattered electron micrographs of $(K_{0.5}Na_{0.5})NbO_3$ ceramics sintered at 1040°C for 2 h in: (e) O_2 and (f) $75 N_2$ - $25 H_2$ (mol%).

Fig. 3. Grain size distributions of $(K_{0.5}Na_{0.5})NbO_3$ ceramics sintered at 1040°C in: (a) O_2 , (b) $75 N_2$ - $25 H_2$ (mol%), and (c) H_2 .

diameter [Fig. 3 (b)]. The grain size distribution broadens further with increased sintering time. The samples sintered in H_2 show similar behaviour to those sintered in 75 N_2 -25 H_2 (mol%), but the grain size distribution is narrower and the maximum grain size smaller [Fig. 3 (c)].

Conventional TEM micrographs are shown in Fig. 4 (a) and (b). Micro-faceting is visible at the grain boundary of the sample sintered in O_2 [Fig. 4 (a)]. Ferroelectric domains are also visible. Micro-faceting is also visible at the grain boundary of the sample sintered in H_2 [Fig. 4 (b)]. In the sample sintered in H_2 , the ferroelectric domains are much reduced in size. The reduction in domain size indicates that the sample is changing from a normal first-order ferroelectric material to a relaxor material,¹⁸⁾ as observed in our previous work.^{15,16)}

Fig. 4. TEM micrographs of $(K_{0.5}Na_{0.5})NbO_3$ ceramics sintered at 1040°C in (a) O_2 and (b) H_2 for 2 h. White arrows show microfaceting. (c) TEM-EELS measurements of O/K ratio across the grain boundaries of $(K_{0.5}Na_{0.5})NbO_3$ samples sintered in O_2 and H_2 at 1040°C for 2 h.

TEM electron energy loss spectroscopy (TEM-EELS) results are shown in Fig. 4 (c). For the sample sintered in O_2 , four grain boundaries were observed and for the sample sintered in H_2 , five grain boundaries were observed. Each set of data represents representative results from one grain boundary. For the sample sintered in O_2 , the O/K ratio increases considerably at the grain boundary, whereas for the sample sintered in H_2 the O/K ratio decreases slightly at the grain boundary. The O/K ratios in the sample sintered in H_2 are lower than those of the sample sintered in O_2 , both in the bulk of the grain and at the grain boundary.

XRD traces of the samples sintered for 10 h are shown in Fig. 5 (a). The patterns can all be indexed with JCPDS card no. 77-0038 for monoclinic $(K_{0.65}Na_{0.35})NbO_3$. No secondary

Fig. 5. (a) XRD traces, (b) unit cell parameters and (c) unit cell volume of $(K_{0.65}Na_{0.35})NbO_3$ ceramics sintered at 1040°C for 10 h in O_2 , 75 N_2 -25 H_2 (mol%) and H_2 .

phases are visible. Unit cell parameters of the samples are shown in Fig. 5 (b). The error bars show the estimated error of the refinement. The a unit cell parameter remains almost constant with changing sintering atmosphere. The b unit cell parameter increases as the sintering atmosphere becomes more reducing. The c unit cell parameter and the angle β , both decrease as the sintering atmosphere becomes more reducing. The unit cell volume also decreases as the sintering atmosphere becomes more reducing [Fig. 5 (c)]. Again, the error bars show the estimated error.

4. Discussion

($K_{0.5}Na_{0.5}$)NbO₃ is well known to be a difficult ceramic to densify.⁹⁾ To achieve high density ($K_{0.5}Na_{0.5}$)NbO₃ ceramics (> 95% theoretical density) by conventional sintering techniques requires careful control of sintering conditions¹⁹⁾ or addition of sintering aids.²⁰⁾ In the present work, densities > 95% theoretical density could be achieved by sintering in 75 N₂-25 H₂ (mol%) and H₂ even at the low sintering temperature of 1040°C (Fig. 1). This is higher than previous results for ($K_{0.5}Na_{0.5}$)NbO₃ sintered in air at low temperature (e.g. a density of 86.9% theoretical density for ($K_{0.5}Na_{0.5}$)NbO₃ sintered at 1030°C for 8 h⁸⁾) and is comparable to samples sintered at 1100°C (e.g. a density of 94.9% theoretical density after sintering at 1100°C for 2 h⁸⁾). Sintering in reducing atmospheres is expected to cause an increase in the concentration of oxygen vacancies,^{21,22)} which may assist densification by increasing the lattice diffusion rate of oxygen.

The SEM and TEM micrographs show that ($K_{0.5}Na_{0.5}$)NbO₃ has faceted grain boundaries (Fig. 2 and Fig. 4), as has also been found in earlier works.^{8,14)} For faceted grain boundaries, grain growth takes place by the step growth mechanism, which is analogous to the growth of crystals by 2D-nucleation.²³⁻²⁷⁾ For 2D-nucleation controlled growth, the growth rate of a grain has an exponential dependence on the driving force for grain growth ΔG .^{26,28)} Below a critical driving force ΔG_C , grain growth is very slow but for driving forces greater than ΔG_C the grain growth rate increases rapidly.²⁶⁾ For $\Delta G > \Delta G_C$, kinetic roughening of the grain boundary takes place and the growth rate assumes a linear dependence on ΔG .^{25,29)} The driving force for grain growth ΔG depends on the difference in size between the growing or shrinking grain and the mean grain size.³⁰⁾ During sintering of a sample there will be a range of values of ΔG which will initially be determined by the particle size distribution of the ceramic powder.

The critical driving force ΔG_C is given by²⁸⁾:

$$\Delta G_C = \frac{\Omega \varepsilon^2}{3hRT} \quad (1)$$

where Ω = molar volume, ε = step free energy of the nucleus, h = step height of the nucleus, R = the gas constant and T = temperature. ε is the excess energy associated with the edge of the 2D nucleus. The value of ΔG_C is very dependent on the step free energy ε . ε in turn is affected by sintering temper-

ature^{17,31,32)} and atmosphere.^{14,33-35)} Sintering ($K_{0.5}Na_{0.5}$)NbO₃ in reducing atmospheres is expected to cause an increase in oxygen vacancy concentration.^{21,22)} From the TEM-EELS results [Fig. 4 (c)], it can be seen that the O/K ratio is lower in the ($K_{0.5}Na_{0.5}$)NbO₃ sample sintered in H₂ than in the sample sintered in O₂. This indicates that the sample sintered in H₂ has an increased oxygen vacancy concentration. The dip in the O/K ratio at the grain boundary also indicates that the grain boundary core contains more oxygen vacancies than the grain interior. This is expected if oxygen is migrating from the grain interior to the boundary and then from the boundary to the external atmosphere. The changes in unit cell parameters and volume [Fig. 5 (b) and (c)] are also consistent with an increase in vacancy concentration, as explained in our previous works.^{15,16)}

The grain growth behaviour of the ($K_{0.5}Na_{0.5}$)NbO₃ samples can be explained by considering the effect of the sintering atmosphere on the vacancy concentration. An increase in vacancy concentration lowers the configurational entropy³⁶⁾ which in turn lowers ε .³⁷⁻³⁹⁾ When the samples are sintered in O₂, the vacancy concentrations are relatively low and ε is relatively high. This causes the value of ΔG_C to be high. Most of the grains have $\Delta G < \Delta G_C$ and can only grow very slowly. A small number of grains have $\Delta G \geq \Delta G_C$. These grains grow rapidly to form abnormal grains [Fig. 2(a) and Fig. 3 (a)]. As the sintering time increases, the abnormal grains continue to grow. In addition, some of the slowly growing matrix grains grow large enough to have $\Delta G \geq \Delta G_C$. These grains then grow rapidly to form abnormal grains. Therefore both the size and number of abnormal grains increase with sintering time [Fig. 3 (a)].

When the sintering atmosphere changes to 75 N₂-25 H₂ (mol%), the concentration of oxygen vacancies increases, as seen in the TEM-EELS and XRD results. This causes a decrease in ε and ΔG_C . The number of grains which have $\Delta G > \Delta G_C$ and which can grow rapidly increases. All of the matrix grains are consumed by the rapidly growing abnormal grains and even after 0.5 h of sintering, the microstructure consists of coarse grains [Fig. 3 (b)]. With increased sintering time, the abnormal grains grow further; however their growth rate is limited because of their impingement upon each other. For the samples sintered in H₂ the oxygen vacancy concentration increases further, causing a further decrease in ε and ΔG_C . This causes a further increase in the number of grains which have $\Delta G > \Delta G_C$. Because the number of rapidly growing grains increases, impingement occurs earlier than in the case of the samples sintered in 75 N₂-25 H₂ (mol%) and this results in a reduction of average grain size after impingement of the abnormal grains [Fig. 2 (d) and Fig. 3 (c)].

Therefore, by sintering at 1040°C and controlling the sintering atmosphere, the microstructure of ($K_{0.5}Na_{0.5}$)NbO₃ can be varied from a bimodal microstructure to a coarse grained microstructure. As grain size is known to affect piezoelectrical properties,⁴⁰⁾ this provides a way of controlling the piezoelectric properties of ($K_{0.5}Na_{0.5}$)NbO₃. In addition, the present work shows that samples can be sintered to

high density in reducing atmospheres even at low temperatures.

5. Conclusions

(K_{0.5}Na_{0.5})NbO₃ ceramics have been sintered in atmospheres of O₂, 75 N₂-25 H₂ (mol%) and H₂ at 1040°C and their grain growth behaviour characterised. (K_{0.5}Na_{0.5})NbO₃ displayed abnormal grain growth and as the sintering atmosphere became more reducing, the number of abnormal grains tended to increase. The change in grain growth behaviour with decreasing oxygen partial pressure is caused by an increase in vacancy concentration in the samples. This lowers the step free energy ϵ and critical driving force ΔG_c necessary for rapid grain growth, increasing the number of grains which can grow rapidly to form abnormal grains. By controlling the sintering atmosphere at low sintering temperature, the microstructure can thus be varied from bimodal to coarse-grained. In addition, samples could be sintered to high density in reducing atmospheres even at low sintering temperature.

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