Research on Abnormal Grain Growth in the Conventional Sintering of (K$_{0.5}$Na$_{0.5}$)NbO$_3$ Nano Powders

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Abstract. About 30nm grain sized (K$_{0.5}$Na$_{0.5}$) NbO$_3$ powders were used as the raw materials, and the solid phase method was used to prepare potassium sodium niobate ceramics at 750~950℃ under normal pressure sintering. The abnormal grain growth (AGG) at process of powder sintering was investigated. The consequences demonstrate that when the sintering temperature is greater than 850℃, AGG can be clearly observed. As the sintering temperature increases, the number of areas where abnormal grain growth occurs increases as well as the size. When the sintering temperature is 950℃, the area of abnormal grain growth has a maximum of approximately 1mm × 1mm, and it has good (111) orientation. The difference in the sintering driving force caused by the size distribution in the potassium sodium niobate nano powder is the root cause of abnormal grain growth.

Keywords: Potassium sodium niobate powder; Atmospheric pressure sintering; Abnormal grain growth; Sintering driving force.

1. Introduction
Development lead-free piezoelectric ceramics with super research performance to take the place of lead-based piezoelectric ceramics are the hotspots of piezoelectric ceramics research. In recent years, due to the (K$_{0.5}$Na$_{0.5}$)NbO$_3$ (KNN) based ceramics with elevated curie temperature ($T_c$>400℃), piezoelectric constant ($d_{33}$>200PC/N), and electro-mechanical coupling coefficient ($k_p$≈45%) has become a research hotspot of lead-free piezoelectric ceramics and is pondered as a conceivable substitute for lead-based piezoelectric ceramics$^{[1,2]}$. Using nano powder as a raw material is an effective method to improve the powder sintering activity, which can obviously decrease the sintering temperature of ceramics and effectively suppress the volatilization of K and Na in the traditional solid phase method$^{[3,4]}$. Due to the large sintering activity of the nano powder, if the growth of grains is not suppressed during the sintering process, an abnormal grain growth (AGG) phenomenon will occur. As an important phenomenon in powder sintering, the AGG phenomenon has been extensively studied$^{[5-7]}$. The study found that the regions that produce AGG generally have high density and orientation$^{[8,9]}$. On the other hand, taking advantage of this feature, AGG has been used to grow a variety of metals, barium titanate and PMN-PT single crystal materials$^{[10-13]}$, and KNN single crystal materials might have super piezoelectric property because of the optimal domain structure and crystal orientation. Therefore, it is very important to study the AGG phenomenon in the sintering of KNN nano powders for the preparation of high-density KNN based ceramics and single crystals.
2. Experimental Procedure

2.1. Experimental Method
The complex method is used to convert Nb₂O₅ into soluble niobium salt instead of expensive niobium ethanol as a niobium source. The sol-gel method is used to synthesize nano KNN ultrafine powder at 500°C[14]. Fig.1 shows a TEM photograph of the prepared nano KNN powder, the grain size of the nano powder is nearly 30 nm. Using this nano powder as raw material, PVA blended and granulated, using an oil press under 200 MPa pressure to dry press to form a disc with a diameter of 11.5mm, after degumming, sintered in a muffle furnace at 750°C~950°C for 2h into porcelain.

Figure 1. TEM photograph of KNN powders as raw materials.

2.2. Sample Character
The microscopic morphology of the sample was observed by SEM and EDS spectrum analysis was performed. The instrument model used was Hitachi S-3500N; the bulk density of the ceramic was measured by the Archimedes drainage procedure, and its calculation formula is expressed as follows:

\[ \rho = \rho_0 \frac{M}{M - m} \]

Where, \( \rho \) is density of ceramics, \( M \) is dry weight of ceramics, \( m \) is the suspended weight of ceramics in water, \( \rho_0 \) is the density of distilled water.

The phase structure and orientation of the ceramics were analyzed by XRD. The instrument used was a Bruker AXS D8 Advance X-ray diffractometer. The radiation source was Cu K. The Olympus BX51M metallographic microscope was used to observe the orientation of the ceramic grains under polarized light.

3. Results and Discussion
Surface grinding and polishing of KNN ceramics sintered at different temperatures found that when the sintering temperature was 850°C, black spots began to assume on the ceramic surface. As the sintering temperature added, the number of black spots on the ceramic surface increased rapidly (Fig. 2 shows a typical photo of KNN ceramic surface prepared by sintering at 950°C). When the sintering temperature is 950°C, a large number of black spots appeared on the ceramic surface, and the maximum black spot area is about 1mm × 1mm. SEM and EDS analysis were performed at the interface of the black spot area on the ceramic surface prepared by sintering at 950°C. The results are demonstrated in Fig. 3, the grains in this area are much larger than those in other areas region. The presence of AGG area will reduce the density and strength of the ceramic as a whole. In the experiment, the ceramic prepared at 1000°C cracked during grinding. From the EDS composition analysis results, it can be seen that the content of each element in the AGG region and the normal
growth region of the grains does not change significantly, indicating that they have the same composition.

**Figure 2.** The photograph of KNN ceramics sintered at 950°C.

**Figure 3.** SEM and EDS analysis photograph of the dark spot interface.

Fig. 4 shows the change curve of ceramic density prepared by different sintering temperature. It can be seen from Fig. 4 that within a certain sintering temperature range, the density of the ceramic increases with the increase of the sintering temperature. When the sintering temperature is 800°C, the density of the ceramic is the highest, which is 91% of the theoretical density. As the sintering temperature is further increased, the density of ceramics begins to decrease. Referring to the analysis in Fig. 3, the diminishment in ceramic density is primarily due to the presence of the interface in the AGG region. In addition, the increased K and Na volatilization caused by the increase in sintering temperature is also a cause of the decrease in density.

**Figure 4.** The relative densities of KNN ceramics with different sintering temperature.

In addition, the increased K and Na volatilization caused by the increase in sintering temperature is also a cause of the density's decrease.

**Figure 5.** XRD patterns of KNN ceramics sintered at different temperature.

Fig. 5 shows the XRD patterns of ceramic samples sintered at different temperatures. The samples sintered at different temperatures are all pure perovskite phase structures (JCPDS No. 32-0822). For the samples prepared at 900°C and 950°C, the relative strength of the (111) plane in XRD is significantly enhanced, which shows that with the appearance of the AGG phenomenon in ceramic sintering, the (111) oriented crystal plane on the ceramic surface has been significantly increased, so it can be inferred that the AGG region has (111) orientation.

In order to further verify the orientation of the AGG region, a polarizing microscope observation was performed at the interface of the AGG region. Fig. 6 shows that the AGG region (lower right part of Fig. 6) has a consistent orientation compared with the region with normal grain growth (upper left part of Fig. 6). And the abnormally grown grains have clear edges and corners, which indicates that the crystal growth is controlled by the two-dimensional nucleation mechanism.
Figure 6. The polarizing microscope photograph of AGG region interface.

For the grain growth under the two-dimensional nucleation mechanism, the driving force is determined as follows [15]:

$$
\Delta G = \sigma_{gb} \Omega \left( \frac{1}{r} - \frac{1}{R} \right)
$$

(2)

Where, $\Delta G$ is driving force for grain growth, $\sigma_{gb}$ is average grain boundary energy, $\Omega$ is molar volume, $r$ is radius of the grain, $R$ is the radius of the grain that neither grows nor shrinks (generally the average radius of the grain).

It can be seen from formula (2) that its driving force is inversely opposing to the average radius of the crystal grains. Therefore, compared with micron-sized powders, nano-sized powders have a greater driving force for sintering, which is conducive to the rapid growth of grains. When the average grain radius is unchanged, the grains with different grain sizes have different driving forces for sintering, and the grains with larger sizes have larger driving forces. Compared with micron-sized powders, the difference in sintering driving force caused by the size distribution of nano powders is more significant. As can be seen from Fig.1, the distribution of the nano powder grain size used in this experiment is about 10~40nm, so during the sintering process, when the sintering temperature increases, the larger-sized grains will get larger sinter driving force which produces abnormal grain growth.

4. Conclusions

This article regards potassium niobate powder as the main research object, prepares structured piezoelectric ceramics, analyzes the effects of template type, template content, sintering temperature and holding time on potassium niobate ceramics, and draws the following conclusions:

(1) Using KNN powder with an average grain size of about 30nm as the raw material, KNN ceramics sintered by solid phase procedure at 750°C to 950°C under normal pressure sintering, it was found that the content of each element in the AGG area and the normal grain growth area presented no obvious change, indicating that the composition is the same.

(2) Through experiments, it was found that when the sintering temperature is 800°C, the ceramic density is the largest which is 91.9% of the theoretical density. When the sintering temperature is greater than 800°C, AGG phenomenon occurs when the ceramic is sintered. When the sintering temperature is 950°C, the grain growth area of abnormal crystals is the largest which is about 1mm × 1mm, and has (111) orientation.

(3) The difference in sintering driving force caused by the size distribution in KNN nano powders is the root cause of abnormal grain growth.
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