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Comparison of formation behavior of $Ba_2NaNb_5O_{15}$ in air and molten NaCl salt

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The crystal growth of barium sodium niobate, $Ba_2NaNb_5O_{15}$ (BNN), and its electrical properties have been elaborately investigated because of the immense importance in many technological applications such as electro-optic, piezoelectric, and nonlinear optical devices [1–6]. However, its application is limited due to high cost and difficulty in fabrication. In contrast, BNN ceramics are superior because they can be made into larger and more complex parts. In order to fabricate BNN ceramics with high density and uniform microstructure, the preparation of BNN powders with high sintering activity is important and therefore it is necessary to understand the formation behavior of BNN phase. In this work, conventional mixed oxides (CMO) and molten salt synthesis (MSS) were chosen to synthesize BNN powders. Phase assemblages during the formation of BNN were investigated in detail.

High purity powders of $BaCO_3$, Na_2CO_3, Nb_2O_5, and NaCl were used as starting materials. $BaCO_3$, Na_2CO_3, and Nb_2O_5 according to the formula of $Ba_2NaNb_5O_{15}$ were first mixed in alcohol for 3 hr. Then one part of the mixture was hand-ground with NaCI in the weight ratio of 1:2 in ethanol. The dried powders with or without NaCI were placed in covered aluminum crucibles and calcined at 700–100 °C for 3 hr. Afterward, the synthesized products were washed with hot de-ionized water until no chloride ions were detected. For comparison, $BaCO_3$ and Nb_2O_5 were mixed according to the composition of $BaNb_2O_6$ and then NaCI was added, calcined, and washed according to the above-mentioned process.

The phase analysis of the synthesized powders was performed on a Guinier–Hägg camera by means of powder diffraction using Cu K_α radiation as the radiation source ($\lambda = 1.5405981$ Å) and silicon as the internal standard. The negatives obtained were evaluated with a computerized scanner system [7].

The XRD patterns of the synthesized products by CMO at 700–1100 °C for 3 hr are shown in Fig. 1. The powder by CMO at 700 °C is composed of unreacted Nb_2O_5, $BaCO_3$, newly-formed $Na_2Nb_4O_{11}$ and $Na_2Nb_8O_{21}$. When the temperature increases to 800 °C, $Na_2Nb_8O_{21}$ increases owing to the further reaction of $Na_2Nb_4O_{11}$ and Nb_2O_5. In addition, $Ba_5Nb_4O_{15}$ phase occurs at the expense of $BaCO_3$ and Nb_2O_5. At 900 °C, Nb_2O_5, $BaCO_3$, and $Na_2Nb_4O_{11}$ disappear, while $BaNb_2O_6$, $NaNbO_3$, and $Ba_2NaNb_5O_{15}$ form. Subsequently, $Ba_2NaNb_5O_{15}$ gradually increases with the increase of calcination temperature, accompanied by the decrease of $Na_2Nb_8O_{21}$, $BaNb_2O_6$, and $NaNbO_3$. At last, single-phase $Ba_2NaNb_5O_{15}$ is obtained at 1100 °C. The reaction processes of $BaCO_3$, $NaCO_3$ and Nb_2O_5 in air can be described as follows:

$$Na_2CO_3 + 2Nb_2O_5 \xrightarrow{<700\,^\circ C} Na_2Nb_4O_{11} + CO_2\uparrow \quad (1)$$

$$Na_2Nb_4O_{11} + 2Nb_2O_5 \xrightarrow{600\text{–}800\,^\circ C} Na_2Nb_8O_{21} \quad (2)$$

$$5BaCO_3 + 2Nb_2O_5 \xrightarrow{700\text{–}800\,^\circ C} Ba_5Nb_4O_{15} + 5CO_2\uparrow \quad (3)$$

$$15BaCO_3 + 2Na_2Nb_8O_{21} \xrightarrow{800\text{–}900\,^\circ C} 3Ba_5Nb_4O_{15} + 4NaNbO_3 + 15CO_2\uparrow \quad (4)$$

$$Na_2Nb_8O_{21} + Ba_5Nb_4O_{15} \xrightarrow{900\text{–}1100\,^\circ C} 2Ba_2NaNb_5O_{15} + BaNb_2O_6 \quad (5)$$

$$2BaNb_2O_6 + NaNbO_3 \xrightarrow{900\text{–}1100\,^\circ C} Ba_2NaNb_5O_{15} \quad (6)$$

As seen above, at low temperatures (<700 °C), Na_2CO_3 reacts with Nb_2O_5 to form $Na_2Nb_4O_{11}$, which further reacts with Nb_2O_5 to form $Na_2Nb_8O_{21}$ phase at 600–800 °C. The newly synthesized $Na_2Nb_8O_{21}$ reacts with $BaCO_3$ to form $Ba_5Nb_4O_{15}$ and $NaNbO_3$ at 900 °C (reaction (4)), while the remnant Nb_2O_5 also reacts with $BaCO_3$ to form $Ba_5Nb_4O_{15}$ at 800 °C. At the same time, further reaction between the remaining $Na_2Nb_8O_{21}$ and $Ba_5Nb_4O_{15}$ results in the formation of $BaNb_2O_6$ and $Ba_2NaNb_5O_{15}$ at 900 °C. This newly developed $BaNb_2O_6$ reacts with $NaNbO_3$ from reaction (4) to form $Ba_2NaNb_5O_{15}$ at temperatures above 1000 °C. Therefore, single phase $Ba_2NaNb_5O_{15}$ is synthesized at 1100 °C. Huang investigated the formation behavior of $Sr_{0.4}Ba_{0.6}Nb_2O_6$ and found that $Ba_5Nb_4O_{15}$ occurs at 700 °C [8]. However, in this investigation $Ba_5Nb_4O_{15}$ begins to form at 800 °C during the formation of $Ba_2NaNb_5O_{15}$, which probably results from the preferred reaction between Nb_2O_5 and

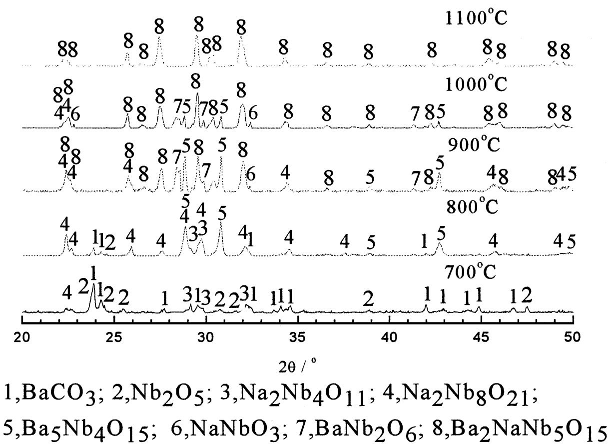

Figure 1 XRD patterns of the synthesized products by CMO calcined at 700–1100 °C for 3 hr.

Na_2CO_3 to form niobium-rich phases $Na_2Nb_4O_{11}$ and $Na_2Nb_8O_{21}$.

The XRD patterns of the synthesized products by MSS at 700–1100 °C are shown in Fig. 2. The synthesized product at 700 °C is composed of $BaNb_2O_6$ and $NaNbO_3$. It shows that both $BaNb_2O_6$ (formed by the reaction of $BaCO_3$ and Nb_2O_5) and $NaNbO_3$ (formed by the reaction of Na_2CO_3 and Nb_2O_5) occur at 700 °C with the aid of NaCl, indicating the reaction process in MSS is quite different from CMO. $Ba_2NaNb_5O_{15}$ begins to form at 800 °C in MSS, which is lower than for CMO. When $BaNb_2O_6$ and $NaNbO_3$ coexist in molten NaCl salt, two possible reactions can occur. One is that $Ba_2NaNb_5O_{15}$ directly develops from newly synthesized $BaNb_2O_6$ and $NaNbO_3$ according to reaction (6). The other is that Na^+ in NaCl substitutes for Ba^{2+} in $BaNbO_6$ to develop $Ba_2NaNb_5O_{15}$. However, it can be seen from Fig. 2 that with the development of $Ba_2NaNb_5O_{15}$, only $BaNb_2O_6$ phase decreases and disappears, while the content of $NaNbO_3$ is almost invariable from 800–1100 °C. These results indicate that the reaction between $BaNb_2O_6$ and $NaNbO_3$ to form $Ba_2NaNb_5O_{15}$ cannot occur in molten NaCl salt. Therefore, $Ba_2NaNb_5O_{15}$ can only be developed by the substitution of Na^+ in NaCl for Ba^{2+} in $BaNb_2O_6$. To verify the reaction, the reaction process of $BaCO_3$ and Nb_2O_5 in molten NaCl salt was investigated.

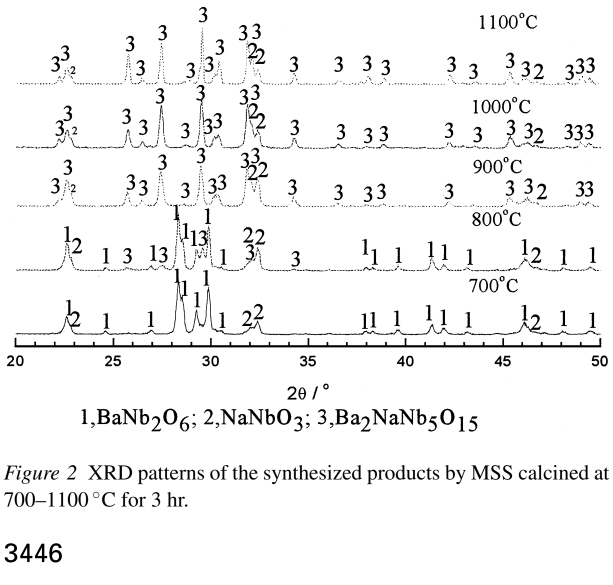

Figure 2 XRD patterns of the synthesized products by MSS calcined at 700–1100 °C for 3 hr.

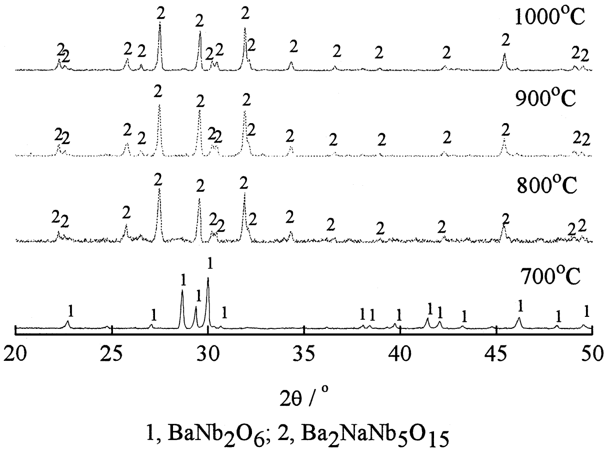

Figure 3 XRD patterns of the synthesized products calcined at 700–900 °C using $BaCO_3$ and Nb_2O_5 as starting materials in molten NaCl salt.

Fig. 3 shows the phase assembly of powders calcined at 700–900 °C using $BaCO_3$ and Nb_2O_5 as starting materials in molten NaCl salt. It can be seen that $BaNb_2O_6$ phase forms at 700 °C with the disappearance of $BaCO_3$ and Nb_2O_5. Single-phase $Ba_2NaNb_5O_{15}$ is formed at 800 °C, which further proves that Na^+ ions in NaCl replace Ba^{2+} ions in $BaNb_2O_6$ to form $Ba_2NaNb_5O_{15}$. Therefore, the reaction of $BaCO_3$, $NaCO_3$, and Nb_2O_5 in NaCl salt can be described as follows:

$$\mathrm{BaCO_3 + Nb_2O_5 \xrightarrow{<700\,^{\circ}C} BaNb_2O_6 + CO_2 \uparrow} \tag{7}$$

$$\mathrm{Na_2CO_3 + Nb_2O_5 \xrightarrow{<700\,^{\circ}C} 2NaNbO_3 + CO_2 \uparrow} \tag{8}$$

$$\mathrm{5BaNb_2O_6 + 2NaCl \xrightarrow{>800\,^{\circ}C} 2Ba_2NaNb_5O_{15} + BaCl_2} \tag{9}$$

In conclusion, five intermediate phases, $Na_2Nb_4O_{11}$, $Na_2Nb_8O_{21}$, $NaNbO_3$, $Ba_5Nb_4O_{15}$, and $BaNb_2O_6$, occur in CMO using $NaCO_3$, $BaCO_3$, and Nb_2O_5 as starting materials and single-phase $Ba_2NaNb_5O_{15}$ can be synthesized at 1100 °C. In contrast, when the same starting materials are calcined in molten NaCl salt, only $NaNbO_3$ and $BaNb_2O_6$ occur. Unfortunately, the final synthesized products consist of $NaNbO_3$ and $Ba_2NaNb_5O_{15}$ due to the substitution of Na^+ in NaCl for Ba^{2+} in $BaNb_2O_6$. By choosing $BaCO_3$ and Nb_2O_5 as starting materials, single-phase $Ba_2NaNb_5O_{15}$ can be successfully synthesized in molten NaCl salt at 800 °C after 3 hr.

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