

Structural and thermal properties of potassium niobate glasses for an application in electro-optical product design and manufacture

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Research in the field of ferroelectric materials has significantly increased in recent years because of exceptional electronic and optical properties. In this study, amorphous materials of potassium niobate (KNbO_3) for an application in an electro-optical product design and manufacture were fabricated by a twin-roller quenching method, and structural and thermal properties were studied through various post-annealing processes. Four anomalies of crystallization were observed in the DTA results of the amorphous KNbO_3 . The activation energies calculated by the Ozawa method were approximately 164 kJ/mol, 251 kJ/mol, 150 kJ/mol, and 216 kJ/mol. To investigate the process of crystallization structurally, the amorphous KNbO_3 was post-annealed and the intermediate phase of $\text{K}_4\text{Nb}_6\text{O}_{17}$ was found when heat-treated in the temperature range 550 °C to 800 °C before the formation of the perovskite KNbO_3 phase.

Key words: Ferroelectric, KNbO_3 , glass, crystallization, activation energy, amorphous, perovskite, pyrochlore.

Introduction

Glass-ceramics containing ferroelectrics seem to be an interesting alternative due to their relative low preparation time and cost, since the amorphous state of ferroelectric materials shows excellent properties such as high permeability, large ionic conductivity, high chemical stability, and high fracture strength [1, 2]. Moreover, due to the considerable preparation difficulties and costs of making single crystals, much interest in the preparation of glass-ceramics with the ABO_3 crystal phase exists [3]. A theoretical study of an amorphous ferroelectric material was published by Lines in 1977, and the thermal and electric properties of ABO_3 -type amorphous ferroelectrics such as $\text{Li}(\text{Nb,Ta})\text{O}_3$, $\text{Na}(\text{Nb,Ta})\text{O}_3$, and $\text{K}(\text{Nb,Ta})\text{O}_3$ produced by a twin-roller quenching apparatus were investigated by Glass *et al.* in 1977 [4, 5].

Potassium niobate (KNbO_3) is an excellent nonlinear optical material with second harmonic generation, electro-optic, acousto-optic, and photorefractive properties [6, 7]. KNbO_3 crystals are actually used as optical waveguides, frequency doublers, holographic storage systems, phase conjugations, nonvolatile ferroelectric memories, dielectrics for microelectronics and in wireless communications [7, 8]. Recently, niobate glasses have attracted much attention, because several quenching techniques which enabled glass materials to be produced containing no former network have been developed and some new oxide glasses that have

many orders of magnitude greater ionic conductivity and dielectric constant than those of the single crystals have been found [9–12].

The purpose of the present study is to establish the crystallization process and to clarify crystalline phases in amorphous materials of KNbO_3 for an application in an electro-optical product design and manufacture. The amorphous KNbO_3 was fabricated by a twin-roller quenching method and confirmed structurally. The influence of the treatment temperature on the microstructure, which is an important property of electric and optic devices, was investigated structurally and thermally. In particular, the formation of various metastable phases such as the pyrochlore $\text{K}_4\text{Nb}_6\text{O}_{17}$ phase was clarified and their activation energies were calculated in this study.

Experimental

To prepare the amorphous sample of KNbO_3 , K_2CO_3 (Aldrich Co., 99.9 %) and Nb_2O_5 (Aldrich Co., 99.9 %) were mixed congruently and calcined in an alumina crucible at 900 °C for 24 h. Subsequently, the reaction ratio was confirmed by an XRD experiment, as shown in Fig. 1. The prepared powder was melted in a quartz tube using an electroresistant heater and quenched using a twin roller-quenching apparatus. The twin-roller of tungsten carbide had a diameter of 70 mm and a length of 75 mm, and the rotation speed of the rollers was 800 to 2000 revolutions per minute (rpm). The quenched samples were transparent and colorless flakes, approximately 10 mm in width, 15 to 100 mm in length, and 20 to 50 μm in thickness.

The microstructure and morphology of the amorphous

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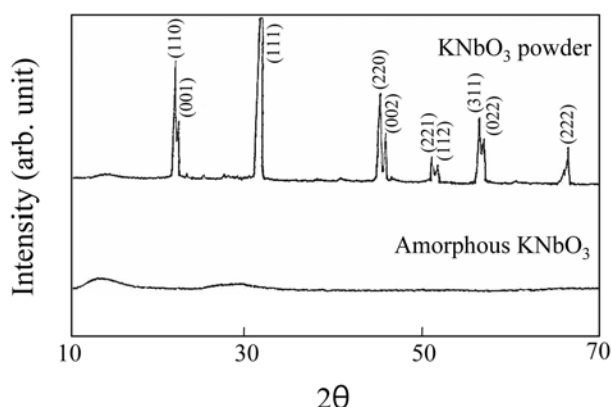


Fig. 1. XRD patterns of calcined and amorphous samples of KNbO_3 . The amorphous KNbO_3 was fabricated by melting and quenching the calcined powder by a twin roller-quenching method.

states were analyzed using X-ray diffraction (XRD, Rigaku, Japan) and a scanning electron microscope (SEM, JOEL, USA), respectively. The XRD experiments were performed every 50 °C from room temperature to 800 °C in order to investigate the crystallization temperature and to check that the prepared samples were indeed amorphous. The endothermic and exothermic properties of the samples were measured by differential thermal analysis (DTA, SEIKO Co., Japan). The crystallization temperature was also measured more precisely by DTA experiments with various heating rates.

Results and Discussion

Fig. 1 shows the typical XRD patterns of calcined and as-quenched KNbO_3 samples. The calcined sample identified by XRD using nickel-filtered $\text{CuK}\alpha$ radiation showed the powder pattern of the KNbO_3 single phase. The phase was in agreement with the JCPDS card (No. 35-795) with orthorhombic symmetry [13]. However, the result from the as-quenched sample showed the absence of crystalline peaks, which is a representative property of an amorphous phase.

The XRD patterns of amorphous and post-annealed KNbO_3 samples are shown in Fig. 2. The samples were post-annealed for 1 hour from room temperature to 800 °C in flowing nitrogen to form a crystalline sample. The interval of annealing temperatures was 50 °C. Below 450 °C, no diffraction peaks were shown, meaning that crystallization had not occurred. Upon elevating the annealing temperature above 550 °C, some diffraction lines were detected in the XRD patterns. The XRD peaks were not exactly the same as for a stoichiometric crystal of KNbO_3 and a mixture of phases was obtained, such as KNbO_3 and $\text{K}_4\text{Nb}_6\text{O}_{17}$. $\text{K}_4\text{Nb}_6\text{O}_{17}$ is well-known as a pyrochlore phase, which is made in a Nb-rich composition. These results agree with those of the glass ceramics studied by Graça *et al* [14].

Because of the problem of melting the amorphous KNbO_3 sample, a post-annealing temperature above 800 °C was not used but the post-annealing time was increased from 1 hour to 10 hours, as shown in Fig. 2. When the time

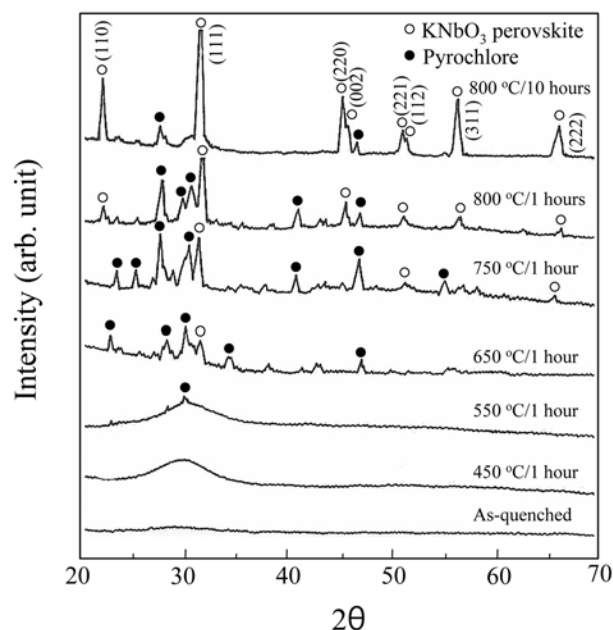


Fig. 2. XRD patterns of amorphous KNbO_3 . Patterns were obtained on heating the samples at 50 °C intervals from room temperature to 800 °C, but the patterns below 450 °C are not shown here because there was no crystallization.

reached 10 hours, the diffraction lines from the pyrochlore phases almost vanished and those of the KNbO_3 crystalline phase were obtained. This means that the amorphous KNbO_3 becomes ultimately crystalline after it passes through some metastable states.

Figs. 3(a), (b), (c), and (d) illustrate the SEM images of specimens as-quenched, post-annealed at 400 °C, post-annealed at 600 °C, and post-annealed at 800 °C, respectively. The post-annealing time was 10 hours. The image of the amorphous KNbO_3 shows as only a dark region. In the case of the 400 °C annealed sample, some crystallite-like bodies were detected in the amorphous base and their average size was approximately 0.5 μm . When the annealing temperature was taken to 600 °C, the shape of the bodies changed to a needle-like as shown in Fig. 3(c). From the XRD results, these bodies in the amorphous KNbO_3 might be the crystals of perovskite and pyrochlore phases. The average width and length of the needle-like crystals were approximately 0.2 μm and 1.3 μm , respectively. At 800 °C, various shapes of crystals were observed and the residual amorphous regions disappeared completely. This means that many crystallites nucleate, grow, and overlap in the whole sample heat-treated at elevated temperatures above a crystallization temperature (T_c). The largest crystal detected in Fig. 3(d) had a size just above 3.5 μm .

To investigate the crystallization processes and various metastable states obtained from heat-treated samples in detail, their thermal properties were measured with the parameter of heating and cooling rates by DTA. Typical DTA curves of amorphous KNbO_3 are shown in Fig. 4. Solid and dashed lines appear on the first heating and

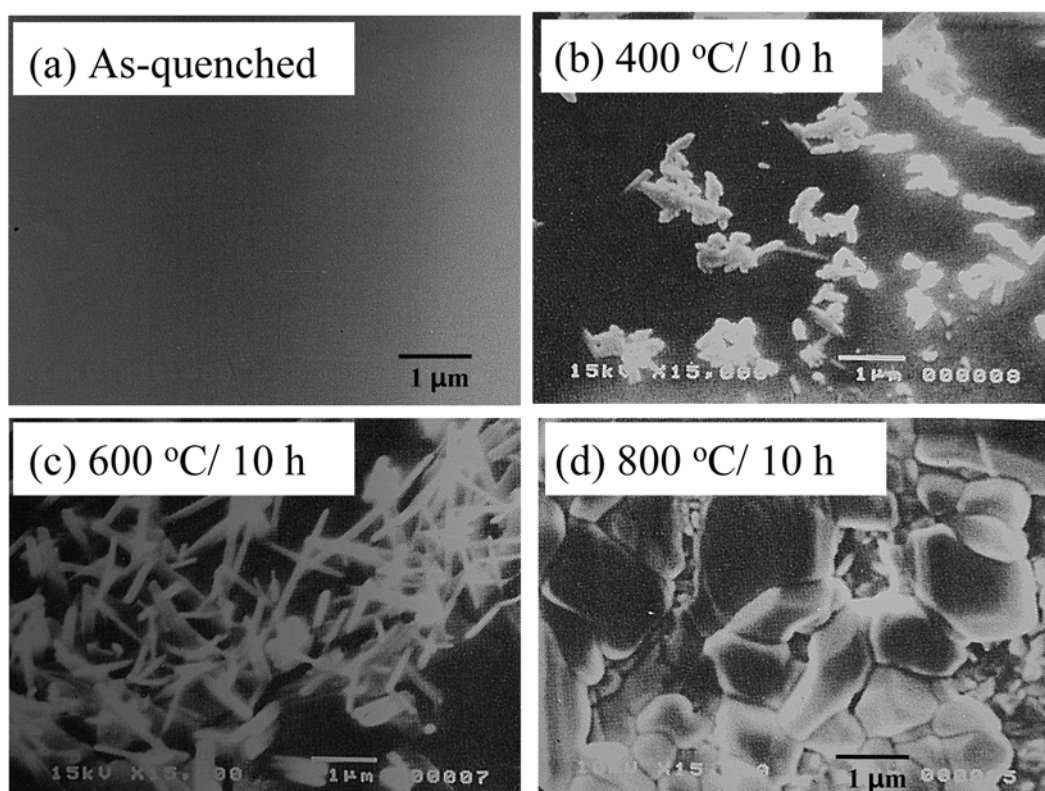


Fig. 3. SEM images of four specimens: (a) as-quenched, (b) annealed at 400 °C for 10 hours, (c) annealed at 600 °C for 10 hours, and (d) annealed at 800 °C for 10 hours.

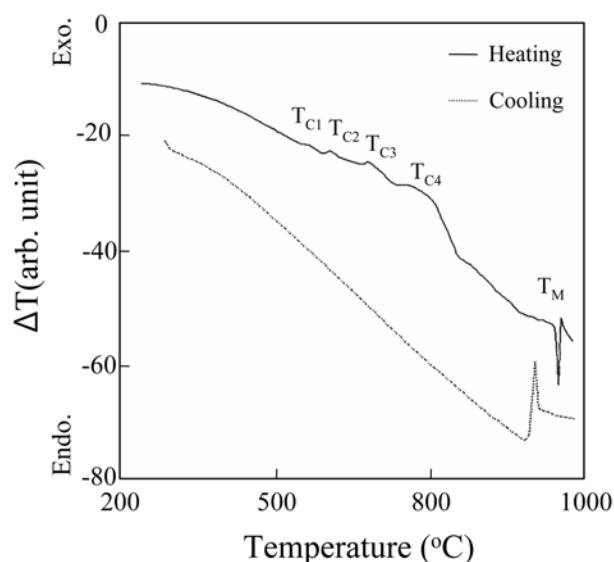


Fig. 4. DTA curves of amorphous KNbO_3 . The heating rate was 10 Kminute^{-1} and a Pt pan was used. Peaks of crystallization were observed at 576 °C, 615 °C, 682 °C, and 798 °C. Solid and dashed lines appear on first heating and cooling, respectively.

cooling processes, respectively. The ramping rate was 10 Kminute^{-1} and a Pt pan was used. In the first heating process, a strong endothermic peak was observed at 1045 °C because of the melting of the sample. Four exothermic anomalies besides the melting signal were measured in the first heating process, but no signal was detected in the first cooling process. Therefore, these anomalies corre-

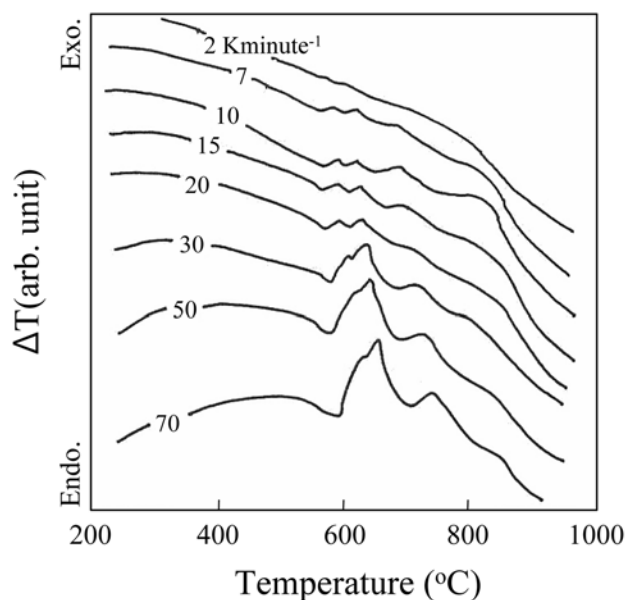


Fig. 5. DTA curves of amorphous KNbO_3 depending on heating rates. The heating rate was from 2 Kminute^{-1} to 70 Kminute^{-1} .

sponded to the crystallization processes and various metastable states. The peaks of crystallization labeled T_{C1} , T_{C2} , T_{C3} , and T_{C4} for convenience were observed at 576 °C, 615 °C, 682 °C, and 798 °C, respectively.

The crystallization temperature was also measured more precisely by DTA experiments with various heating rates. Fig. 5 gives the DTA curves of amorphous KNbO_3 with

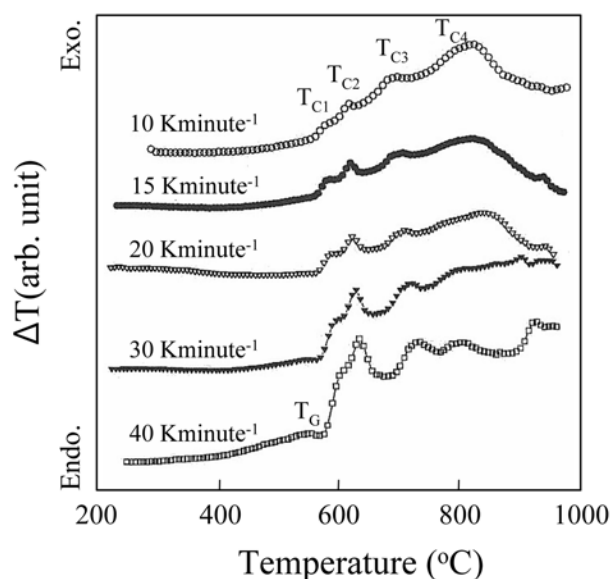


Fig. 6. DTA curves of amorphous KNbO_3 corrected by their base lines. The crystallization temperatures were changed according to the heating rate between 10 Kminute^{-1} and 40 Kminute^{-1} .

a parameter of the heating rate between 2 Kminute^{-1} to 70 Kminute^{-1} . The anomalies of crystallization changed according to the heating rates. To get the sophisticated peak-value of the anomalies, the DTA curves of amorphous KNbO_3 were corrected by the base line, as shown in Fig. 6. The activation energies of crystallizations were calculated by the non-isothermal Ozawa method [15]. As the heating rate increased, the crystallization temperature shifted to higher temperatures and the intensity of anomalies also increased. Ozawa's equation can be obtained directly from the relation between the heating rate and the crystallization temperature as follow:

$$\log(B) = -0.4567 \frac{\Delta E}{R T_C} + \text{const.}, \quad (1)$$

where B is the heating rate, R is the gas constant, T_C is the crystallization temperature, and E is the activation energy. Plots of $\log(B)$ versus $1000/T_C$ for the crystallizations are given in Fig. 7. Solid lines in Fig. 7 fitted the results of Eq. (1), and the activation energies calculated from the slopes of T_{C1} , T_{C2} , T_{C3} , and T_{C4} were approximately 164 kJ/mol, 251 kJ/mol, 150 kJ/mol, and 216 kJ/mol, respectively.

Conclusions

After producing amorphous KNbO_3 by a twin-roller quenching method, crystallization temperatures labeled T_{C1} , T_{C2} , T_{C3} , and T_{C4} for convenience were obtained by DTA to be 576°C , 615°C , 682°C , and 798°C , respectively.

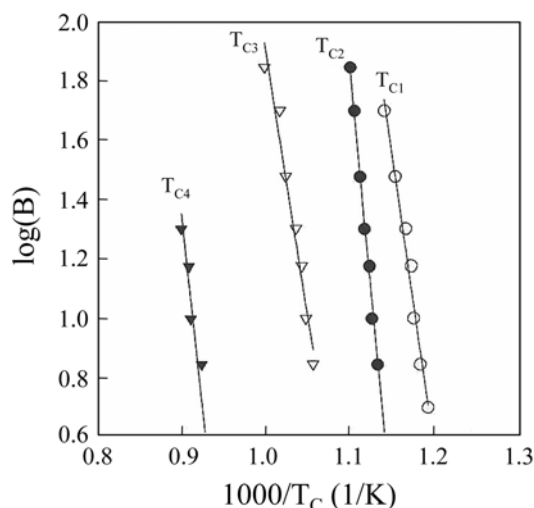


Fig. 7. Plots of $\log(B)$ versus $1000/T_C$. Solid lines are the fitting lines calculated by the Ozawa method.

Activation energies of all these crystallizations were calculated as 164 kJ/mol, 251 kJ/mol, 150 kJ/mol, and 216 kJ/mol, respectively, by the Ozawa method, which is a non-isothermal analysis method. To investigate the process of crystallization structurally, the amorphous KNbO_3 was post-annealed and the intermediate phase of $\text{K}_4\text{Nb}_6\text{O}_{17}$ was found when heat treated in the temperature range 550°C to 800°C .

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