Non-isothermal Crystallization Kinetics of the BaTiO$_3$-KNbO$_3$-SiO$_2$ Glass

H. Y. Yang and Y. S. Yang$^*$
Department of Nano Fusion Technology, Pusan National University, Busan 609-735, Korea

H. W. Choi
Department of Physics, Pusan National University, Busan 609-735, Korea

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We have investigated the non-isothermal formation kinetics of nanocrystals from the BaTiO$_3$-KNbO$_3$-SiO$_2$ (BKSO) glass at temperatures from room temperature to 800 °C. The thermal characteristics and the structural transformations of the BKSO glass have been studied by means of a differential thermal analysis and X-ray diffraction. The crystallization of BKSO glass is found to accompany a single-step occurrence of a tetragonal Ba$_3$TiNb$_4$O$_{15}$ nanocrystal structure. During the crystallization, a nanocrystals with a size of ∼40 nm at the initial stage grow with increasing temperature and reach a size of ∼120 nm by the time the crystallization finishes. We use the non-isothermal model of Johnson-Mehl-Avrami-Kolmogorov to characterize the kinetics of the crystallization process for the BKSO glass. The Avrami exponent of 3.5 indicates that the crystallization mechanisms is an increasing nucleation rate with diffusion-controlled growth. In the view of applications, providing information on how to control the size of nanograins systematically by simply controlling the annealing temperature of the glass state, as described in this study, should be useful.

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I. INTRODUCTION

Recently much attention has been paid to the design of new ferroelectric, piezoelectric, and pyroelectric materials that are lead free because lead is toxic and gives rise to environmental problems [1–4]. Some possible ways of designing such new materials include the replacement of atomic species, a structural change such as glass-ceramics instead of poly or single crystals, and the formation of composite compounds by mixing different compositions together. Among these, the investigation of the physical properties of glasses and of glass-ceramics of ferroelectric materials has attracted significant interest due to their technological importance. BaTiO$_3$ and KNbO$_3$ crystals are examples of those important ferroelectric materials and are applicable to surface acoustic wave, non-linear optical, and electromechanical transducer devices [5–8].

BaTiO$_3$ undergoes sequential phase transitions from the paraelectric cubic perovskite structure at high temperature to the ferroelectrics tetragonal (120 °C), orthorhombic (−5 °C) and rhombohedral (−90 °C) structures [9,10]. KNbO$_3$ has an orthorhombic structure at room temperature. The melting and the Curie temperatures of KNbO$_3$ are 1100 °C and 435 °C, respectively [8]. Most studies on BaTiO$_3$ and KNbO$_3$, such as studies on their structural, thermal and electrical properties, have been performed on the crystalline state. Studies on the fundamental properties for the BaTiO$_3$ and the KNbO$_3$-related glass and glass-ceramics are lacking.

In the case of glass ceramics, the physical properties depend very much on the crystal volume fraction and the crystal size in the glass matrix, and optimum properties can often be obtained by controlling those parameters through the synthesis process, with the volume fraction and the size being controlled by using a heat treatment during the crystallization of a glass [11,12]. Thus, an understanding of the crystallization process is essential. Moreover, ferroelectric materials with sizes in the nano-range are in high demand in industries for applications in advanced technology. As the electrical and the mechanical properties of nanomaterials are much different from those of bulk materials, more of the materials made from nanoparticles are required before using them for applications. Concerning the preparation of a glass sample, the use a sufficient amount of a glass former is often required to overcome the high cooling rate and to lower the melting temperature. BaTiO$_3$ crystal powder melts at 1618 °C achieving the high cooling rate that is necessary to
make glass as a compound with a low thermal conductivity is difficult. We have used SiO\textsubscript{2} as a glass former as its physical properties and its role of in glass forming are well established [13,14].

In this paper, we present the results of non-isothermal studies on the phase transition process of a BaTiO\textsubscript{3}-KNbO\textsubscript{3}-SiO\textsubscript{2} (BKSO) glass to a crystal. We use the Johnson-Mehl-Avrami-Kolmogorov model to analyze the non-isothermal experimental data.

II. EXPERIMENTS

The BKSO glass was fabricated by using the melt quenching method. BaTiO\textsubscript{3}, KNbO\textsubscript{3} and SiO\textsubscript{2} powders were well mixed. The polycrystalline powder was made by using a solid state reaction during the heat treatment at 1300 °C for 1 h. This was quenched with twin rollers at a cooling rate of about 4 × 10\textsuperscript{4} °C/s. The color was bright yellow, and the thickness of this sample was 0.025 mm. The non-isothermal crystallization kinetics of the BKSO glass was investigated by using a differential thermal analysis (DTA; TG-DTA2020s, Mac. Science) in the temperature range from 30 to 800 °C. For non-isothermal experiments, a sample of 20 mg was encapsulated in a platinum pan and was heated at different rates. Continuous heating experiments were conducted at a scanning rate of 5 °C/min. The empty sample pans for each measurement were used for a baseline subtraction. The crystal grain sizes were calculated by using X-ray diffraction (XRD; Miniflex II, Rigaku) data and an image calculating program of scanning electron microscopy (SEM; S-4700, Hitachi).

III. RESULTS AND DISCUSSION

Among the theoretical models that can be applied to the non-isothermal DTA results to interpret the transformation kinetics from a glass to a crystal phase, the Johnson-Mehl-Avrami-Kolmogorov (JMAK) model was used. The JMAK equation with linear heating is written as

\[ x(t) = 1 - \exp(-Kt^n), \]  

with

\[ K(\beta, t) = K_0\beta^n \exp \left( -\frac{E}{k_B\beta t} \right) \]  

where \( x(t) \) is the transformed crystalline volume fraction after time \( t \), \( n \) is the Avrami exponent, \( K(\beta, t) \) is the crystallization rate constant with non-isothermal parameter \( K_0 \), \( E \) is the activation energy describing the overall crystallization process, \( \beta \) is the heating rate, \( T = \beta t \) with heating temperature \( T \), and \( k_B \) is the Boltzmann constant. Both \( n \) and \( K(\beta, t) \) reflect the nucleation and the growth mechanisms of the sample. From Eq. (1), plotting \( \ln(-\ln(1-x)) \) vs. \( \ln \beta \) at a given temperature gives a linear dependence on the Avrami exponent \( 2n \). By combining Eqs. (1) and (2), one can obtain the activation energy for the crystallization of a glass by plotting \( \ln(-\ln(1-x)) \) vs. \( 1/T \) with the following relationship [15–19]:

\[ \frac{d(\ln(-\ln(1-x)))}{d(\frac{1}{T})} = -2nT - \frac{E}{k_B} \approx -\frac{E}{k_B} \]  

(3)

when \( E/2n \gg k_BT \).

Figure 1 shows the DTA curve during the crystallization of BaTiO\textsubscript{3}-KNbO\textsubscript{3}-SiO\textsubscript{2} (BKSO) glass at a heating rate of 10 °C/min, where the glass transition temperature \( T_g \), the crystallization temperature \( T_c \) and the maximum crystallization temperature \( T_p \) are shown. One exothermic peak indicates that only one crystalline phase from glass occurs with heating.

![Figure 1. (Color online) Non-isothermal DTA curve for the BaTiO\textsubscript{3}-KNbO\textsubscript{3}-SiO\textsubscript{2} glass for a heating rate of 10 °C/min. The glass transition temperature \( T_g \), the crystallization temperature \( T_c \) and the maximum crystallization temperature \( T_p \) are shown. One exothermic peak indicates that only one crystalline phase from glass occurs with heating.](image)

Figure 2 shows XRD patterns taken at room temperature for the samples obtained by annealing the BKSO glass at temperatures up to a given temperatures in an electric furnace at a heating rate of 10 °C/min, which is the same heating rate as that used for the DTA measurement in Fig. 1. By rapidly quenching the samples to room temperature from the selected temperatures, we determined the crystal structure corresponding to the exothermic peak in the DTA curve. Diffraction patterns measured with the stoichiometric compositions of