

TRANSPARENT BARIUM TITANATE GLASS CERAMIC NANOCOMPOSITES FOR OPTOELECTRONIC DEVICE APPLICATIONS

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Received: June 02, 2024; Revised: September 05, 2024; Accepted: November 18, 2024

Abstract

The glass crystallization process was applied to create a nanocomposite material composed of crystallites within a glass-like matrix. The structural optical and dielectric properties of crystals embedded in a glassy matrix, the BaTiO₃-Na₂O-B₂O₃-SiO₂ system generated by the melt quenching process, were investigated in this study. The heat treatment procedure was used to convert the prepared glass to glass-ceramic samples at temperatures ranging from 700 to 800°C. After being quenched between stainless steel plates, the X-ray diffraction results reveal the presence of crystalline phase in a glassy matrix. Scanning electron micrography and transmission electron micrography were used to investigate the crystal morphology. The glass transition and crystallization temperatures were investigated by using the differential thermal analysis. The optical transmittance spectra in the wavelength range of 300-1000 nm were then recorded using UV-Vis spectrophotometer. A precise LCZ meter was used to measure the dielectric characteristics at various frequencies. It was demonstrated that crystallites form using a specific method, resulting in anisotropic glass ceramic. The shape and crystallinity of the produced samples influence their optical and dielectric properties.

Keywords: Optoelectronics; Nanocomposite; Transparent Glass; BaTiO₃

Introduction

Piezoelectric materials possess a remarkable ability to convert mechanical energy into electrical signals and vice versa. Among these materials, inorganic variants like lead zirconated titanate (PZT) (Li *et al.*, 2021) and barium titanate (BaTiO₃) (Charoonsuk *et al.*, 2019; Pongampai *et al.*, 2021) demonstrate this effect through the rearrangement of ions within their crystal structures, which lack

inversion symmetry (Sriphan and Vittayakorn, 2022; Sriphan *et al.*, 2023). Widely utilized across industries, these materials serve as integral components in ultrasonic motors, actuators, precision motion control devices, microfluidics, implantable medical devices, and piezoelectric nanogenerators (Sriphan and Vittayakorn, 2022; Sriphan *et al.*, 2023). Despite their widespread

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application, piezoelectric materials have some limitations, including constraints on strength and durability, inadequate temperature stability, high production costs, processing complexities, limited biocompatibility, and potential environmental and health risks, rendering them less favorable for biomedical and related purposes (Sriphan and Vittayakorn, 2022; Sriphan *et al.*, 2023).

In contrast, glass ceramics emerge as promising alternatives, distinguished by their fabrication from pore-free precursor glasses and possessing favorable thermal, mechanical, optical, magnetic, and electrical properties. This versatility enables their deployment across various domains, encompassing electrical and magnetic engineering, electronics, aerospace engineering, lighting and optics, as well as biomaterials.

Glass ceramics with integrated ABO₃ nanocrystals provide a transparent nano ferroelectric crystal. It is possible that self-frequency doubling laser sources might be designed using this oxide in conjunction with the intrinsic nonlinear optical characteristics of ferroelectric crystals. As a result, researchers have paid a lot of attention to this novel material as they look for new uses for optoelectronic devices (Tarafder *et al.*, 2009; Tarafder *et al.*, 2010). Thus, these ABO₃ glass ceramics might be useful in a wide variety of contexts, such as electro-optical modulators, pyroelectric detectors, optical waveguides, piezoelectric transducers, etc.

The main crystalline phase of perovskite lead titanate was first precipitated by Herczog and Stookey in the glass system SiO₂-Al₂O₃-TiO₂-PbO (Herczog and Stookey, 1960). Subsequently, Kokubo and Tashiro crystallize the fine-grained PbTiO₃ as the predominant phase and study the dielectric characteristics of the glass ceramic system PbO-TiO₂-Al₂O₃-SiO₂ (Kokubo and Tashiro, 1974). The dielectric characteristics of the glass ceramic system BaO-PbOTiO₂-B₂O₃-SiO₂ have also been investigated by Mandal *et al.* (Mandal *et al.*, 1987). This study discovered that the dielectric constant at 1 kHz and room temperature is merely on the order of 25. Glass ceramics based on PbO with Bi₂O₃ are hygroscopic, although they have a higher dielectric constant at room temperature (Golezardi *et al.*, 2010). Because of the toxicity of lead (Pb) in the environment and the emergence of global protectionism, the development of lead-free radiation-protecting glasses is crucial in order to enable novel glass ceramic uses for optoelectronic devices (Tanaka *et al.*, 2003).

ABO₃ structures based on perovskite metal oxides have found applications in catalytic responses, piezoelectric, photoelectric, and other

fields. One of the most important ceramic substances is barium titanate (BaTiO₃). Due to its ferroelectric polarization and excellent dielectric responsiveness, barium titanate (BaTiO₃) is regarded as a significant perovskite material. BaTiO₃ has the benefits of being inexpensive and safe for the environment. Actuators, random access memory (RAM), and integrated optical and electronic components are only some of the many applications for BaTiO₃'s substantial opto-electric and non-linear optical coefficients (Cai *et al.*, 2009; Takenaka and Nagata, 2018; Zhang *et al.*, 2018). The crystalline structure of the material is crucial for these applications, but it can change depending on the temperature and other circumstances of synthesis (Zhang *et al.*, 2017; Zhang *et al.*, 2018). However, few studies have been conducted to investigate the optoelectronic properties of perovskite barium titanate in glass systems (Thakur *et al.*, 2015; Singh *et al.*, 2020).

Commercial borosilicate glass is a major contributor to the industry. They're transparent and have low melting points, excellent thermal and chemical stability, and low thermal expansion coefficients. Both its dielectric constant and its softening temperature is significantly better than those of soda-lime-silica glasses. According to Gowda *et al.* 2007, boron can be found in trigonal and tetrahedral coordination with oxygen. Even though their glassy network and physical qualities, such as high transparency, low melting point, high thermal stability, and a good capacity for glass formation (Dos Santos *et al.*, 2007; Murugesan and Bergman, 2007; Keller *et al.*, 2007), are well-coordinated in borate glasses.

This work, therefore, demonstrated the investigation of the transparent glass ceramic nanocomposites with the BaTiO₃ added in (100-x) Na₂O-B₂O₃-SiO₂ glass (where x = 80 wt%) with the consideration of its phase formation, microstructure, crystal sizes, optical, ferroelectric and dielectric properties.

Experiment details

Synthesis of the glass ceramic samples

The glass with the composition of 80 wt% BaTiO₃ (BT): 20 wt% Na₂O-B₂O₃-SiO₂ was utilized to make BT-Na₂O-B₂O₃-SiO₂ glass ceramics. The solid-state reaction approach was used to produce pure BT powder with a perovskite structure. As starting materials, BaCO₃ and TiO₂ reagent powders were employed. The combined powder was calcined for 3 h at 1100°C. The glass in the system 25Na₂O-13B₂O₃-62SiO₂ (in wt.%) (Ghanbari-Ahari, and Cameron, 1993) was created

by combining the raw ingredients Na_2CO_3 , B_2O_3 , and SiO_2 , and melting the mixture in a Pt crucible at 1200°C for 2 h in an air atmosphere using an electric furnace. The molten glass was cooled in water. The glass frits were then ball-milled to make a fine powder. The glass powder was then combined with BT powders. The glass batch was then melted in a Pt crucible at 1500°C for 4 h in an air atmosphere using an electric furnace and quenched between stainless steel plates to produce glass pieces, followed by annealing at 450°C for 2 h to remove the glass's internal tensions. The resultant glasses were then heat treated for 2 h to make glass ceramics at 700, 725, 750, and 800°C . The glass ceramics were designated HT 700, HT 725, HT 750, and HT 800 in that order.

Characterization techniques

Differential thermal analysis (DTA)

DTA curves were measured in an air environment under static circumstances using $\alpha\text{-Al}_2\text{O}_3$ powder as a reference material and at a constant heating rate using differential thermal analyzers (DTA: 1600 DTA, Du Pont Instrument). For the glass transition (T_g), crystallization (T_c), and melting temperatures (T_m) experiments, the finely milled sample powder with particle size less than $45\text{ }\mu\text{m}$ of 30 mg was put into an alumina crucible and heated at a rate of $10^\circ\text{C}/\text{min}$ from room temperature to 1200°C .

X-ray powder diffraction analysis (XRD)

In X-ray powder diffraction investigation, an X-ray diffractometer (XRD, PANalytical X'Pert Pro MPD) was used to capture data from 10° to 80° 2θ with a step size of 0.012° in flat plate geometry, utilizing Ni filtered Cu K radiation. JCPDS numbers (from the ICDD-PDF2 data source) were utilized to identify the crystalline phases present in samples.

Field emission scanning electron microscopy (FE-SEM)

Field emission scanning electron microscopy was used to examine the microstructure of the heat-treated samples (FE-SEM: JSM-6335F). Prior to FE-SEM observation, the heat-treated samples were etched with 3% hydrofluoric acid for 15 seconds to allow the crystals to protrude from the surface and provide a high contrast of the crystal microstructure of the etched glass matrices.

Transmission electron microscopy (TEM)

The transmission electron microscope was used to obtain the TEM image of the powdered BT- $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$ glass ceramics (TEM: JEM 2010).

UV-Visible studies

The UV-Vis spectrophotometer was used to record the optical transmittance spectra in the wavelength range of 300-1000 nm. The optical transmission spectra of 3 mm thick glass samples were recorded at room temperature.

Tauc's plots are used to calculate the optical band gap of BT- $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$ glass ceramics. The optical band gap of BT- $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$ glass ceramics was determined using equation (1) (Ghosh *et al.*, 2007):

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu} \quad (1)$$

Absorption coefficient (α), constant (A), Planck constant (h), photon frequency (ν), optical band gap (E_g), and index (n), which can take on the values 2, 3, $1/2$, or $1/3$ depending on the kind of transition. Beer's law (Davis and Mott 1970) expresses the relationship between sample thickness and transmittance as a function of the absorption coefficient (equation (2)). The connection is described as follows:

$$\alpha = -\left(\frac{1}{t}\right) \ln T \quad (2)$$

T stands for transmittance, and t stands for thickness.

Electrical property studies

Both sides of the glass crystals were coated with gold and then polished so that they could be used as electrodes in electrical measurements. The BT- $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$ glass ceramic's dielectric constant (ϵ_r) and dielectric loss ($\tan\delta$) were measured in an LCZ meter (Model 4276A, Hewlett Packard) at room temperature. Finally, a Sawyer Tower circuit (Radiant Technologies, Inc.) was used to measure the ferroelectric hysteresis loops at room temperature.

Results and Discussion

Appearance

The HT700 glass ceramic sample was clear and white, with no discernible flaws or blemishes. Additionally, the HT725 glass ceramic sample seemed translucent and white. Glass ceramic samples from HT750 and HT800, on the other hand, were both opaque and colorless. In Figure 1, we see how the BT- $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$ glass ceramic samples change in appearance as the heat treatment temperature is increased or decreased. Transparency is greatest in glass ceramics treated at

700°C, whereas increasing the temperature to 725°C makes them less see-through. In addition, it was found that raising the heat treatment temperature, particularly heating the sample to the greatest temperature (800°C), increased the opaqueness.

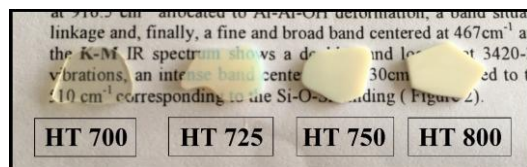


Figure 1. Appearance of the BT-Na₂O-B₂O₃-SiO₂ glass ceramic samples

Differential thermal analysis (DTA)

The glass particles were used to evaluate the thermal parameter are shown in Figure 2. First and second crystallization temperatures (T_{c1} and T_{c2}) were observed at 812 and 900°C, respectively, whereas the glass transition temperature (T_g) was measured at 684°C. There is a little endothermic peak around 1182°C. For the purpose of determining the glass's peak melting temperature (T_m), this temperature was taken into account. Nucleation typically begins at temperatures around or slightly above T_g , while the optimal rate of crystal growth tends to occur at higher temperatures. Understanding the temperature dependency of both nucleation and growth processes allows for the regulation of glass crystallization, facilitating the attainment of desired properties in the resulting glass-ceramic material. Subsequently, the glass underwent a heat treatment regimen spanning temperatures between 700 and 800°C to investigate its crystallization behavior. In the case of the glass-ceramic samples treated within the temperature range of 700 to 725°C (referred to as HT700-HT725), although they displayed an amorphous X-ray diffraction (XRD) pattern, small spherical-like grains were discernible within the samples. This observation suggests the potential occurrence of phase separation or nucleation within the glass matrix instead of the formation of crystallites. Conversely, the HT 750 sample (referenced as Figure 6 (HT 750)) exhibited a morphology similar to that of the HT700-HT725 glass-ceramic samples. However, its corresponding XRD analysis revealed slight traces of crystalline phases, potentially indicating an increase in the crystallinity of this heat-treated sample.

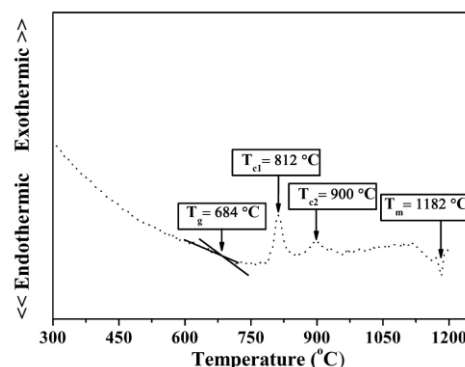


Figure 2. DTA curves of the glass sample BT-Na₂O-B₂O₃-SiO₂ at a heating rate 10°C/min

UV-Visible Studies

The ultraviolet-visible-near-infrared (UV-VIS-NIR) transmittance spectra of the HT700, HT725, HT750, and HT800 glass ceramic samples are demonstrated in Figure 3. Samples of glass ceramics HT700, HT725, HT750, and HT800 were tested for transparency and were found to have wavelengths of 80%, 60%, 2.5%, and 0% at 700 nm. As the temperature of the heat treatment was raised, the trend of transmittance decreased. Furthermore, the figures show that UV cutoff wavelength gradually increases as the heat treatment temperature increases. The glass was amorphous at 700°C, but at 725°C, it becomes minutely crystalline and the UV-cut-off wavelength moves from 360 to 500 nm. This was caused by the Rayleigh and Mie scattering effects shown by the small crystals contained within it (Mie, 1908; Young, 1982).

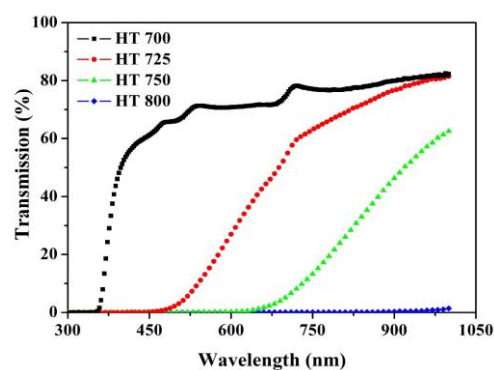


Figure 3. Transmittance spectra of the BT-Na₂O-B₂O₃-SiO₂ glass ceramic samples

The Tauc's plot $[(\alpha h\nu)^2 \text{ vs. } h\nu]$ for heat-treated samples at various temperatures is shown in Figure 4. By projecting the linear component of the curve to intersect the photon energy axis at zero absorption, the optical band gap energies (E_g) can be calculated from the Tauc's figure. The values of E_g are given by the intersection of the slope of the linear segment of the plot $[(\alpha h\nu)^2 \text{ vs. } h\nu]$ (in eV). E_g value for the HT700 glass ceramic sample is 3.55 eV. This value decreases to 1.15 eV as the heat-treatment temperature rises. This is because the crystallinity of the glass ceramic samples has increased (Shasmal and Karmakar, 2015). The reliance on optical properties, such as UV-cut-off and optical band gap, on the heat-treatment parameters, is extremely relevant for the glass-ceramics in terms of the uses they have in optoelectronic devices.

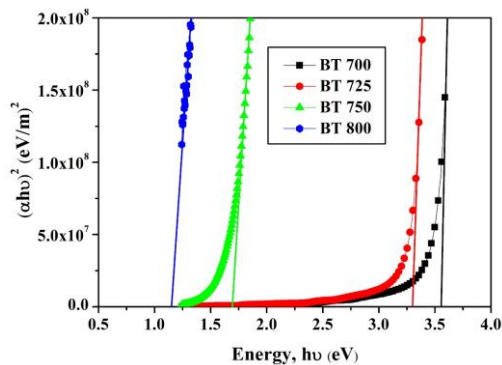


Figure 4. Tauc's plot of the BT-Na₂O-B₂O₃-SiO₂ glass ceramic samples

X-ray diffraction analysis

Figure 5 displays the XRD patterns of the acquired BT-Na₂O-B₂O₃-SiO₂ glass ceramic samples. The HT700 and HT725 samples both show a broad XRD pattern, confirming its amorphous nature, whereas the HT750 sample shows some low-intensity peaks, showing the occurrence of some crystals inside the glass matrix. There is an obvious increase in crystallinity in the HT800 sample, as seen by the clear diffraction patterns and strong, sharp diffraction peaks. Crystallite diameters were estimated to be between 10 and 100 nm, and this range was found to hold true across a wide range of heat treatment temperatures. Figure 6 presents the FE-SEM imaging result showing the correlation between crystallite size and heat treatment temperature. The XRD patterns reveal the presence of two crystalline phases, a tetragonal phase of Ba₂TiSi₂O₈ (JCPDS

No. 22-0513) and a tetragonal phase of BaTiO₃ (JCPDS no. 79-2264) (Intawin *et al.*, 2017).

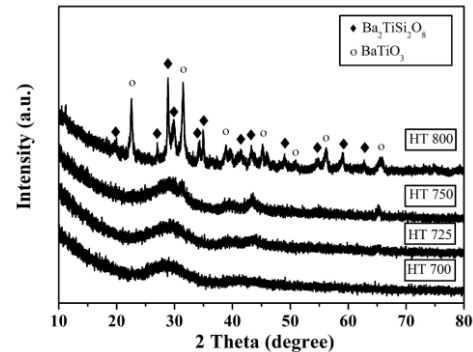


Figure 5. XRD patterns of the BT-Na₂O-B₂O₃-SiO₂ glass ceramic samples

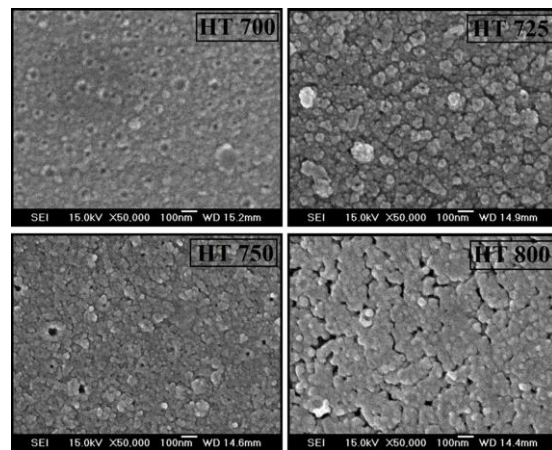


Figure 6. FE-SEM images with $\times 50,000$ magnification of the BT-Na₂O-B₂O₃-SiO₂ glass ceramic samples.

FE-SEM and TEM image analyses

Field-emission scanning electron microscopy (FE-SEM) was used to investigate the microstructures of heat-treated glass ceramics. Micrographs of heat-treated samples at 700, 725, 750, and 800°C for 2 h are shown in Figure 6. At low temperatures of 700, 725, and 750°C, tiny spherical particles with an average diameter of 20-30 nm are visible as spherical clusters with an average diameter of 100 nm. The diameter of the particles grows as the temperature rises to 800°C. Individual particles with an average diameter 60 nm are obtained. Spherical clusters are found in Figure 6 (HT700, HT725 and HT750), which with the increase in heat treatment temperature,

increased both the crystal volume fractions, as well as the size of the particles increased. At the maximum temperature, more particles are created, resulting in a larger assembly.

Transmission electron microscopy (TEM) was also used to determine the HT 750 microstructures, as seen by the TEM image and the SAED pattern of the BT-Na₂O-B₂O₃-SiO₂ glass ceramic sample that was heat-treated for 2 h at 750°C. Micrographs show the nanocrystalline particles. A typical particle size of 50 nm is shown in Figure 7. This finding confirms that the size of particles can be affected by temperature, as seen in a FE-SEM image. There is a lack of uniformity in the crystallites' shape. There are spherical ones, spheroid ones, and some with odd shapes. It occurs due to several crystallization mechanisms (Shasmal *et al.*, 2007). It has been shown that the proportion of spheres increases with increasing heat treatment temperatures. The presence of Ba₂TiSi₂O₈ nanocrystallites in the glassy matrix was confirmed by the d-spacings computed from the SAED pattern (inset of Figure 7). This finding agrees with what is shown in Figure 5 for the diffraction peaks of the Ba₂TiSi₂O₈ phase.

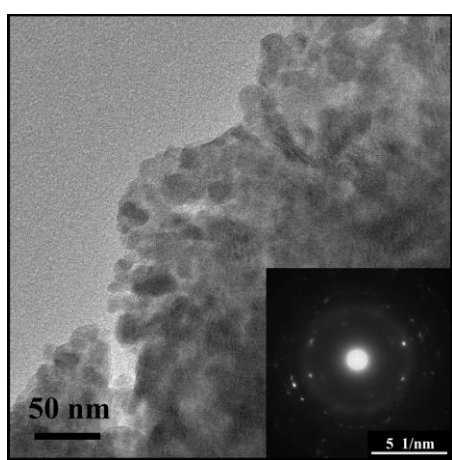


Figure 7. TEM image and SAED pattern with $\times 100,000$ magnification of the sample (HT 750) heat treated at 750°C for 2 h

Dielectric properties

Figure 8 displays the relationship between frequency and the dielectric constant and dielectric loss of BT-Na₂O-B₂O₃-SiO₂ glass ceramic samples subjected to a range of heat treatment temperatures. It is clear from the graph that there is a slight decrease in dielectric constant across all samples with increasing frequency. This result agrees with those of earlier studies (Prasad and Varma, 2001).

According to Maxwell's and Wagner's predictions, a glass crystal structure will exhibit interfacial polarization because it is a heterogeneous material. It was noted that the hopping mechanism in each interstice, when subjected to alternating current, was the primary contributor to dielectric constant at high frequencies. As a result of being unable to keep up with the frequency of the applied field, the hopping frequency between ions falls behind. Therefore, the dielectric constant values fall as frequency increases (Kumar and Buddhudu, 2010). For heat treatment temperatures of 700, 725, 750, and 800°C, the corresponding dielectric constant values at 10 kHz are 25.0, 27.5, 37.5, and 80.0, respectively. Figure 8 (HT 700)-(HT 750) shows, and prior work (Chaliha *et al.*, 2009) confirms, that as the temperature of the glass rises, the amount of crystallinity in the matrix also rises. In contrast, the existence of Ba₂TiSi₂O₈ and BaTiO₃ phases is likely to blame for the increased dielectric constant in the heat-treated 800°C sample. Also, the dielectric loss values were quite low across the board, ranging from around 0.01 to about 0.20 depending on frequency and heat treatment temperature.

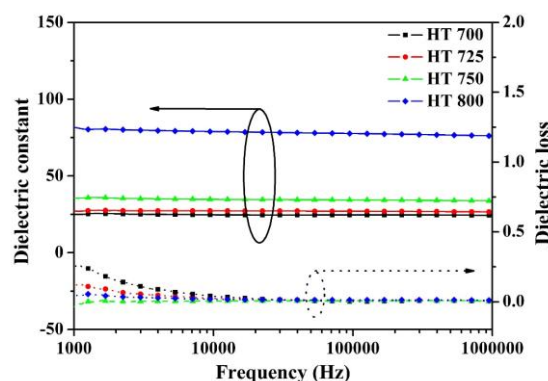


Figure 8. Frequency dependence of dielectric constant measured at room temperature of the BT-Na₂O-B₂O₃-SiO₂ glass ceramic samples.

Ferroelectric properties

In Figure 9, we can see the loops of the ferroelectric hysteresis for the BT-Na₂O-B₂O₃-SiO₂ glass ceramics at different heat treatments. All of the tests were done at room temperature and 50 Hz. Both the HT700 and HT725 samples showed enormous, rugby ball-shaped loops in the hysteresis curve, indicating a high leakage current. This finding further verified that the HT700 and HT725 samples include a significant proportion of amorphous matrices, resulting in a greater number

of ions that are able to diffuse in the presence of an electric field. The glass-ceramic samples' ferroelectric behavior improved after being heated to 750-800°C, as seen by the transition of the large rugby ball-like loop into narrow hysteresis loops. Increased concentrations of $\text{Ba}_2\text{TiSi}_2\text{O}_8$ and BaTiO_3 crystalline phase in the glass matrix may explain their enhanced ferroelectric behavior. The loss value of the investigated samples also decreased as a result of the improved ferroelectric behavior at room temperature of the $\text{BT-Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$ glass ceramic samples.

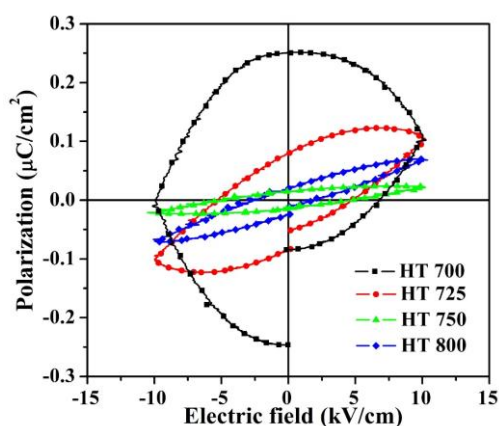


Figure 9. Ferroelectric hysteresis loops

Conclusions

Melt quenching was successfully used to create $\text{BaTiO}_3\text{-Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$ glass-ceramic nanocomposites. After deducing the appropriate thermal parameter from the DTA result, the glasses were heated to 700-800°C for 2 h in order to create glass ceramics. When the amorphous phase of glass can be transformed into polycrystalline material through heat treatment, the glass will crystallize. X-ray diffraction patterns show that the HT700 and HT725 samples are in an amorphous phase, whereas the HT750 and HT800 samples are in a crystalline precipitation of $\text{Ba}_2\text{TiSi}_2\text{O}_8$ and BaTiO_3 phases. FE-SEM reveals that crystal size grew as heat treatment temperatures rose. SAED pattern and TEM image confirm the presence of $\text{Ba}_2\text{TiSi}_2\text{O}_8$ nanocrystals in the amorphous glass support. As a glass ceramic, the $\text{BaTiO}_3\text{-Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$ system displays ferroelectric properties. Using the current method, novel glass ceramics can be synthesized for use in optoelectronic devices.

Acknowledgment

The authors would like to thank The Reinventing University Program 2022 from Ministry of Higher Education, Science, Research and Innovation, Thailand, Rajamangala University of Technology Phra Nakorn, Thailand. This work (Grant No. RGNS 65 - 093) was financially supported by Office of the Permanent Secretary, Ministry of Higher Education, Science, Research and Innovation. We would also like to thank the Division of Physics, Faculty of Science and Technology, Rajamangala University of Technology Thanyaburi, Pathum Thani, Thailand.

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