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Eu³⁺ doped ferroelectric CaBi₂Ta₂O₉ based glass-ceramic nanocomposites: Crystallization kinetics, optical and dielectric properties

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ABSTRACT

We report Eu³⁺ doped transparent glass-ceramics (GCs) containing bismuth layer-structured ferroelectric (BLSF) CaBi₂Ta₂O₉ (CBT) as the major crystal phase. The CBT crystal phase was generated in a silica rich glass matrix of SiO₂-K₂O-CaO-Bi₂O₃-Ta₂O₅ glass system synthesized by melt quenching technique followed by controlled crystallization through ceramming heat-treatment. Non-isothermal DSC study was conducted to analyze crystallization kinetics of the glass in order to understand the crystallization mechanism. The optimum heat-treatment protocol for ceramization of precursor glass that has been determined through crystallization kinetics analysis was employed to fabricate transparent GCs containing CBT nanocrystals, which was otherwise difficult. Structural analysis of the GCs was carried out using XRD, TEM, FESEM and Raman spectroscopy and results confirmed the existence of CBT nanocrystals. The transmittance and optical band gap energies of the GCs were found to be less when compared to the precursor glass. The refractive indices of the GCs were increased monotonically with increase in heat-treatment time, signaling densification of samples upon heat-treatment. The dielectric constants (ϵ_r) of the GCs were progressively increased with increase in heat-treatment duration indicating evolution of ferroelectric CBT crystals phase upon heat-treatment.

1. Introduction

Mixed bismuth oxide layer compounds (known as Aurivillius compounds) were reported first by Bengt Aurivillius [1] in 1949, which was followed by investigation of ferroelectricity in these compounds by Smolensky et al. [2]. A member of the Aurivillius family, bismuth layered-structure ferroelectrics (BLSFs) has attracted great attention in recent years due to their unique properties, such as large dielectric breakdown strength (BDS), high Curie temperature (T_c) and excellent fatigue free polarization [3,4]. These properties make them a promising candidate for application in ultrasound transducers, high temperature piezoelectric devices, thin film capacitors, pyroelectric sensors, optical memories, displays and non-volatile ferroelectric random access memories (FE-RAM).

The BLSF crystals are represented by the general formula $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{x-1}\text{B}_x\text{O}_{3x+1})^{2-}$, where $(\text{A}_{x-1}\text{B}_x\text{O}_{3x+1})^{2-}$ are the pseudo-perovskite unit cells interspaced between bismuth oxide $(\text{Bi}_2\text{O}_2)^{2+}$ layers along the c-axis. In the pseudo-perovskite block 'A' can be a monovalent (Na^+ , K^+), bivalent (Ca^{2+} , Ba^{2+} , Sr^{2+} , Pb^{2+}) or trivalent cation (Bi^{3+}), 'B' represents a tetravalent, pentavalent, or hexavalent ion (Ti^{4+} , Nb^{5+} , Ta^{5+} , W^{6+} , and V^{6+}) and x can be any integer or $\frac{1}{2}$ integer. The $\text{CaBi}_2\text{Ta}_2\text{O}_9$ (CBT) crystal belongs to the BLSF family which

consists of double TaO_6 octahedral units within the $(\text{CaTa}_2\text{O}_7)^{2-}$ perovskite blocks stacked between the $(\text{Bi}_2\text{O}_2)^{2+}$ layers [5]. It is a polar orthorhombic crystal phase with $A2_1am$ space group [6]. The presence of small sized Ca^{2+} ion (ionic radius 1.00 Å) in the A-site of $(\text{ATa}_2\text{O}_7)^{2-}$ layers leads to a significant lattice mismatch between the CaO and TaO_2 planes of the layers which caused structural distortion of crystals. Due to this structural distortion, the CBT crystals become non-centrosymmetric which contributes to larger spontaneous ferroelectric polarization [7]. CBT also exhibits higher Curie temperature ($> 600^\circ\text{C}$). Das et al. [8] synthesized CBT thin films and reported some of its ferroelectric and dielectric properties. A maximum polarization of $13.4 \mu\text{C}/\text{cm}^2$, remanent polarization of $3.44 \mu\text{C}/\text{cm}^2$, coercive field strength of $112 \text{ kV}/\text{cm}$, dielectric constant of 116 at 100 kHz and low dielectric loss of 0.01 were reported. Photoluminescence properties of rare earth doped CBT ferroelectrics synthesized through conventional solid state reactions technique have been reported in recent times. Ruirui et al. observed outstanding tunable emissions and generation of warm white color in $\text{Eu}^{3+}/\text{Tb}^{3+}$ co-doped CBT powders [9]. Strong red emission peaks at 622 nm for Pr^{3+} and 615 nm for Eu^{3+} were observed for CBT powders doped with 0.02 mol% of Pr^{3+} and 0.15 mol% of Eu^{3+} respectively [10]. They also reported significant enhancement of luminescence intensity of Eu^{3+} ion in CBT by co-doping with La^{3+} and the

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highest emission intensity was reported for europium ion concentration of 0.15 mol% [11]. Such rare earth doped non-centrosymmetric CBT crystals along with their inherent ferroelectric and non-linear optical (NLO) properties could be useful for designing of future generation opto-electronic devices [12].

In comparison to ferroelectric ceramics, fabrication of ferroelectric glass-ceramics (FGCs) through melt-quenching technique offers several advantages like zero/low porosity, higher mechanical and dielectric breakdown strengths and the possibility of altering the properties by varying the volume fraction of the ferroelectric phase and size of the crystals dispersed in the glass matrix. Transparency in FGCs can be achieved through homogenous nucleation and controlling growth of crystallites in nanometer range that are too small for Rayleigh scattering. However, for application of transparent FGCs in integrated optical devices, the size of the crystallites must be large enough to generate a reasonably good ferroelectric response. A tradeoff between these two attributes remains a big challenge for the researchers [13]. Very recently we have reported the optical and dielectric properties of Eu^{3+} doped $\text{BaBi}_2\text{Ta}_2\text{O}_9$ (BBTE) glass and glass-ceramics and observed favorable properties, like, a five-fold increase in photoluminescence intensity in the BBTE glass-ceramics and higher dielectric constant (ϵ_r) (> 100) along with low dielectric losses and dissipation factors [14]. To the best of our knowledge, there is no report available in the literature on rare earth doped transparent nanostructured glass-ceramics containing ferroelectric CBT ($\text{CaBi}_2\text{Ta}_2\text{O}_9$) crystal phase, in spite of its favorable properties making it suitable for various advanced applications.

In the present work, we report for the first time synthesis of Eu^{3+} doped ferroelectric $\text{CaBi}_2\text{Ta}_2\text{O}_9$ (CBTE) glass-ceramics using conventional melt quenching and ceramming technique. A comparative study of crystallization kinetics of the CBTE glass has been made through linear (Kissinger, Augis-Bennett, Ozawa, Matusita) and multivariate nonlinear (n^{th} dimension Avrami-Erofeev) model-fitting approaches to ascertain the nature of nucleation and mechanism of crystal growth. A novel approach of isothermal prediction has been adopted through the nonlinear kinetics study in order to optimize the heat-treatment protocol for controlled crystallization. The theoretically optimized heat-treatment protocol was successfully exploited experimentally to synthesize transparent CBTE GCs by controlled crystallization. The microstructure, thermal, optical and dielectric properties of the CBTE GCs has been correlated to their processing conditions.

2. Experimental procedure

Precursor CBTE glass was prepared using a molar composition of $17.5\text{K}_2\text{O}-51.3\text{SiO}_2-10\text{BaO}-10\text{Bi}_2\text{O}_3-10\text{Ta}_2\text{O}_5$ doped with 0.5 mol% of Eu_2O_3 and 0.7 mol% of CeO_2 . The glass was synthesized through melt quenching technique by preparing glass batch of 120 g and melting in a platinum crucible at 1475°C for 2 h employing an electric furnace. High purity raw materials are used for synthesis of glass, such as silica, SiO_2 (99.8%; Sipur A1 Bremtheler Quarztzwerk, Usingen, Germany), anhydrous potassium carbonate (GR, 99.5%; Loba Chemie, Mumbai, India), calcium carbonate, CaCO_3 (99.0%; Fluka Biochemica, India), bismuth (III) oxide, Bi_2O_3 (99.0%; Loba Chemie, Mumbai, India), tantalum (V) oxide, Ta_2O_5 (99.85%; Alfa Aesar, Ward Hill, MA), europium (III) oxide, Eu_2O_3 (99.99%; Sigma Aldrich, Zeppelinstr, Karlsruhe, Germany) and cerium (IV) oxide, CeO_2 (99.99%; Indian Rare Earth Limited, Mumbai, India). Intermittent stirring of the glass melt was done with a silica glass rod at regular intervals for homogenization. The melt was cast on to an iron mould. The casted block was re-melted twice following the same procedure to ensure good homogeneity of glass. The final casted block was annealed at 520°C for 3 h followed by slow cooling to room temperature in order to relieve internal stresses in the glass. The as-prepared glass was cut, polished with CeO_2 powders

and shaped into dimensions of $(12 \times 12 \times 2) \text{mm}^3$. The polished glass samples were subjected to single-stage heat-treatment for crystal growth at 660°C for varying durations of 1, 3, 6, 18 and 30 h. Heating and cooling rates of $1^\circ\text{C}/\text{min}$ was kept constant throughout the ceramization process. The coefficient of thermal expansion (α), glass transition temperature (T_g), and dilatometric softening temperature (T_d) of the precursor glass sample were evaluated using a horizontal push-rod dilatometer (Model DIL 402 PC; NETZSCH- Gerätebau GmbH, Selb, Germany). Non-isothermal Differential scanning calorimetry (DSC) analysis has been performed on 20–30 mg precursor bulk glass samples in platinum crucibles from room temperature to 1200°C using a NETZSCH instrument (Model STA 449 F3; NETZSCH- Gerätebau GmbH, Selb, Germany), using different heating rates of 10, 20, 30 and 40 K/min. The thermal property data obtained from DSC analysis have been used for crystallization kinetics study using Netzsch Thermokinetics 3.1 software (version – 072010). Archimedes principle was applied to measure the densities of the precursor glass and the glass-ceramics, using water as the buoyancy liquid. Structural analysis of the CBTE glass-ceramics was done using a X-ray diffractometer, XPERT-PRO MPD diffractometer (PANalytical, Almelo, the Netherlands) with CuK_α radiation of 1.5406 \AA at 25°C , having a source power of 40 kV and 30 mA to identify the developed crystalline phases. The 2θ scan was carried out in the range of 10° – 80° with a step size of 0.02° . Raman spectra of the base glass and heat-treated glass-ceramic samples were recorded using a Raman spectrometer (HORIBA Jobin Yvon, France; Model: Lab Ram HR 800 EV) in the wave number range of 50 – 1100 cm^{-1} using an excitation source of 785 nm diode laser. TEM analysis was carried out on very finely powdered GC samples dispersed in acetone solvent on a carbon-copper grid. Bright field TEM images and SAED pattern of the nanocrystalline glass-ceramics were obtained using a FEI (Model TecnaiG2 30ST; FEI Company, Hillsboro, OR) instrument. Surface morphologies of the heat-treated glass-ceramics were examined with a high-resolution FE-SEM (Gemini Zeiss Suprat 35 VP model of Carl Zeiss Microimaging GmbH, Berlin, Germany) after etching the samples in 2 vol% aqueous solution of HF for 15–20 min. The optical absorption and transmission spectra were recorded using a Perkin-Elmer UV–Vis–NIR spectrophotometer (Model Lambda 950; Perkin-Elmer Corporation, Waltham, MA) in the wavelength range of 400–800 nm. The fluorescence emission and excitation spectra were recorded using a bench-top modular spectrofluorometer (Quanta Master; Photon Technology International, Birmingham, NJ) attached with a Xe arc lamp as the excitation source. The refractive indices of the base glass and heat-treated glass-ceramics were measured using laser sources by a Prism Coupler (Model 2010/M; Metricon Corporation, New Jersey) at four different wavelengths of 532, 632.8, 1064 and 1552 nm respectively. The dielectric constant, dielectric loss and dissipation factors of the base glass and GCs were measured at room temperature at selected frequencies from 500 Hz to 10 kHz, using a Hioki LCR meter (Model 3532-50 Hitester, Hioki, Ueda, Nagano, Japan), after coating both sides of the samples with conducting silver paint followed by drying. The hardness of the base glass and glass-ceramic samples was measured using micro-indentation hardness testing systems (Clemex CMT, Longueuil, Canada) equipped with a conical Vicker's indenter at an indent load of 100 g. The average length of the diagonals of Vicker's indents was measured under an optical microscope after taking 10 indents for each sample for 11 s. The hardness was calculated using the standard equation for the Vickers geometry as follows:

$$HV = 1.8544 \frac{P}{d^2} \quad (1)$$

where HV is the Vicker's hardness number, P is the load in kg and d is the average length of the diagonals of indentations in mm.

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