Structural and dielectric characteristics of 0.50 Bi_2O_3 - 0.25 V_2O_5 - 0.25 SrB_4O_7 glass-ceramic.

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Abstract - Novel 0.50 Bi_2O_3-0.25 V_2O_5-0.25 SrB_4O_7 glasses have been prepared via conventional splat-quenching technique. Differential thermal analysis (DTA) carried out on the as-quenched samples confirms their glassy nature and shows a prominent exothermic peak at 400°C. The X-ray powder diffraction (XRD) pattern of the heat treated sample could be indexed to an orthorhombic ferroelectric $Bi_2VO_{5.5}$ phase with the lattice parameters a=5.543, b=5.615 and c=15.321Å. The presence of nano-crystallites of bismuth vanadate, $Bi_2VO_{5.5}$ (BiV) dispersed in the glassy matrix of strontium tetraborate, SrB_4O_7 (SBO) is confirmed in the heat treated (at 400°C for 12h) samples, by high resolution transmission electron microscopy (HRTEM). The dielectric constant (ϵ_r) , measured as a function of temperature, exhibits an anomaly around the transition temperature of the parent crystalline BiV. The ϵ_r of the glass-ceramic at 300K is comparable with that predicted by Maxwell's model and logarithmic mixture rule.

I. INTRODUCTION

Ever since the first report of electro-optic effect in transparent materials containing a ferroelectric perovskite-like crystalline phase within a glass matrix by Borrelli [1], transparent glass-ceramics comprising of ferroelectric crystals have been in great demand for nonlinear optical (NLO) applications . Strontium tetraborate, SrB_4O_7 (SBO) which is a recently reported member of the borate family, offers itself as an ideal glass host matrix by virtue of its easy glass forming tendency, thermal stability and optical transmission characteristics [2]. Bismuth vanadate, $Bi_2VO_{5.5}$ (BiV), which is a n=1 member of the Aurivillius family of oxides, is ferroelectric at room temperature [3] and glass-ceramics comprising of BiV nanocrystallites dispersed in SBO glass matrix possess interesting physical properties [4,5] and are promising materials for NLO applications. In this paper, we report the details regarding the crystallization of ferroelectric BiV phase in Bi_2O_3-V_2O_5-SBO glasses and the subsequent characterization of the transparent glass-ceramics for their structural and dielectric properties.

II. EXPERIMENTAL

Samples for the present study were prepared from Bi_2O_3, V_2O_5 and pre-reacted SrB_4O_7 (SBO) according to the stoichiometry 0.50 Bi_2O_3 - 0.25 V_2O_5 - 0.25 SBO. Homogeneous mixtures of these compositions taken in molar ratios were melted in a platinum crucible in an electrically heated furnace at $1100°C$ for 1h and then the melt was poured onto a stainless steel plate and pressed to obtain flat plates. The amorphous nature of the as-quenched samples and the crystallinity in the annealed samples were confirmed by X-ray powder diffraction (XRD) studies using CuK_α radiation. Electron diffraction and microscopic studies were carried out using a high resolution JEOL 200CX microscope. Differential thermal analysis (DTA) measurements were carried out at a heating rate of $10°C$/min for a chip of the sample weighing $\approx$ 20mg. The volume fraction of the crystallized phase was estimated based on the density of the samples determined by the Archimedean method. The dielectric measurements were performed, using Keithley 3330 LCZ meter, in the frequency range 100Hz-100kHz. For this purpose, gold was sputtered on either side of the annealed glass plates. Subsequently silver epoxy was employed to bond the leads to the samples. Among the various compositions in the 2x Bi_2O_3 - x V_2O_5 - (1-3x) SBO ternary system, that form stable glasses and yield the ferroelectric BiV phase on crystallization, we have chosen the representative composition x=0.25 for the present investigation. The glasses of the composition 0.50 Bi_2O_3 - 0.25 V_2O_5 - 0.25 SBO and the glass-ceramics obtained by the crystallization of these glasses have been characterized for their structural and dielectric properties.

III. RESULTS AND DISCUSSION

The differential thermal analysis (DTA) carried out on the as-quenched samples confirms their glassy nature (Fig.1 a) and the glass transition temperature T_g is estimated to be $\approx 530°C$. Two prominent exothermic peaks, one at $400°C$ and another at $715°C$ were observed. The exothermic peak at $400°C$ is absent in the DTA trace of the sample preheated at $400°C$ for 12h (Fig. 1b).

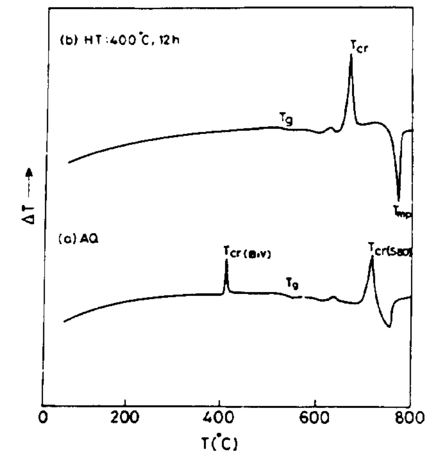

Fig. 1. The DTA for the (a) as-quenched and (b) heat treated (400°C for 12h) samples.

The X-ray powder diffraction (XRD) patterns recorded at room temperature for the as-quenched sample (Fig. 2 a) confirm its amorphous nature. The broad peak observed at $2\theta \approx 28°$ is attributable to the centpercent peak of BiV (4). The prominent peaks in the XRD pattern (Fig. 2 b) recorded for the sample obtained by crushing the glass heated at $400°C$ for 12h, could be indexed to the crystalline BiV phase with lattice parameters a = 5.543, b = 5.615 and c = 15.321 $\mathring{A}$ (4). The XRD pattern recorded for the sample heated at $725°C$ for 12h indicates the coexistence of both the SBO and BiV crystalline phases. These studies confirm that the second exothermic peak observed at $715°C$ in the DTA to be the crystallization temperature of the SBO phase. Indeed the sample loses its transparency completely at this stage.

The high resolution transmission electron micrographs of the as-quenched sample show the presence of spherical particles of BiV finely dispersed in the SBO matrix and both the matrix and the dispersed phases are amorphous. A high resolution image of the heat treated sample (Fig. 3) shows the presence of BiV crystallites in the SBO glass matrix. The corresponding electron diffraction pattern is shown as inset.

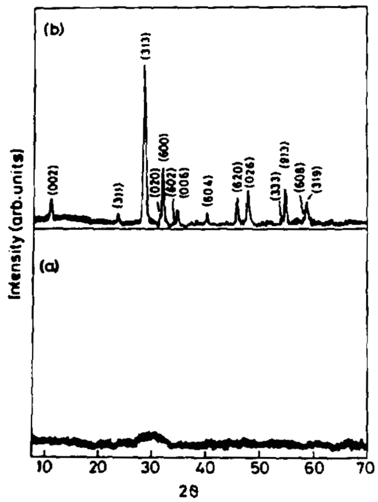

Fig. 2. The XRD patterns for the (a) as-quenched and (b) heat treated samples.

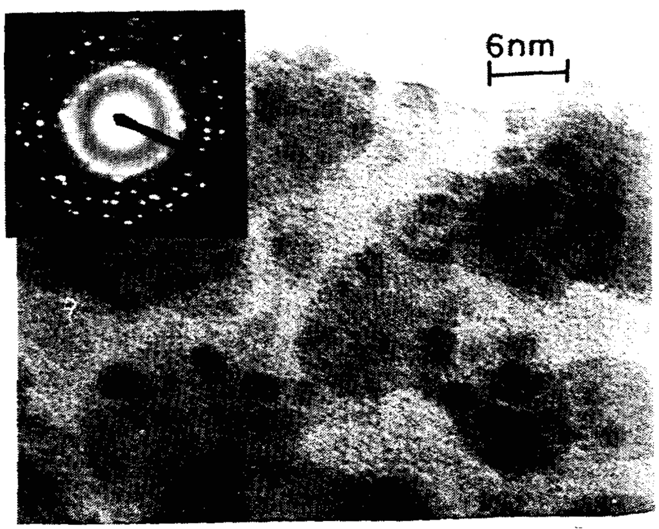

Fig. 3. Transmission electron micrograph and the corresponding electron diffraction pattern of the sample heat treated at 400°C for 12h.

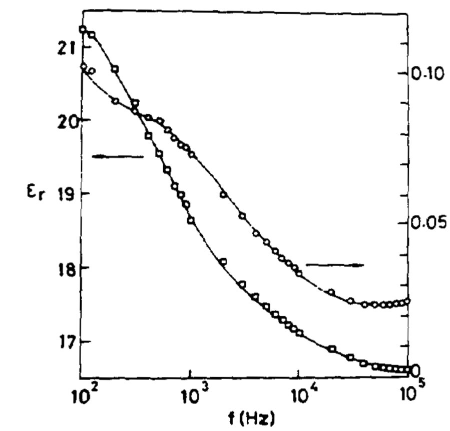

Fig. 4. The variation of ϵ_r and tanδ with frequency for the heat treated sample.

The variation of ϵ_r and tanδ with frequency, in the range 100Hz-100kHz, for the heat treated sample is shown in Fig. 4. The temperature dependence of ϵ_r, measured at three frequencies: 100kHz, 10kHz and 1kHz (Fig. 5) indicate the existence of a pronounced dielectric anomaly at 475°C which is 25°C higher than the phase transition temperature of the parent crystalline BiV. The dielectric loss (tan δ) also exhibits an anomaly around the same temperature. This implies that the crystalline BiV phase exhibits a phase-transition even when it is embedded in the glass matrix. Since the temperature at which the dielectric anomaly is observed is well below the glass-transition temperature (T_g), the possibility of interfacial polarization contributing to the observed dielectric anomaly is remote. The magnitude of the anomaly, which is smaller than that of BiV single crystal, may be attributed to the presence of intercrystalline layers with lower dielectric constant.

The dielectric constant could be predicted based on Maxwell's model, in which spherical particles of higher dielectric constant (ϵ_{rd}=90 at 100 kHz) are dispersed in a matrix of lower dielectric constant (ϵ_{rm}= 10 at 100 kHz):

$$\epsilon_r = \frac{V_m\epsilon_{rm}(2/3 + \epsilon_{rd}/3\epsilon_{rm}) + V_d\epsilon_{rd}}{V_m(2/3 + \epsilon_{rd}/3\epsilon_{rm}) + V_d} \quad (1)$$

where ϵ_r is the dielectric constant of the sample, V_m (=0.75) and V_d (=0.25) are the volume fractions of the matrix (SBO) and the dispersed phase (BiV), respectively [4]. The value of ϵ_r obtained using the above equation is 16.66 which is very close to the experimentally measured value of 16.5 at 100 kHz. The value obtained by fitting the present data into the logarithmic mixture rule ($log\epsilon_r = \sum_i V_i \, log\epsilon_{ri}$) is 17.3.

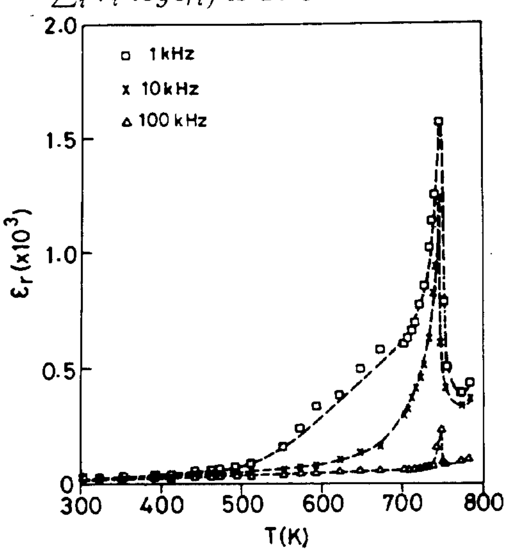

Fig. 5. The variation of ϵ_r with temperature for the heat treated sample.

IV. CONCLUSIONS

Transparent glasses of the composition 0.50 Bi_2O_3 - 0.25 V_2O_5 - 0.25 SBO have been prepared and BiV has been crystallized in these glasses by heat treatment. The temperature dependence of ϵ_r of these transparent glass-ceramics indicates the existence of a prominent dielectric anomaly at 475°C, which is 25°C higher than the phase-transition temperature of the crystalline BiV. Studies are in progress, to characterize these samples for their ferroelectric and electro-optic properties to assess their suitability for device applications.

V. REFERENCES

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