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Study of Structural and Mechanical Properties of the Transparent Bismuth Borate Glass Ceramic

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ABSTRACT

Structural and mechanical properties of the photocatalytic transparent $2Bi_2O_3$-B_2O_3glasses were studied.X-ray diffraction substantiated the presence of photocatalytic $Bi_4B_2O_9$ crystalsembedded in the glass matrix of bismuth borate glass ceramics heat treated for 2 hr, 3 hr, 4 hr, 5 hr and 6 hr at 400°C. The size of $Bi_4B_2O_9$ crystals decresed with the increase in the time of heat treatment.Fouriertransform infrared spectroscopy revealed the bending vibration of B-O-B bonds in (BO_3)triangle,vibration of Bi-O-Bi in (BiO_6) octahedron,stretching vibration of (BO_4) tetrahedron,stretching vibrations in BiO_6 units and stretching vibration of (BO_4) tetrahedron. Microhardnessof the heat treated glass demonstrated the increasing trend with the increase in the time of heat treatment.

keywords-BBO,glass ceramic, optical transparent, photocatalytic glass ceramic, transparent glass.

1. INTRODUCTION

Now a day,promoting clean energy initiatives and urge for eco-friendly innovative materials for their use in the present day worldhavebrought the researchers from all around the world on the common ground to develop eco-friendly innovativematerials which is simple to fabricate with sufficient mechanical and chemical properties and economically viable. These materials are now the need of the hour. The glass ceramics are one of them.

Various authors exhibited that a number of photocatalyst have been developed either in the powder form or thin film or the photocatalytic crystals embed in the matrix[1-3].These photocatalyst came into existence as efficient and economically viable in the clean energy and environment applications. Since the finding of TiO_2as photocatalyst it has been extensively used as photocatalyst[4-8].

Huang et al. revealed that $Bi_2O_2CO_3$tuned with carbonate ion possessessatisfactory photocatalytic properties[9]. Huang et al. also exhibited that $Bi_4B_2O_9$ crystals showedsatisfactory photocatalytic properties and $Bi_4B_2O_9$was formed using the solid state reaction. He also observed degradation of methylene blue under simulated solar irradiation [10].

Sharma et al. found that $Bi_4B_2O_9$ crystals embedded in the glass matrix prepared by the melt quenching technique showedsatisfactory photocatalytic activity along with the photo induced hydrophilicity thereby making the transparent glass ceramics use in the selfcleaning application[11].

Authors have exhibited that glass ceramics have been used as a photocatalyst to treat waste water.[12-13].

Authors have alsoidentified glass and glass–ceramics as key elements to most of the great engineering advancements of the 20th century, following the development of solid state lasers and optical glass fibers, biomaterials, glasses for imaging technologies, glass films in microelectronic devices [14].Glass and glass ceramics being a structural material have found to be having inherent advantages such as low cost, easy to fabricate, transparency, mechanical and chemical stability. Glass-ceramics contain crystallites in the amorphous matrix and possess some additional properties.

Glass-ceramics were discovered in 1953. Since then, a lot of research papers have been published on glass-ceramics by research institutes, and varsities.

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Glass-ceramics are mostly produced in two steps:In First step, a glass is formed by a glass-manufacturing process. The glass is cooled down and is then reheated in a second step. In this heat treatment the glass partly crystallizes.Glass-ceramics are produced by controlled crystallization of glasses with addition of nucleating additives, in most cases nucleation agents (e.g., noble metals, fluorides, ZrO_2, TiO_2, P_2O_5,Cr_2O_3 or Fe_2O_3) are added to the base composition of the glass-ceramicin contrast to a spontaneous crystallization, which is not wanted in glass manufacturing.These nucleation agent aids and control the crystallization process. They always contain a residual glassy phase and one or more embedded crystalline phases. Controlled crystallization gives an ordered series or arrangement of crystals in the materials with interesting combinations of properties.Glass-ceramics are vested with the fabrication advantage of glass, as well as special properties of ceramics.

Therefore, towards the study of photocatalytic transparent bismuth borate based glass ceramics, we have selected the composition of $2Bi_2O_3$-B_2O_3(BBO) having borate oxide which is one of the good glass formers. In the present work, $2Bi_2O_3$-B_2O_3 (BBO) transparent glass ceramics have been fabricated to have photocatalytic $Bi_4B_2O_9$ crystals and their inherent and mechanical properties have been studied.

2. Experimental

$2Bi_2O_3$-B_2O_3 (BBO) glasses were fabricated using the conventional melt-quenching method. For glass preparation, Bi_2O_3 and B_2O_3 were weighed and ball milled for 1 hour at 1000 rpm. Table.1 depicts the chemical composition of $Bi_2O_3$and B_2O_3 in gm.

Table 1. Chemical composition of glass sample

material	Chemical Composition in gm
Bi_2O_3	9.3063
B_2O_3	0.6937

After homogeneous mixing, a batch of 10 g was used for melting in alumina crucible in the furnace at 1000℃ for 1 hour. After melting, the melt was poured onto a stainless steel plate preheated up to 250℃ and was flattened with another steel plate maintained at the same temperature. The details of processing parameters are shown in Table 2.

Table 2. List of processing parameters for preparation of glass sample

Ball milling time	1 h
Ball milling speed	100 rpm
temperature in furnace	1000°C
Holding temperature in furnace	1 h
Preheat temperature of lower plates	250°C
Preheat temperature of upper plates	250°C
Type of crucible	25 ml alumina

Stainless steel 304 grade plates of dimension 150×70×8 mm each have been used for the base and upper part of the setup. Each plate has been subject to grinding, buffing and polishing process so that the surface of the glass formed would be of high finish.

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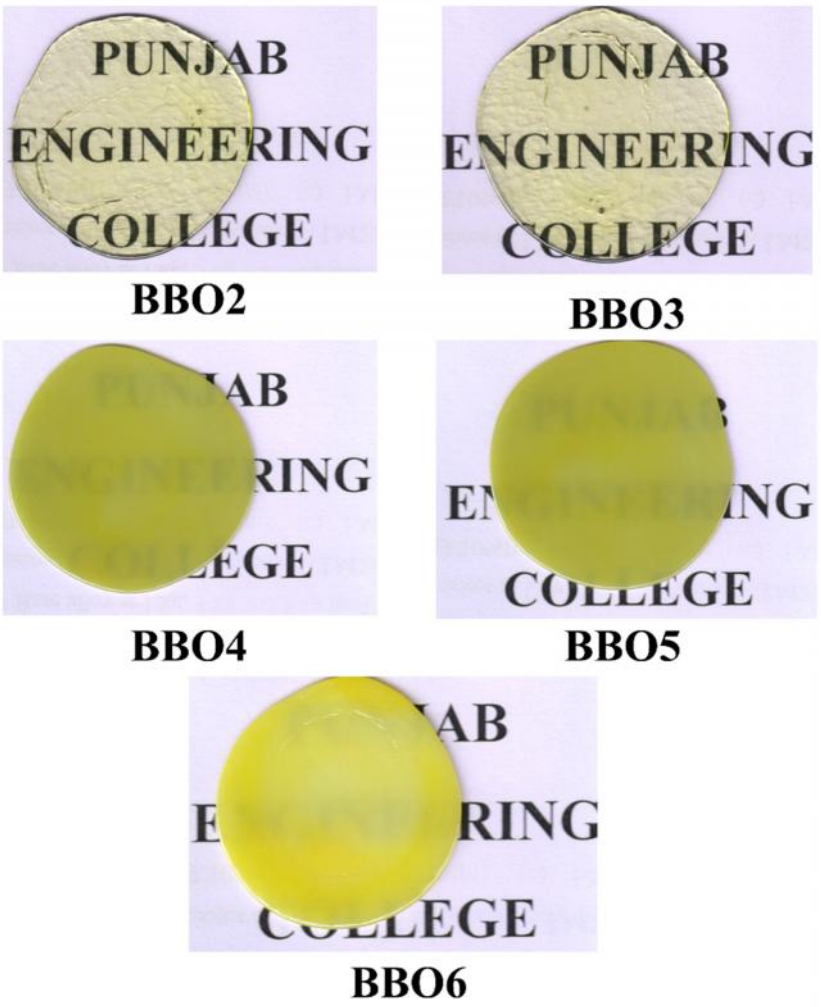

Fig.1 Optical images of the BBO glass ceramic (a) BBO2, (b) BBO3, (c) BBO4, (d) BBO5, (e) BBO6.

3. CHARACTERIZATION AND TESTING DETAILS

The heat treated samples were Characterised by X-ray diffractionPANalytical (Cu Kα1 radiationλ =1.54 A˚,40 mA, 45 kV) at a scanning rate of 2° per min, Step Size 2θ equal to 0.0170 with 2θ ranging from 10.008°to 89.9934°. Crystallization was controlled by heat treating (HT) the samples at 380℃ for 2 hr, 3 hr, 4 hr, 5 hr and 6 hr which have been referred in the manuscript as BBO2, BBO3, BBO4, BBO5, BBO6 respectively as shown in the fig.1. FTIRPerkinElmer was used to perform Fourier transform infrared spectroscopy of the samples under study. Microhardness values were measured using Vickers hardness testing machine. Microhardness was performed at room temperature using the square-based pyramid diamond indenter.

4. RESULTS AND DISCUSSION

4.1 Crystal size of the photocatalytic $Bi_4B_2O_9$ crystals

Fig.2 shows the XRD patterns of crystallized samples where sharp peaks mark the presence of micro/nano crystallitesand all peaks in the heat-treated samples have been matched with the $Bi_4B_2O_9$ crystals (JCPDS cardNo.01070-1458).

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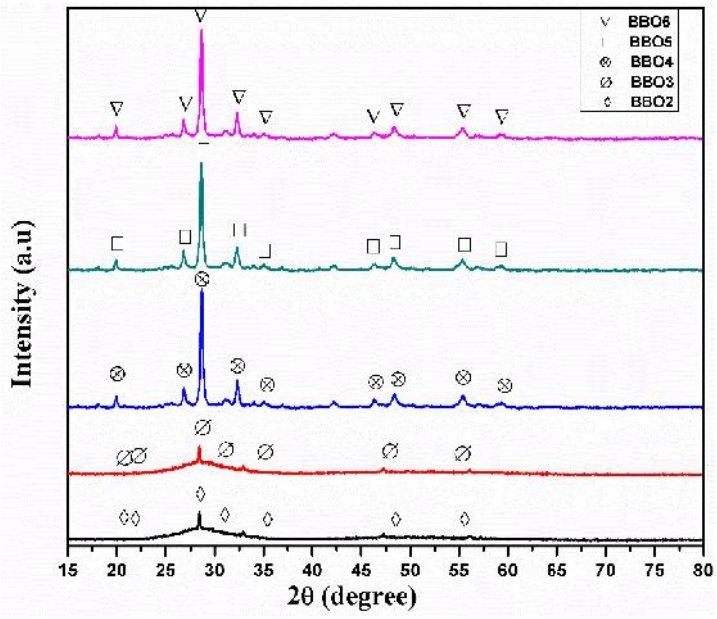

Fig.2 XRD patterns of the heat treated glass sample.

$Bi_4B_2O_9$ crystals size is calculated by the Scherrer equation. It is a formula that relates the size of crystallites, in a solid to the broadening of a peak in a diffraction pattern. It is used in the determination of size of particles of crystals in the form of powder.

The Scherrer equation can be written as:

$$D = \frac{k\lambda}{\beta C\theta} \quad (1)$$

Where, θ is the Bragg angle.K is the constant of proportionality, K (the Scherrer constant) depends on the how the width is determined, the shape of the crystal, and the size distribution.

K actually varies from 0.62 to 2.08 is a dimensionless shape factor, with a value close to unity. The shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite. λ is the X-ray wavelength. Full Width at Half Maximum (FWHM)β–the width of the diffraction peak, in radians, at a height half-waybetween background and the peak maximum β is the line broadening at half the maximum intensity (FWHM). D is the mean size of the crystallite domain.

Calculation of the mean crystallite domain for BBO2 by taking observed bragg angle and the FWHM values at the corresponding bragg angles and thereby the size of the crystal domain is calculated by the scherrer formula as shown in (1). The observed angle varied from 20.849° to 55.686°. The size of the crystal domain varied from 68.1796 nm to 146.7470 nm and the average size of the crystal have been found out to be 100.0613875 nm for BBO2 glass ceramic.

Similarly, Calculation of the mean crystallite domain for BBO3 by taking observed bragg angle and the FWHM values at the corresponding bragg angles. The observed angle varied from 20.849° to 55.686°. The size of the crystal domain varied from 60.2273 nm to 146.7470 nm and the average size of the crystal have been found out to be 98.6968 nm for BBO3 glass ceramic.

For BBO4, the observed angle varied from 19.914° to 59.402°. The size of the crystal domain varied from 11.20382 nm to 40.1787 nm and the average size of the crystal have been found out to be 26.4431 nm for BBO4 glass ceramic. For BBO5, the observed angle varied from 19.888° to 59.341°. The size of the crystal domain varied from 9.33369 nm to 33.4800 nm and the average size of the crystal have been found out to be 22.533063 nm for BBO5 glass ceramic.

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For BBO6, the observed angle varied from 28.661° to 59.322°. The size of the crystal domain varied from 12.62671 nm to 36.52514 nm and the average size of the crystal have been found out to be 21.5514 nm for BBO6 glass ceramic.

Fig .3 shows the decreasing trend in average crystal size with the increase in the time of heat treatment. More the time of heat treatment more is the rate of nucleation. It can be attributed from the results that nucleation rate increased at a very fast rate after 3 hr. However, the difference in rate of nucleation for 4 hr, 5 hr and 6 hr was approximately the same.Hence it is evident from the X ray diffraction results of the bismuth borate glass ceramic that there is presence of micro to nano photocatalytic $Bi_4B_2O_9$ crystals embedded in the BBO glass host matrix.

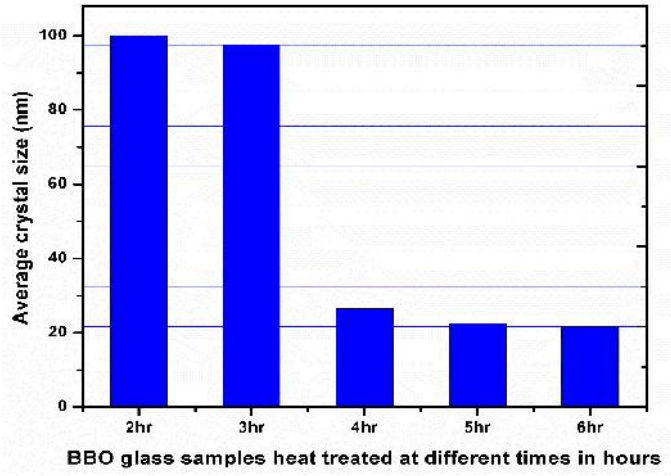

Fig. 3 Variation of average crystal size with time

4.2 FTIR spectra of the heat treated glass samples

Figure 4 shows atomic vibrational modes examined by FTIR spectroscopy. Usually, the atomic vibrations in all bismuth borate glasses show almost similar pattern. Cheng et al. performed the structural investigations of Bi_2O_3-B_2O_3 glasses using infrared spectroscopy[15].Stone et al.have found asymmetricB-O bonds for the BO_3 and BO_4 coordination in the Bi_2O_3-B_2O_3glass system [16]. Hyman et al. examined the crystal structure using X-ray diffraction and showed that BO_3^{3-} anions are arranged in discrete planes and held in coordination with bismuth atoms[17]. In the case of Bi_2O_3-B_2O_3 glass sample sharp peaks in band (420–576) cm^{-1} correspond to the vibration of Bi-O-Bi in BiO6 octahedron [18-19].A sharp band at (590–725)$cm^{-1}$is due to B–O–B bending vibrations in BO3 triangular units [20]. The sharp band at (750–1000)$cm^{-1}$with a shoulder represents the symmetric bonds stretching of B–O in (BO4) tetrahedral units.[18,20]. The shoulder belonging to another broad band at 1031–1326$cm^{-1}$is due to symmetric stretching of B–O-B in BO3 triangles under BO4 coordination [18,21]. Similarly, bands at 1350–1600 cm^{-1}belong to asymmetric stretching relaxation of the B–O bonds in tetrahedral BO4 coordination. FTIR results shows the well coordination of B-O-B linkages.Table 3shows the FTIR bands assigned for heated glass samples.

Table 3. Assignment of FTIR bands spectra analyzedin heat treated glass samples

Wavenumber (cm^{-1})	FTIR assignment
420–576	Vibration of Bi-O-Bi in [BiO6] octahedron
590–725	Stretching vibrations of Bi-O in BiO6 units, bending vibration of B-O-B in [BO3]triangle
750–1000	Stretching vibration of [BO4] tetrahedron
1031–1326,1350–1600	Stretching vibration of B-O-B in [BO3] triangles

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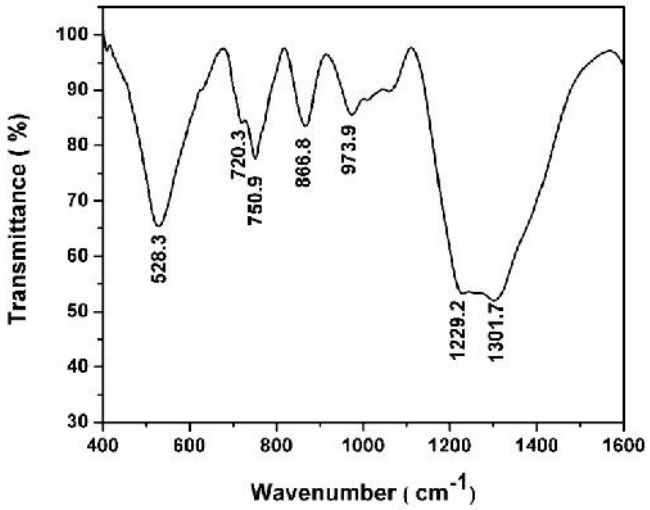

Fig.4 FTIR bands spectra observed in heat treated glass samples.

4.3 Microhardness studies

Microhardness was performed at room temperature using the square-based pyramid diamond indenter. For the better estimation of the surface hardness, each sample was subjected to indents at different positions by varying the load from 10gf to 100 gffor each indent so that indenter shape should be capable of producing geometrically similar pattern andhave well-defined points of measurement. At 100 gf geometrical impressions were fine and measuring points were clearly visible. The loading force of 100 gf, loading rate and dwell time were kept constant for all the samples understudy.Table 4 summarizes the hardness values obtained for BBO glass sample heat treated for 2 hr, 3 hr, 4 hr, 5 hr and 6 hr at 400°C. Fig 5 shows the variation of hardness value at different times.

Table 4. Hardness value of BBO glass sample at different times

Heat treatment time	Hardness (HV)				
	BBO2	BBO3	BBO4	BBO5	BBO6
2h	70	-	-	-	-
3h	-	89	-	-	-
4h	-	-	238	-	-
5h	-	-	-	277	-
6h	-	-	-	-	290

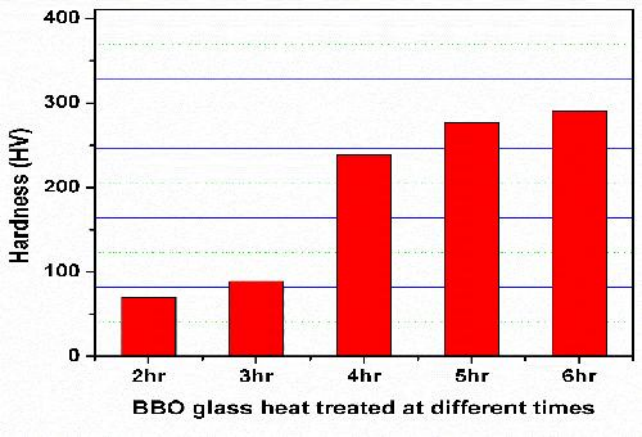

Fig.5Variation of the hardness of BBO glass sample at different time

5. CONCLUSIONS

The study of the effect of crystallization time on the structural and mechanical properties of the bismuth borate glass ceramic have shown the following results which are as follows:

1. Heat treatment of $2Bi_2O_3$-B_2O_3glass ceramic at increasing order of time has resulted approximately 21-26 nm **photocatalytic** $Bi_4B_2O_9$ crystals in the $2Bi_2O_3$-B_2O_3 glass matrix.
2. Fourier transform infrared spectroscopy resulted well coordination of B-O-B linkages in BO_3 and BO_4 units.
3. Microhardness of the $2Bi_2O_3$-B_2O_3 glass ceramic have found to be increased with the increase in the heat treatment time.

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