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Structural investigation of iron doped bismuth borate glasses and effect of heat treatment on FTIR Spectra

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Abstract

Glasses of composition $\text{Fe}_2\text{O}_3 \cdot \text{Li}_2\text{O} \cdot \text{B}_2\text{O}_5 \cdot \text{Bi}_2\text{O}_3$ in the system doped with cobalt ion were prepared by quenching technique [1]. Heat-treatment of the parent glasses was performed at 400 C for 4 and 6 h. The glass structure evolution was examined by FT-IR spectroscopy analysis. The FT-IR data propose for these glasses and heat-treated glass network structures mainly built by: di-, tri-, tetra-, penta- and ortho-borate groups.

Keywords: Structural investigation, iron doped bismuth FTIR Spectra

Introduction

A glass can thus be defined as "an amorphous solid completely lacking in long range, periodic atomic structure, and exhibiting a region of glass transformation behavior." Any material inorganic, organic or metallic, formed by any technique and exhibits glass transformation behavior is glass [2]. Glass-ceramics are polycrystalline materials produced through controlled crystallization of base glass. Glass-ceramic materials share many properties with both glasses and ceramics. Glass-ceramics have an amorphous phase and one or more crystalline phases and are produced by a so-called "controlled crystallization" in contrast to a spontaneous crystallization.

The borate glasses are the category of glasses in which the major constituent is the B_2O_3 up to 70-80%. Bismuth borate glass is of great interest optoelectronic devices due to its low melting temperature (600-800 °C), extensive glass formation range, high refractive index ranging from 1.9 to 2.3, high physical and chemical stability, and nonlinear optical property. Borate glasses containing a large amount of Bi_2O_3 possess a high refractive index & large polarizability, high optical basicity, small metallization and large optical susceptibility [3]. Borate glasses are suitable optical materials because of high transparency, low melting point, high thermal stability & good solubility. For their easier working and lower thermal expansion, borate glasses are widely used in electronics industry such as scaling and solder glasses [4].

Experimental work

Glass samples have been prepared using melt quench technique. Two or more than two materials are first mixed, then melted and finally allow to rapid cooling with the help of stainless steel plates, because stainless steel plates are good absorber of heat. It will give rise to an amorphous material [1].

Sample Composition



Where $x = 0, 5, 10, 15$

Sample with 0% Co is CFLBB1, 5% Co as CFLBB2, 10% Co as CFLBB3, 15% Co as CFLBB4 and 20 % Co as CFLBB5.

FTIR Analysis

The prepared samples were characterized by IR spectroscopy as follows:

- (i) As prepared samples
- (ii) On annealing at 400 °C for 4 hours
- (iii) On annealing at 400 °C for 6 hours.

The FTIR spectra of as prepared samples are shown. The vibrational modes of bismuth borate glasses are determined by the vibrations of bismuth–oxygen and boron–oxygen structural units ^[5]. A broad envelop in the metal–oxygen stretching region in the IR spectrum of a powdered material is attributed to the highly polar bonds and a large longitudinal mode separation ^[6].

De-Convolution

The analysis of samples has been done through De-Convolution. This helps in correct determination of band

position and peaks. Fitting of the actual curve is done in such a way that it minimizes the square of difference i.e. Cod (R^2) between the curves. The fitting is continued as long as the Cod (R^2) is of the order of ~ 0.999 . It is done for all the samples. Figure shows the De-Convolution for one of the samples CFLBB2. Table shows the various parameters obtained through it.

Table 1: Parameters obtained by De-Convolution for CFLBB2

Area	Center	Width	Height
0.6364	718.5	68.372	0.0074
1.4806	901.4	115.344	0.0102
1.9891	1030.3	116.838	0.0135
3.2539	1191.2	137.153	0.0189
6.3482	1345.4	198.237	0.0255
0.0008	1431.8	0.0082	0.0858

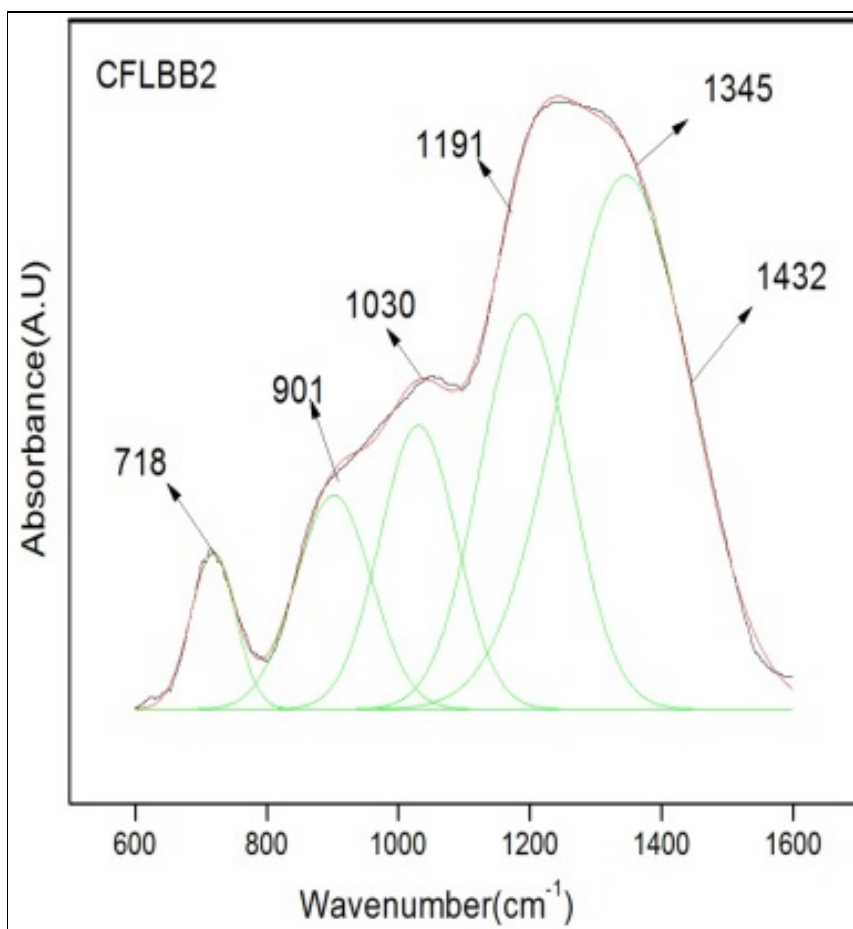


Fig 1: Convolution of the sample CFLBB2

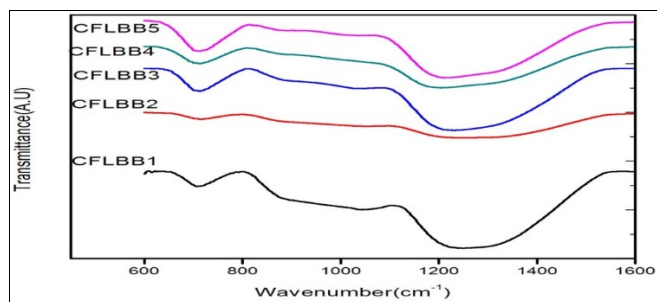


Fig 2: FTIR spectra of as prepared samples

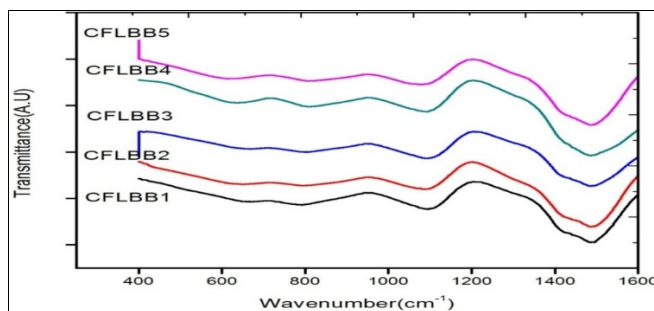


Fig 3: FTIR spectra of the samples annealed at 400 °C for 4 hours

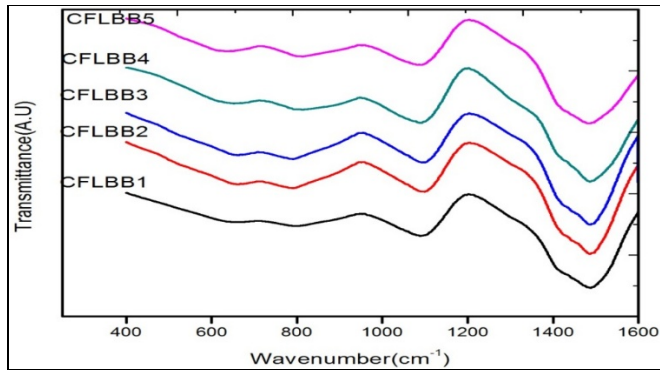


Fig 4: FTIR spectra of the samples annealed at 400 °C for 6 hours

Effect of annealing

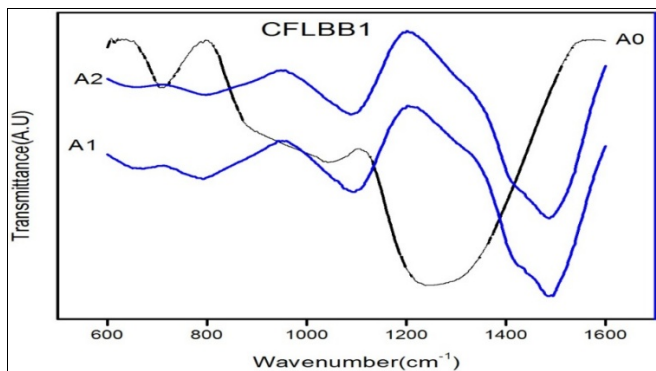


Fig 5: FTIR spectra of CFLBB1 for as-prepared (A0), annealed at 400 °C for 4h (A1) and for 6h (A2)

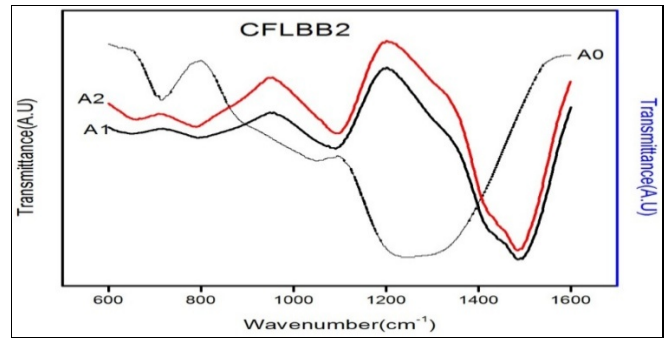


Fig 6: FTIR spectra of CFLBB2 for as-prepared (A0), annealed at 400 °C for 4h (A1) and for 6h (A2)

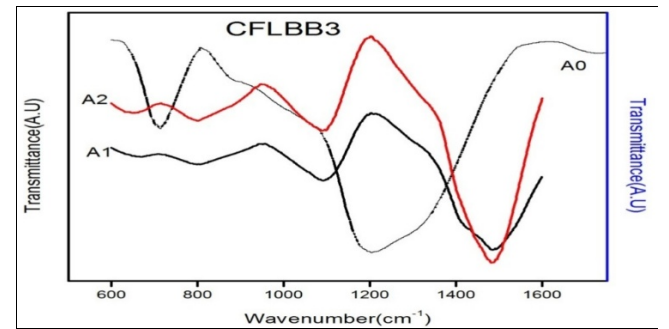


Fig 7: FTIR spectra of CFLBB3 for as-prepared (A0), annealed at 400 °C for 4h (A1) and for 6h (A2)

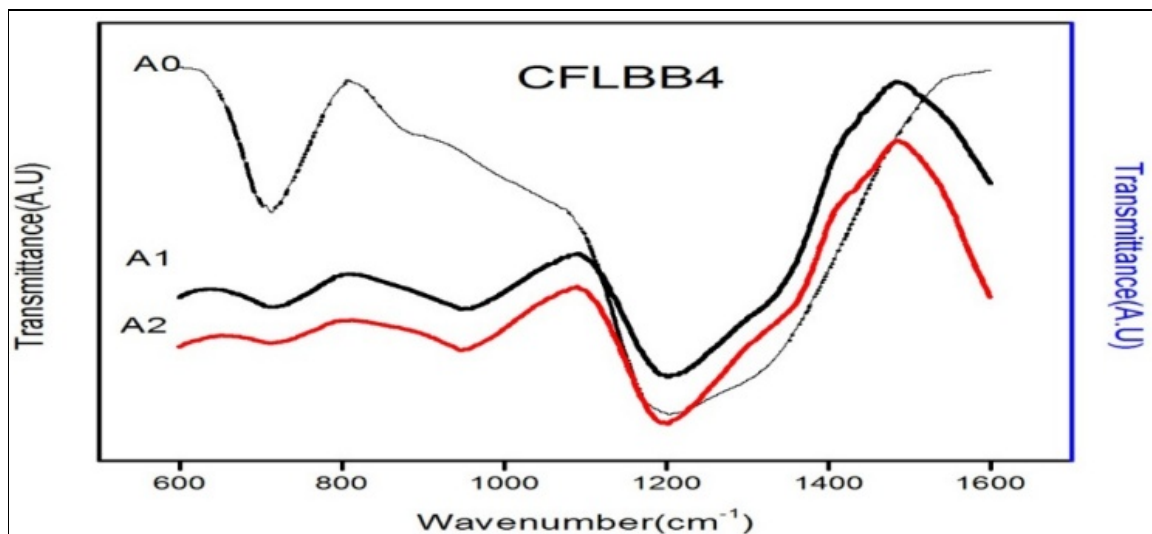


Fig 8: FTIR spectra of CFLBB4 for as-prepared (A0), annealed at 400 °C for 4h (A1) and for 6h (A2)

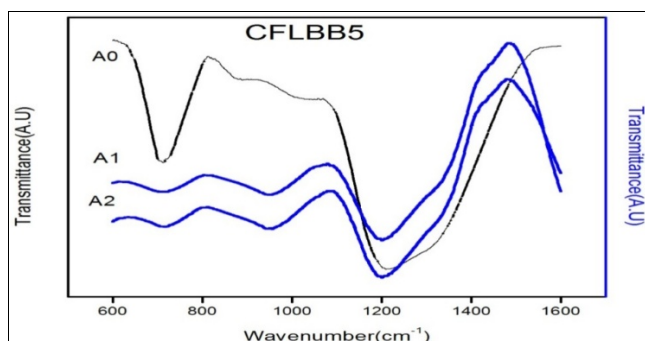


Fig 9: FTIR spectra of CFLBB5 for as-prepared (A0), annealed at 400 °C for 4h (A1) and for 6h (A2)

Discussion

FTIR analysis showed that the peak position at $\sim 700\text{ cm}^{-1}$ corresponds to B-O-B bending and broad peak at $800\text{--}1200\text{ cm}^{-1}$ result due to combined contribution of stretching vibrations of B-O bonds in BO_3 units from pyro-orthoborate groups and stretching vibration of B-O bonds in tetrahedral BO_4 units in tri-borate, tetra-borate and penta-borate groups. Another band around $1200\text{--}1600\text{ cm}^{-1}$ attributes to vibrations attached to large segments of borate network.

- In our present study glass sample shows absorption peak $\sim 900\text{ cm}^{-1}$ are attributed to vibrations of BO_4 tetrahedra in diborate group. The BO_4 tetrahedra vibration in diborate group give rise to absorption in the $900\text{--}1000$

- cm⁻¹ region [7]. The broad band observed in sample in 900-1000 cm⁻¹ region could be due to vibrations of BO₄ tetrahedra in diborate group.
- Stretching vibrations of trigonal BO₃³⁻ units in metaborate, pyroborate and orthoborates. IR band at 1300 cm⁻¹ and above was assigned to B-O stretching vibrations of trigonal BO₃³⁻ units in metaborate, pyroborate and orthoborates [8].
 - The glass samples shows absorption band at 1222 cm⁻¹, 1277 cm⁻¹, can be assigned to B-O stretching vibration involving mainly boroxol and tetra borate groups. Kamitsos *et al.* assigned a band at 1250 cm⁻¹ to B-O stretching vibrations involving mainly boroxol and tetra borate groups [9].
 - The glass samples shows peak at ~610 cm⁻¹ can be attributed to Cationic vibrations in the network or to various modes of Bi-O vibration in BiO₆ [10].
 - The FTIR absorption of samples shows peaks at 1301 cm⁻¹. and others are attributed to asymmetric stretching vibrations of B-O bonds in BO₃ and B₂O⁻ units. The FTIR absorption spectra at ~1295 cm⁻¹ are assigned to asymmetric stretching vibrations of B-O bonds in BO₃ and B₂O⁻ units [11].
 - The Absorption peak at ~555 cm⁻¹ can be assigned to specific bending vibration of Fe-O bonds [10].
 - FTIR shows absorption peak at ~863 cm⁻¹ can be assigned to stretching vibration of BO₄ in diborate group [12].
 - FTIR shows absorption peak at ~709 cm⁻¹ can be assigned to B-O-B bending vibrations [13].
 - The absence of peak at 806 cm⁻¹ indicate absence of boroxol rings. This suggest that system consist of randomly connected BO₃ and BO₄ groups [14].

The position of the band at 1200-1600 cm⁻¹ is shifting towards the higher wavenumber at higher content of iron oxide in samples from CFLBB5 to CFLBB1. Intensity of the bands decreases with increase in iron content. The presence of iron oxide modifies the structural network by providing more oxygen, which results in conversion of [BO₃] to [BO₄] units [14]. As a result, introduction of iron increases the cross linking of the glass matrix due to the increasing the number of tetrahedral [BO₄] groups in the glass system [15].

The as-prepared samples shows IR bands, whereas after annealing IR peaks were appeared in the FTIR spectra of systems under investigation i.e. becomes more crystalline. The vibrations which were dependent on each other became independent after annealing. That is why the band at ~1200-1600 cm⁻¹ gets further split and shows new absorbance peaks which were missing in the untreated samples.

The FTIR study shows that B₂O₃ play the network former role and the iron ions play role of network modifier in the studied samples. The glass network consists of randomly connected BO₃ and BO₄ structural unit.

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