



Studies on Raman Spectra of Cu^{2+} Ion Doped $\text{B}_2\text{O}_3\text{-K}_2\text{O-ZnO-BaO}$ Glasses

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ABSTRACT

Glasses with compositions $59\text{B}_2\text{O}_3\text{-}10\text{K}_2\text{O}\text{-}(30\text{-}x)\text{ZnO}\text{-}x\text{BaO}\text{-}1\text{CuO}$ were prepared using melt quenching technique. The effect of BaO content in present glass system doped with copper ion in place of ZnO has been studied with respect to structural properties. Raman spectroscopy is an experimental technique appropriate for providing information about the structure, local arrangement of the atoms in the present glasses. The Raman spectra of glasses were recorded at room temperature in the range $200\text{-}1800\text{ cm}^{-1}$ using a He-Ne excitation source having wavelength 632.81 nm . The Raman peaks appeared around 760 cm^{-1} assigned symmetric breathing vibrations of six-membered ring with both BO_3 triangle and BO_4 tetrahedral. The intensity of these peaks is slightly varied with the addition of BaO content while the broadness is found to be larger at 30 mol% of BaO than 30 mol% ZnO. This indicates that certain BO_4 units could be preferentially converted while those in ring groups could be stabilized. Raman studies it is concluded that present glasses are composed of $[\text{BO}_4]$ and $[\text{BO}_3]$ units in metaborate, orthoborate, diborate groups.

Indexing terms/Keywords

Borate glasses, Raman spectroscopy.

Academic Discipline And Sub-Disciplines

Physics

SUBJECT CLASSIFICATION

Material Science

TYPE (METHOD/APPROACH)

Experimental work

1. INTRODUCTION

It is known that $\text{B}_2\text{O}_3\text{-ZnO}$ glasses are attractive host materials to various kinds of dopants (TM and rare-earth metal ions) for potential applications in the field of optoelectronics and optical fibers etc. [3]. The properties of B_2O_3 glass can often be altered by the addition of network modifiers. The most commonly used network modifiers are the alkali and alkaline earth oxides [4]. Therefore present study has selected K_2O and BaO as network modifiers. Moreover, the addition of BaO and ZnO to B_2O_3 provides large glass formation domain and form stable glasses. EPR probe due to its EPR spectrum is sensitive enough to detect minute changes in the $59\text{B}_2\text{O}_3\text{-}10\text{K}_2\text{O}\text{-}(30\text{-}x)\text{ZnO}\text{-}x\text{BaO}$ structure around the coordination sphere (CuO_6) was studied by incorporating Cu^{2+} ions [5,6]. There are reports regarding EPR and optical absorption studies of Cu^{2+} ions in tellurite, bismuth and borate based glasses [7-10]. The physical properties, optical absorption EPR and ESR spectra have been well studied [11]. The effect of Cu^{2+} ions on structural changes $59\text{B}_2\text{O}_3\text{-}10\text{K}_2\text{O}\text{-}(30\text{-}x)\text{ZnO}\text{-}x\text{BaO}\text{-}1\text{CuO}$ glasses using Raman spectra was remain as an objective.

In view of the aforesaid reason, it is of interest to study the structural changes induced by the addition of BaO at the expense of ZnO into B_2O_3 glass matrix at 10 mol% K_2O content using Raman techniques.

2. Experimental

The conventional melt quenching technique was used for preparation of present glass system. Glasses with compositional formula $59\text{B}_2\text{O}_3\text{-}10\text{K}_2\text{O}\text{-}(30\text{-}x)\text{ZnO}\text{-}x\text{BaO}\text{-}1\text{CuO}$ (where $x = 0, 6, 12, 18, 24$ and 30 mol%) were prepared. The composition of the prepared samples were prepared by mixing together the appropriate amounts of H_3BO_3 (Loba Chemie, 99.9% purity), Na_2CO_3 (Merck-99.9% purity), K_2CO_3 (Merck-99.9% purity), Li_2CO_3 (Merck-99.9% purity), ZnO (Merck-99.9% purity), CdO (Merck-99.9% purity) and BaCO_3 (Merck-99.9% purity). 1 mole% of copper oxide (CuO) (99.9% purity) was added. The experimental technique was discussed in earlier publication [6,11].

3. Results and Discussion

Raman studies:

Fig. 3.1 shows the Raman spectra of present glass system in the spectral range $200\text{-}1800\text{ cm}^{-1}$ consisting of broad peaks and shoulders. The Raman peak positions are summarized in Table 3.1. The assignments of Raman peaks of the glasses are given in Table 3.2. Raman spectra of borate glasses are very complex as the structure of borate



network consists of more borate structural units. The Raman peak at around $466\text{-}496\text{ cm}^{-1}$ is assigned to pentaborate and diborate groups [12, 13]. The peak appeared at around 620 cm^{-1} is due to ring-type metaborate groups [14]. This band is not seen in BKZB1 glass. This indicates that ring-type metaborate groups are not present in high ZnO content glass (BKZB1). The peak at around $760\text{-}775\text{ cm}^{-1}$ is assigned to symmetric breathing vibrations of six-membered rings with both BO_3 triangles and BO_4 tetrahedra (tri-, tetra- or pentaborate groups) [15,16]. The intensity of these peaks is slightly varied with the addition of BaO content while the broadness is found to be larger at 30 mol% of BaO than 30 mol% ZnO. This indicates that certain BO_4 units could be preferentially converted while those in ring groups could be stabilized. The weak Raman peaks appeared at around 845 cm^{-1} is due to symmetric stretching of the B-O-B bridges in pyroborate groups ($\text{B}_2\text{O}_5^{4-}$) whose intensity almost disappears with the addition of BaO content up to 30 mol%. This may be an indication of pyroborate groups are present with ZnO content and are disappears when BaO content substitutes ZnO from 6 to 30 mol%. In a pure borate glass the Raman peak is always present at 806 cm^{-1} the vibration associated with boroxol rings [17-18] but this peak is absent in the BKZB glass system. Therefore, all the boroxol units could be converted into BO_3 and BO_4 units [20]. The peaks observed in the range $\sim 940\text{-}960$ are ascribed to pentaborate and tetraborate groups [17]. These spectra show a broad band around 1450 cm^{-1} , which is usually assigned to the B-O $\bar{\text{O}}$ bonds attached to the large number of borate groups or $\text{B}\bar{\text{O}}_2\bar{\text{O}}$ triangles linked to $\text{B}\bar{\text{O}}_4$ units, where $\bar{\text{O}}$ stands for an oxygen atom bridging two boron atoms [18,19]. It is clear from spectra that the intensity of the peak at $\sim 1450\text{ cm}^{-1}$ is found to be slightly increased with the increase of BaO content up to 30 mol%. This may be attributed to $\text{B}\bar{\text{O}}_2\bar{\text{O}}$ triangles linked to other borate triangles [20]. As BaO content increases from 0 to 12 mol% causes a shift in the Raman peak at 466 cm^{-1} of BKZB1 toward lower frequencies; from 466 to 460 and then to 453 cm^{-1} . This peak shifts to 457 , 489 and then to 496 cm^{-1} (BKZB6) with further addition of BaO content from 12 to 30 mol%. The observed rise in intensity and shift in the peak $\sim 460\text{ cm}^{-1}$ towards higher wave number indicates the formation of more penta or diborate groups in the glasses.

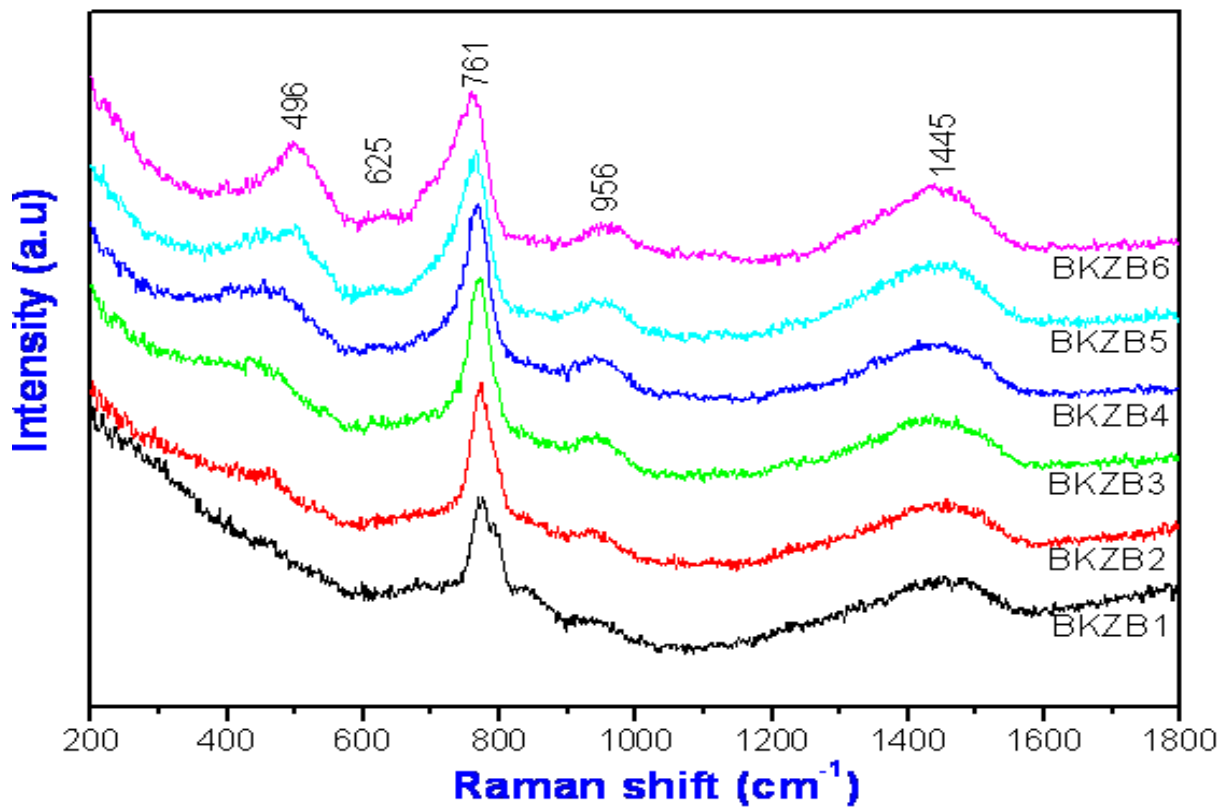


Fig 3.1. Raman spectra of $59\text{B}_2\text{O}_3\text{-}1(\text{K}_2\text{O}\text{-}(30\text{-}x)\text{ZnO}\text{-}x\text{BaO}\text{-}1\text{CuO}$ ($0 = x = 30\text{ mol}\%$) glass system.

The intensity of the peak at $\sim 940\text{ cm}^{-1}$ increases while shifts to higher wavenumber with increase in BaO content. This may indicates the presence of more number of pentaborate groups and bond lengths of B-O bonds of pentaborate groups could be reduced. The above results suggest more metaborate, penta or diborate groups than pyroborate groups are present in the glasses with addition of BaO group.



Table 3.1 Raman peak positions of $59\text{B}_2\text{O}_3\text{-}10\text{K}_2\text{O}\text{-}(30\text{-}x)\text{ZnO}\text{-}x\text{BaO}\text{-}1\text{CuO}$ ($0 \leq x \leq 30$ mol%) glass system, with error $\pm 1 \text{ cm}^{-1}$.

| Sample code | IR bands (cm^{-1}) | | | | | |
|-------------|-------------------------------|-----|-----|-----|-----|------|
| BKZB1 | 466 | - | 768 | 845 | 945 | 1458 |
| BKZB2 | 460 | 618 | 770 | - | 946 | 1457 |
| BKZB3 | 453 | 621 | 770 | - | 946 | 1450 |
| BKZB4 | 457 | 618 | 768 | - | 947 | 1445 |
| BKZB5 | 489 | 618 | 764 | - | 951 | 1445 |
| BKZB6 | 496 | 626 | 761 | - | 956 | 1445 |

Table 3.2 Assignments of Raman peaks of $59\text{B}_2\text{O}_3\text{-}10\text{K}_2\text{O}\text{-}(30\text{-}x)\text{ZnO}\text{-}x\text{BaO}\text{-}1\text{CuO}$ ($0 \leq x \leq 30$ mol%) glass system.

| Peak positions | Assignment |
|----------------|---|
| 466-496 | pentaborate and diborate groups |
| ~620 | ring-type metaborate groups |
| 760-775 | symmetric breathing vibrations of six-membered rings with both BO_3 triangles and BO_4 tetrahedra |
| ~845 | symmetric stretching of the B-O-B bridges in pyroborate groups |
| 940-960 | pentaborate and tetraborate groups |
| 1440-1460 | B-O ⁻ bonds attached to various borate groups |

Conclusion

Transparent glasses with the composition $59\text{B}_2\text{O}_3\text{-}10\text{K}_2\text{O}\text{-}(30\text{-}x)\text{ZnO}\text{-}x\text{BaO}\text{-}1\text{CuO}$ (where $x = 0, 6, 12, 18, 24$ and 30 mol%) were prepared by melt- quenching technique. The Raman peak appeared at around 620 cm^{-1} is due to ring-type metaborate groups. This band is not seen in BKZB1 glass. This indicates that ring-type metaborate groups are not present in high ZnO content glass (BKZB1). The above results suggest more metaborate, penta or diborate groups than pyroborate groups are present in the glasses with addition of BaO group.

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