Optical and EPR Spectroscopy Characteristics of Molybdenum Doped Alkali-Cadmium-Zinc-Borate Glasses

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Abstract:

The focus of the current review is on the application of optical and EPR spectroscopy tools to cadmium zinc borate glasses that have been altered with MoO_3 ions. The melt quenching procedure is used to generate the samples with compounds of B_2O_3-CdO-ZnO-K_2O-MoO_3, in which the amount of MoO_3 grew at the expense of the amount of K_2O content. The XRD spectra that were acquired for these samples revealed that there were no strong peaks, which verified that the material was in an amorphous phase. In order to investigate the many transitions and ligand field concepts surrounding the transition metal ions, optical absorption and EPR spectra were both recorded and evaluated. Tauc and Urbach plots have been drawn, and the relevant energies and disorder of the samples have been analyzed. It has been shown that as the mole percentage of MoO_3 in these glasses grows, the band gap decreases, going from 3.036eV to 2.919eV, and the refractive index increases, going from 2.387 to 2.419, both of which are advantageous for optical applications. The EPR spectra revealed two unique and substantial signals, one at g = 4.3 and the other at g = 1.9, which referred to the presence of Mo^{5+} ions at octahedral coordination sites with C_{4V} point group symmetry and partially distorted axial symmetry. A second signal's existence adds validity to this interpretation. This is shown by the presence of the second signal.

Key words: Potassium borate glasses, XRD, optical and Electron paramagnetic resonance (EPR) spectra, Refractive Index.

1. Introduction:

Amorphous characters of glasses are optically transparent and thermally stable due to the occurrence of small array order in the structure [1]. In the current technical applications, glasses made of borate are prominent among the many glasses.Borate glasses, which are modified by alkali oxides such as Na_2O, K_2O, and Li_2O, exhibit distinct physical and thermal properties and have gained increasing importance in glass research.[2, 3]. Among K_2O has the effect of preventing glass from crystallizing and promoting glass formation. Additionally, the increased alkali ion conductivity in the glass network of these glasses makes them suitable for application in optoelectronic devices [4]. The existence of PbO, CdO, and ZnO oxides transforms the network of glasses by incorporating non-bridging oxygen's [5, 7]. Metal oxide-based glasses including Bi_2O_3, CdO, PbO and ZnO are gaining popularity in a wide range of applications, especially in optical and shielding materials.Heavy metal oxides (CdO & MoO_3) containing glasses are having high density and refractive index, which is essential characteristics, used in

shielding and optical materials application [8, 9].Transition metal oxide doped glasses have been extensively studied in recent years, with particular attention given to borate glasses containing MoO_3 as a dopant. These glasses have gained significant prominence in various research fields. Borate glasses with Mo ions are used in large-area displays like smart windows, high-density memory, light modulation, and electrochemical devices. Due to the multiple valence states of molybdenum, the presence of molybdenum ions in glasses as Mo^{3+}, Mo^{4+}, Mo^{5+}, and Mo^{6+} adds semiconductor qualities to the glass with n-type conduction [10]. The present paper investigates the significant impact of MoO_3 doped B_2O_3-CdO-ZnO-K_2O glasses through the optical UV absorption and EPR spectra.

2. Experimental Methodology:

A typical melt quenching procedure was used to make glasses with nominal compositions of $60B_2O_3$-20CdO-10ZnO-(10-x)K_2O-x$MoO_3$with x=0 (BCZKM 1), 0.5 (BCZKM 2), 1(BCZKM 3), 1.5 (BCZKM 4), and 2 (BCZKM 5) mole percent as show in the table 1. Commercially available powders of H_3BO_3, CdO, ZnO, K_2O, and MoO_3 from Sigma-Aldrich were used as starting chemicals. The required mole concentrations were accurately weighed using a mono-pan digital balance. These substances were placed in a crucible before being heated to 950 degrees Celsius in a furnace that was operated by electricity. These mixtures finally melted evenly after about half an hour had lapsed. To achieve homogeneity, the molten mixtures were agitated further. After that, the molten metal had been transferred over a plate made of stainless steel that had been heated to a temperature of 100 degrees Celsius and then compressed with a second plate made of stainless steel. Such glasses were annealed at a temperature of 100 degrees Celsius for twenty-four hours in order to relax all of the stress. A screw gauge is used to determine the thickness of the glass samples, typically ranges from 0.5 to 1mm. These samples as shown in the figure 1 were exposed to the X-ray analyses by Bruker D8 advance X-ray diffractometer CSIF, BITS Pilani, GOA. XRD analyses confirmed the amorphous structure of the synthesized glasses. As shown in the figure1, there are no strong peaks in the XRD spectrum.The made samples were polished to provide a smooth surface. The polished samples were analyzed for UV-Visible spectra in the range of 200 nm to 1000 nm using a V-670 UV-VIS spectrophotometer at Osmania University, Hyderabad. Using a Bruker EPR spectrometer, HCU, HYDERABAD the samples' EPR spectra are captured at a 9.7GHz X-band frequency and a 100 kHz modulating frequency.

Glass Code	B_2O_3 Mole%	CdO Mole%	ZnO Mole%	K_2O Mole %	MoO_3 Mole %
BCZKM 1	60	20	10	10	0
BCZKM 2	60	20	10	9.5	0.5
BCZKM 3	60	20	10	9	1
BCZKM 4	60	20	10	8.5	1.5
BCZKM 5	60	20	10	8	2

Table 1. Mole Percentage of the Selected Compositions for Synthesis

BCZKM 1	BCZKM 2	BCZKM 3	BCZKM 4	BCZKM 5

Fig.1. BCZKM Glasses

3. Results & Discussion:

3.1.XRD Spectra:

The following Figure 2 depicts the XRD spectra of a BCZKM glass system.The XRDspectra revealthe lack of distinct lines or sharp peaks indicates a high degree of glassy state.

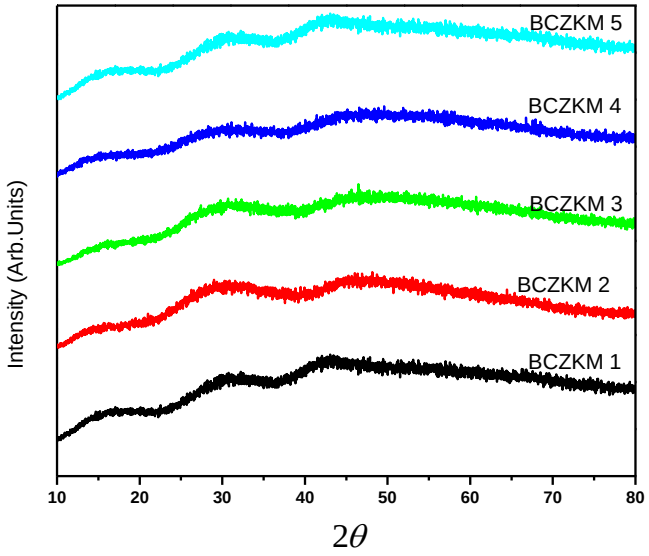

Fig.2. XRD spectra of BCZKM glass system

3.2.Optical absorption:

Figure 3 displays the absorption spectra of BCZKM glasses. The plots of the absorption spectra indicate a change in the absorption edge with a variation in the mole concentration of MoO_3 and K_2O. The un-irradiated glass spectrum shows a broad ultraviolet absorption without any visible bands.The optical spectrum plays a crucial role in the field of material science as it helps to explain the energy level transitions involved. Optical absorption spectra are analyzed to determine the band gap (E_g) and Urbach energy (ΔE) [11].

To explore the optical parameters, initially used to determine the absorption coefficient (α) with following equations

$$\alpha = \frac{Absorption}{thicknessofthesample} x2.303 \quad (1)$$

The band gap of indirect transition in the spectra of the glasses determined by the Tauc [12] proposed relationship as

$$(\alpha h\upsilon) = B^2(h\upsilon - E_g)^2 \quad (2)$$

A graph drawn between $h\upsilon$ verses $(\alpha h\upsilon)^{1/2}$ as shown in the following Figure 4. To determine the E_g (band gap energy) of BCZKM glasses, an extended tangent line was drawn on the linear portion of the Tauc graph. The value of E_g for the matching sample has to be determined by taking the intercept on the energy axis. The band gap values got for the BCZKM glasses were 3.036 eV (BCZKM 1), 3.006 eV (BCZKM 2), 2.988 eV (BCZKM 3), 2.952 eV (BCZKM 4), and 2.919 eV (BCZKM 5). These findings make it abundantly evident that the Eg values dropped as the mole concentration of MoO_3 rose with the result that K_2O was displaced as the dominant molecular species. The results lead one to the conclusion that the amounts of MoO_3 in the currently available BCZKM glasses had an effect on the band gap estimates. The formation of localised states adjacent to the electron conduction band may be the cause of such results. Additionally, the transition of Mo^{6+} ions towards Mo^{5+} ions may be the cause of the band gap reduction. Hence Mo^{5+} ions rise with the composition from BCZKM 1 to BCZKM 5. Further these ions behaves as modifier by taking the positions of octahedral sites that were present in the BCZKM glasses which in turn results in rise in the non-bridging oxygen atoms [13,14].

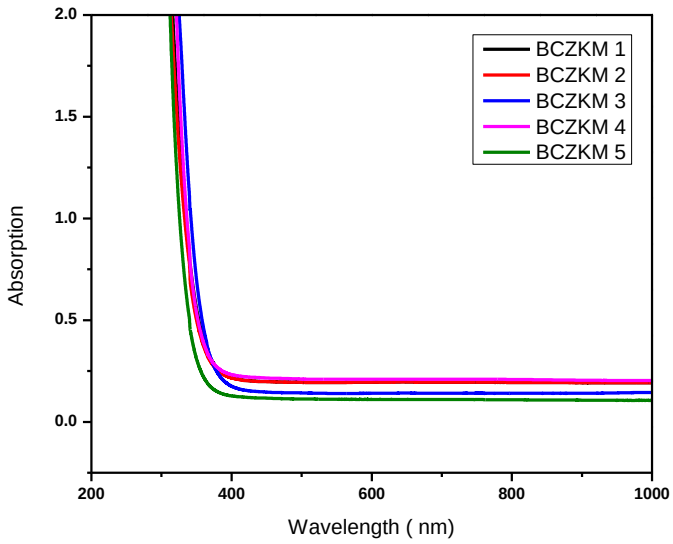

Fig.3. Absorption Vs. Wavelength spectra of BCZKM glasses

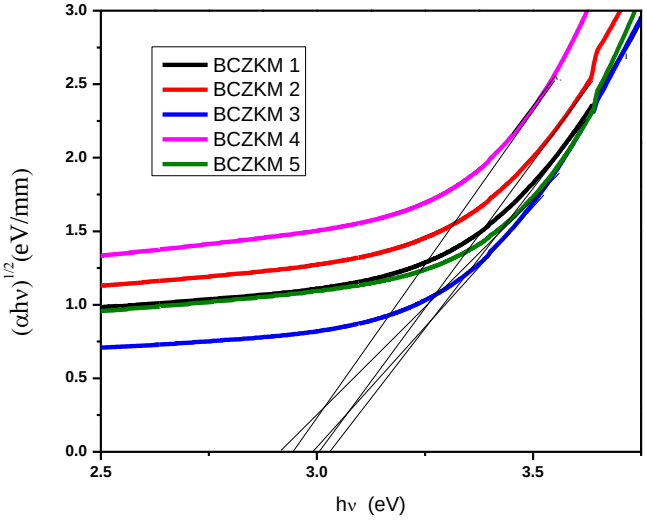

Fig.4. hυ verses $(\alpha h\upsilon)^{1/2}$ plot of BCZKM glasses

The refractive index (n) tabulated in the table determined from the following relation with band gap is [15]

$$\frac{n^2-1}{n^2+2} = 1 - \sqrt{\frac{E_g}{20}} \qquad (3)$$

The plotted graph between refractive index and energy gap is as shown in the Fig.5. And also the calculated values of refractive index, direct band gaps and Urbach energy for the prepared glass system are tabulated in table 2.

S.No.	Sample code	Refractive Index (n)	Optical Band Gap (E_g) eV	Urbach Energy(ΔE) eV
1	BCZKM 1	2.387	3.036	0.610
2	BCZKM 2	2.395	3.006	0.612
3	BCZKM 3	2.400	2.988	0.613
4	BCZKM 4	2.410	2.952	0.615
5	BCZKM 5	2.419	2.919	0.618

Table 2. Refractive Index (n), Optical band gap (E_g) and Urbach Energy (ΔE**)** of BCZKM glasses

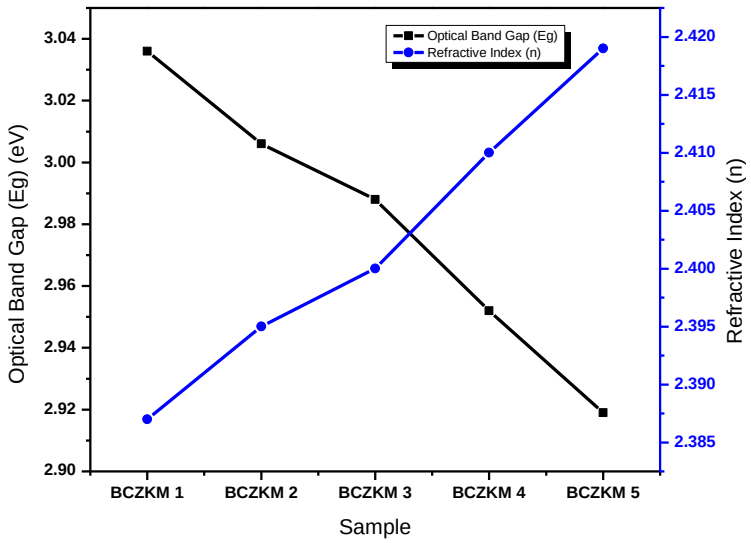

Fig.5 E_g (eV) vs. n plot of BCZKM glasses

The 'n' values increased significantly with the addition of molybdenum oxide, beginning 2.387 (BCZKM 1) to 2.149 (BCZLM 5). This increase in refractive index values can be attributed to the increase in non-bridging oxygen (NBO) species in the glass network. The high concentration of NBOs (Non-Bridging Oxygen) in the network can be linked to the red-shift observed in the UV cut-off wavelength. In the UV region, NBO electrons exhibit weaker binding forces and Madelung potential, which ultimately leads to a red-shift of the cut-off wavelength [16].

The Urbach energy is a helpful tool to assess the level of disorganization that exists in amorphous materials. [17]. The graphs plotted between the parameter ln(α) verses hυ gives the Urbach energy (ΔE) which is as shown in Figure. The slopes of the curves were determined by drawing them from the linear regions of the plots, and the reciprocals of those slopes yielded the Urbach energy. For the BCZKM glasses, the Urbach energy ΔE was approximately 0.6135 eV, obtained from these plots.

3.3. Electron Paramagnetic Resonance:

The EPR spectra of BCZKM glasses as shown in the following Figure 5 are analogous to several described glasses [18, 19]. The EPR spectra displayed two echo pointers at g = 4.3 and g = 1.9. Molybdenum was chosen because it can exist in a variety of oxidation states, including Mo^{6+}, $Mo^{5+,}$ Mo^{4+}, and Mo^{3+}. Among these most contribution towards EPR spectra came from Mo^{5+} and Mo^{6+} states [20, 21].

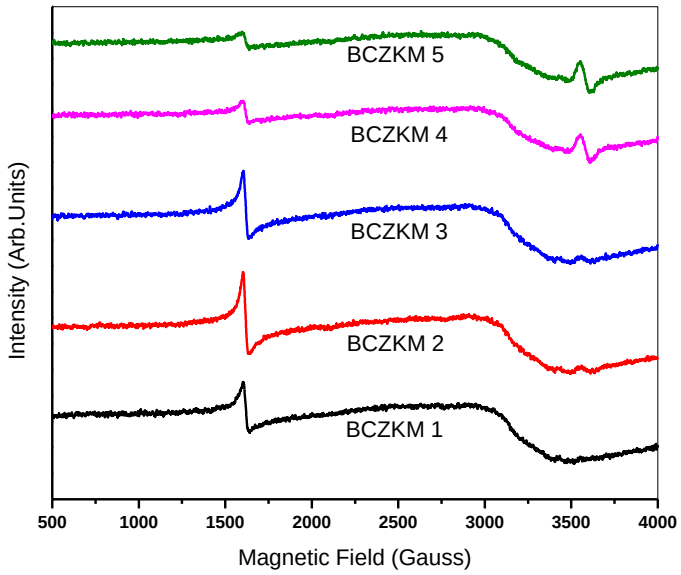

Fig.5. Magnetic Field Vs. Intensity plot of BCZKM glasses

The equation of spin-Hamiltonian provides an appropriate analysis of the electron paramagnetic resonance spectrum i.e.

$$H= \beta SgB+ SAI \quad (4)$$

In which β is the Bohr magnetron, g- is the lande factor, A-being the hyperfine splitting factor, S and I represent electron and nuclear spins respectively.

The ERP spectra have shown an intense central line with g=1.94 is contributed by even molybdenum isotopes. Actually nearly by intense central line a low intensity satellite lines should occur. These are feeble in the present study arising from odd ^{95}Mo or ^{97}Mo isotope [I=5/2]. From the ERP Spectra it can be seen that BCZKM 1 glass has not shown any EPR signal indicating the absence of molybdenum. While BCZKM 2 and BCZKM 3 glass samples contain molybdenum in 0.5 and 1 mole percentage respectively. In these two glass systems a weak EPR central line is seen. Both BCZKM 4 and BCZKM 5 glasses have shown an intense central line with slight satellite lines also. The spectra of BCZKM glasses revealed that the Mo^{5+} ions present in the BCZKM glass network are octahedral coordinated with a weak axial distortion and exhibit C_{4V} symmetry.

4. Conclusion:

BCZKM glasses synthesized by melt-quenching method, where varied mole percentage of Molybdenum oxide (from 0 to 2 mole %) compensate with alkali oxide K_2O. The XRD spectra of BCZKM glassesobserved with no sharp peaks of crystals confirm the amorphous nature. The parameters such as n, E_g, and ΔE were measured, and it was witnessed that the refractive index(n) increased while the optical band gap(E_g) decreased with the increase of MoO_3. This effect could be caused by the shift of Mo^{6+} ions to Mo^{5+} ions.

As the concentration of Mo^{5+} ions increases, they serve as modifiers by occupying octahedral sites in the glass network. This results in a corresponding increase in the number of non-bridging oxygen atoms. The ERP Spectra is depicts that BCZKM 1 glass not shows any EPR signal indicating the absence of molybdenum. While remaining glasses possess the EPR signal for increased mole percentage of molybdenum doped BCZKM glasses. The EPR spectra of MoO_3 doped BCZKM glasses revealed that the Mo^{5+} ions present in octahedral coordinated with a feeble axial distortion and exhibit C_{4V} symmetry.

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