

Influence of Manganese ion Doping on KF-CaO-B₂O₃ Glass Structure

Kassa Belachew, Eyob Daniel, Mengesha Ayene, C. Laxmikanth

Abstract— Glasses with composition 30KF-10CaO-(60-x) B₂O₃: xMnO (where x = 0 to 0.4 wt. %) were prepared by using melt quenching technique. The glassy states of the prepared materials were evidenced from x-ray diffraction studies. Various studies were carried out for the prepared glasses. viz. DTA, IR, and optical absorption. From DTA studies, the calculated stability parameters show an increasing trend of improved stability in the glass network with MnO concentration from 0.1 to 0.4 wt. %. From IR spectral studies, with increasing MnO concentration from 0.1 to 0.4 wt. %, intensity of band due to BO₄ unit increases on the contrary of band due to BO₃, indicates an increase in stability of glass network. Optical absorption spectral analysis shows that, an increase in the optical bandgap with increase in MnO concentration from 0.1 to 0.4 wt. %; the observed trend suggests an increase in the glass stability in the dominant Mn³⁺ ion state.

Index Terms: B₂O₃ glasses, manganese ions, glass-forming ability factor, IR studies, Urbach plot, optical band gap.

1 INTRODUCTION

Borate glasses are the technologically important class of glasses and play a significant role in various applications with a planar BO₃ groups as structural units [1, 2]. Borate glasses containing glass alkali-oxide or modifiers like CaO, ZnO, SrO, PbO, MgO, and BaO are useful materials for many applications in the fields of optical communications (optical fibers), laser hosts, optical filters, X- and γ -ray absorbers, photonic devices, and so forth [3–8]. Recently, the interest in borate glasses has been renewed in views of the fast conductive properties exhibited by some of these glasses containing transition metal ions [9, 10]. This glass system is important in laser and infrared detection applications [11]. Borate glasses containing transition metal oxides are very useful materials for the radiation dosimetry applications in view of the fact their effective atomic numbers is very close to that of human tissue [12]. Network modifier cations, such as alkali, alkaline earth (CaO) and higher valance state ions are accommodated randomly in the network in close proximity to non -bridged anions leading to the increased ability of the glass.

Transition metal ions are very interesting ions to probe the glass network because their outer d-electron orbital functions have rather broad radial distributions and their response to surrounding anions are very sensitive; as a result these ions influence the physical properties of the glasses to a substantial extent. The small amounts of dopants in glasses are found to change properties of the host materials and sometimes it could result in the drastic change with the type of dopant and its concentration. TM doped glasses are of great interest for their optical properties. TM oxides can form homogeneous glasses when mixed with B₂O₃ [13]. Manganese ion, is an interesting one because it exists in different valence states in different glass matrices, for example as Mn³⁺ in borate glass with octahedral coordination whereas in silicate and germanate glasses it exists in Mn²⁺ state with both octahedral and tetrahedral coordination [14]. Further, among different manganese ions, Mn²⁺ and Mn³⁺ ions are well known paramagnetic ions, Mn²⁺ and Mn⁴⁺ ions are identified as luminescence activators [15]. The content of manganese in different forms in different valence states exist in the glass depends on the quantitative properties of modifiers and glass formers, size of the ions in glass structure, their field strength, mobility of the modifier cation etc. Hence, the connection between the state and the position of the manganese ion, physical and optical properties of the glass is highly interesting.

In view of these, it is felt useful to have some understanding over the various physical and optical properties of KF-CaO-B₂O₃: MnO glasses in different oxidations states of manganese ions.

2 EXPERIMENTAL

In the present study, the glasses were prepared by the melt-quenching technique. The starting materials KF, CaO, B₂O₃

- **Kassa Belachew** is currently perusing M.Sc. (Solid State Physics) Degree from Wollo University, Dessie, Ethiopia.
Email: kasabelachew@gmail.com
- **Eyob Daniel** is a faculty member of Department of Physics, Wollo University, Dessie, Ethiopia.
eyoba106@yahoo.com
- **Mengesha Ayene** is a faculty member of Department of Physics, Wollo University, Dessie, Ethiopia.
mengesha.ayene@yahoo.com
- **C. Laxmikanth** is a faculty member of Department of Physics, Wollo University, Dessie, Ethiopia.
prof.cherupally@gmail.com

and MnO that used for the preparation of the present glass systems were with analar grade (larger than 99.9% purity). The chemical composition of these series of glasses is listed in Table 1.

TABLE 1
GLASS COMPOSITIONS OF THE STUDY

Glass Sample	Composition of Glasses
KCBM_0	30KF-10CaO-60 B ₂ O ₃
KCBM_1	30KF-10CaO-59.9 B ₂ O ₃ -0.1MnO
KCBM_2	30KF-10CaO-59.8B ₂ O ₃ -0.2MnO
KCBM_3	30KF-10CaO-59.7B ₂ O ₃ -0.3MnO
KCBM_4	30KF-10CaO-59.6B ₂ O ₃ -0.4MnO

The melting temperature of all these materials was found to be in the range of 610-630°C. The density *d* of the glasses was determined by the standard principle of Archimedes with an accuracy of 0.001 g/cm³, by using O-xylene as working liquid at room temperature. The refractive indices *n_d* of the optically polished glasses was measured using sodium vapour lamp ($\lambda = 589.3$ nm) on a precession Abbe's refractometer. The non-crystalline phases of the glasses were confirmed by shimadzu x-ray diffractometer of model XRD-7000S in 2θ ranges from 10° - 80°. The differential thermal analysis traces were recorded on shimadzu differential thermo gravimetry (DTG) of model DTG-60H with a programmed heating rate of 10 °C/min in the temperature range of 30-700 °C to an accuracy of ±0.1 °C. The IR transmission spectra of these glasses were recorded in the range 200-4000 cm⁻¹ on a Perkin Elmer Spectrometer in the wavenumber range 400-4400 cm⁻¹ by KBr pellet method. The optical absorption spectra of the glasses were recorded by using shimadzu UV-Vis spectrometer at room temperature in the wavelength ranging from 300 to 700 nm.

3 RESULTS AND DISCUSSION

3.1 Physical Parameters

The density *d* of the glass samples was determined at room temperature by using Archimedes principle using O-xylene as the immersion liquid. The concentration of manganese ions *N_i* was calculated from the known densities and compositions of the respective glasses. The refractive index *n_d* of the glass was measured with an Abbe Refractometer at sodium wavelength (589.3 nm). The dopant ion concentration (*N_i*) could be obtained from:

$$N_i(\text{ions/cm}^3) = \frac{N_A M(\text{mol.}\%)d}{\bar{M}} \quad (1)$$

From the obtained values of *N_i*, the inter-ionic distance *r_i* and the polaron radius *r_p* of dopant ions can be evaluated by the following equations [16-18]:

$$\text{Inter-ionic distance } r_i (\text{\AA}) = \left[\frac{1}{N_i} \right]^{1/3} \quad (2)$$

$$\text{Polaron radius } r_p (\text{\AA}) = \frac{1}{2} \left[\frac{\pi}{6N_i} \right]^{1/3} \quad (3)$$

The theoretical dielectric constant (ϵ) was calculated from the refractive index of the glass using

$$\epsilon = n_d^2 \quad (4)$$

The reflection loss from the glass surface was computed from the refractive index by using the Fresnel's formula:

$$R = \left[\frac{(n_d - 1)}{(n_d + 1)} \right]^2 \quad (5)$$

The molar refractivity *R_M* for each glass was evaluated using the formula:

$$R_M = \left[\frac{(n_d - 1)}{(n_d + 2)} \right] V_m \quad (6)$$

The molar volume of the glass samples was calculated using the formula:

$$V_m = \frac{M}{d} \quad (7)$$

The electronic polarizability α_e was calculated using the formula:

$$\alpha = \frac{3(n_d^2 - 1)}{4\pi N_i (n_d^2 + 2)} \quad (8)$$

where *N_i* is the number of manganese ions per unit volume. Table 2 presents data on various evaluated physical parameters useful for understanding the nature of these glasses.

3.2 XRD Studies

Fig. 1 Shows XRD patterns of KF-CaO-B₂O₃: MnO glasses. The absence of sharp peaks in all samples from the XRD recordings confirms the amorphous nature of the prepared materials.

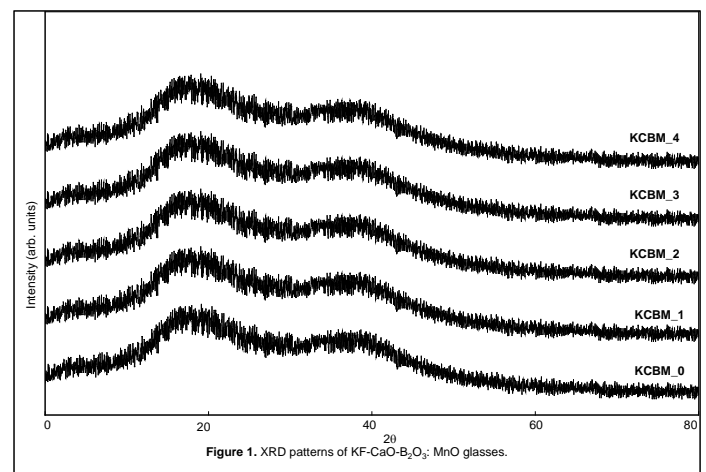


Figure 1. XRD patterns of KF-CaO-B₂O₃: MnO glasses.

TABLE 2
DATA ON VARIOUS PHYSICAL PARAMETERS OF KF-CaO-B₂O₃: MnO GLASSES

Physical Parameters	KCBM_0	KCBM_1	KCBM_2	KCBM_3	KCBM_4
Average molecular weight, \bar{M}	61.383	61.384	61.386	61.387	61.388
Density, d (g/cm ³)	2.545	2.532	2.518	2.509	2.485
Refractive index, n_d	1.503	1.508	1.515	1.519	1.525
Manganese ion concentration, N_i ($\times 10^{20}$ ion/cm ³)	-	0.900	1.000	2.000	3.000
Inter ionic distance, R_i (Å)	-	2.231	2.154	1.709	1.493
Polaron radius, R_p (Å)	-	0.838	0.867	0.688	0.604
Electron polarizability, α_e ($\times 10^{-19}$ ion/cm ³)	-	0.721	0.708	0.529	0.350
Dielectric constant, ϵ	2.259	2.274	2.295	2.307	2.325
Molar refractivity, R_M	3.449	3.490	3.559	3.596	3.656

3.3 DTA Studies

Fig. 2 shows the differential thermal analysis traces of KF-CaO-B₂O₃: MnO glasses. All glasses exhibited an endothermic change between 385°C and 411°C, which is attributed to the glass transition temperature T_g . The appearance of single peak due to the glass transition temperature in DTA pattern of all the glasses indicates the high homogeneity of the glasses prepared. The highest values of the glass transition temperatures for KF-CaO-B₂O₃ glasses containing 0.4 wt. % of MnO indicate their relatively high glass forming abilities. At still higher temperature T_c , an exothermic peak due to the crystal growth in the range 478°C to 530°C followed by another endothermic effect T_m in the region between 610°C and 630°C due to the re-melting of the glasses were observed. The observed glass melting temperature T_m of these glasses was found to increase with increase in concentration of MnO from 0.1 to 0.4 wt. %. From the measured values of T_g , T_c and T_m , the parameter, $K_{gl} = (T_c - T_g) / (T_m - T_c)$, known as Hruby's parameter that gives the information on the stability of the glass network was calculated for all glasses. The value of K_{gl} found to increase as MnO concentration increases in the glass network. The variations of various stability parameters, $(T_c - T_g) / T_m$, $(T_c - T_g) / T_g$ and the Hruby's parameter

$(T_c - T_g) / (T_m - T_c)$ is plotted against MnO concentration and presented as an inset in Fig. 2.

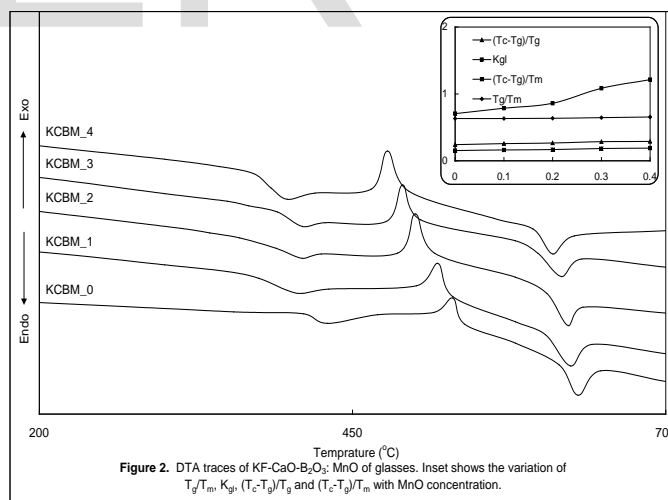


Table 3 presents data on DTA analysis of these glasses. These curves show an increasing trend of stability factors from 0.1 to 0.4 wt. % of MnO concentration; suggesting an increase in stability of the glass network with increase in MnO concentration.

TABLE 3
DATA ON DTA ANALYSIS OF KF-CaO-B₂O₃: MnO GLASSES

Glasses	T _g (°C)	T _c (°C)	T _m (°C)	T _g /T _m	(T _c -T _g)/ (T _m -T _c)	(T _c -T _g)/ T _g	(T _c -T _g)/ T _m
KCBM_0	385	478	610	0.631	0.704	0.241	0.152
KCBM_1	390	490	617	0.632	0.787	0.256	0.162
KCBM_2	395	500	622	0.635	0.860	0.265	0.168
KCBM_3	403	518	624	0.645	1.084	0.285	0.184
KCBM_4	411	530	630	0.654	1.214	0.289	0.189

3.4 IR Spectral Studies

The IR transmission spectra recorded for these glasses (Fig. 3) exhibit two conventional bands:

- Due to the stretching relaxation of the B-O bond of the trigonal BO₃ units in the region 1256-1341 cm⁻¹ (band 1).
- Due to B-O bond stretching of the tetrahedral BO₄ units in the region 890-978 cm⁻¹ (band 2) in the borate network.
- In addition, a band at about 710 cm⁻¹ due to the bending of B-O-B linkages in the borate network.

The observed band positions in the present study are almost similar to those reported in literature [19-28]. With the increase in the concentration of MnO into the glass network 0 to 0.4 wt. % the intensity of the second group of bands (band 2) is found to increase at the expense of first group of bands (band 1). Fig. 4 shows the intensity variations of band 1 and band 2 with MnO concentration for KF-CaO-B₂O₃: MnO glasses. For the case of borate glass, most of the boron atoms generally involve in B₃O₆ boroxol rings, which responsible for networking of the glass [29, 30]. The addition of transition metal ion breaks these rings in to sp² planar BO₃ units and more stable sp³ tetrahedral BO₄ units and possibly with non-bridging oxygens (NBO's). Each BO₄ unit is linked to two such other units and one oxygen from each unit with a metal ion (Ca²⁺) and the structure leads to the formation of long tetrahedron chains. The observations on these studies show that with the increase in MnO concentration from 0.1 to 0.4 wt. % in the glass matrix, there is an increase in the number BO₄ units at the expense of BO₃ units. As mentioned before BO₄ units responsible in making long chain of tetrahedron and which

in turn are responsible for the polymerization of the glass network.

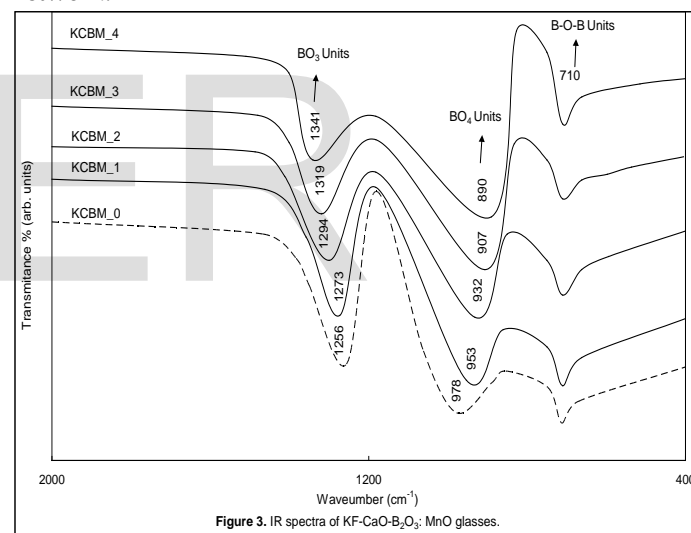


Figure 3. IR spectra of KF-CaO-B₂O₃: MnO glasses.

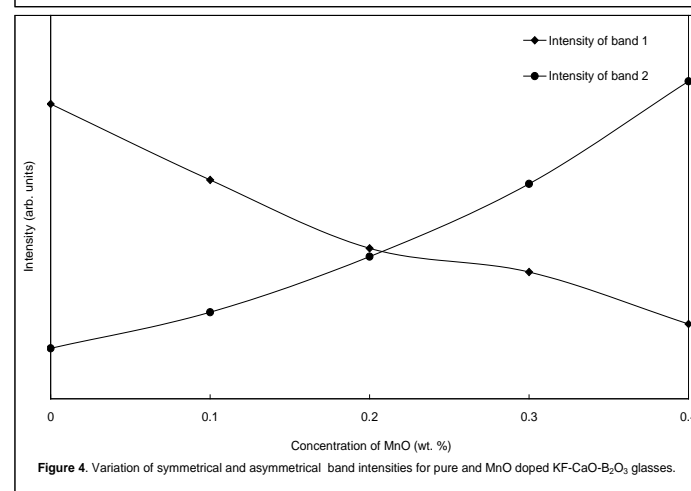


Figure 4. Variation of symmetrical and asymmetrical band intensities for pure and MnO doped KF-CaO-B₂O₃ glasses.

Finally, IR studies on KF-CaO-B₂O₃: MnO glasses showed an increased stability of the glass network with MnO concentration. Table 4 presents the data on various IR band positions (cm⁻¹) for KF-CaO-B₂O₃: MnO glasses.

TABLE 4
DATA ON VARIOUS BAND POSITIONS FROM THE IR SPECTRA OF KF-CaO-B₂O₃: MnO GLASSES

Glass Sample	Bands due to BO ₃ (band 1)	Bands due to BO ₄ (band 2)	Bands due to B-O-B linkages
KCBM_0	1256	978	710
KCBM_1	1273	953	710
KCBM_2	1294	932	710
KCBM_3	1319	907	710
KCBM_4	1341	890	710

3.5 Optical Absorption Studies

Fig. 5 shows the optical absorption spectra of KF-CaO-B₂O₃: MnO glasses in the wavelength region 300-700 nm.

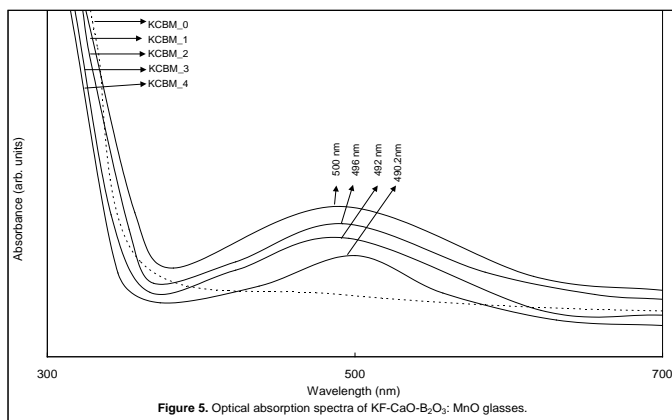


Figure 5. Optical absorption spectra of KF-CaO-B₂O₃: MnO glasses.

The absorption edge observed for KCBM_0 glass is at 328 nm and with increase in concentration of MnO in the glass matrix from 0.1 to 0.4 wt. %, the absorption edge was found to be shift to lower wavelength sides. The spectra of these glasses exhibited absorption bands is due to: (i) Mn²⁺ (d⁵) ion state with octahedral coordination at 500 nm (KCBM_1) and 496 nm (KCBM_2) and (ii) Mn³⁺ (d⁴) ion with tetrahedral coordination at 492 nm (KCBM_3) and 490.2 nm (KCBM_4). These two bands were seen obscured with the appearance of a single broad band in the wavelength range

490.2 nm and 500 nm. When the concentration of MnO is increased from 0.1 to 0.4 wt. %, there is an observed gradual shifting of band position from 500 nm to 490.2 nm; such observation is attributed due to the gradual conversion of manganese ions from Mn²⁺ state into Mn³⁺ state. The absorption bands at 500 and 496 nm are identified due to ⁶A_{1g}(S) → ⁴T_{1g}(G) transition of Mn²⁺ ions [31, 32] and 490 and 490.2 nm are identified due to ⁵E_g → ⁵T_{2g} transition of Mn³⁺ ions [33, 34]. Fig. 6 shows the Urbach plot of KF-CaO-B₂O₃: MnO glasses.

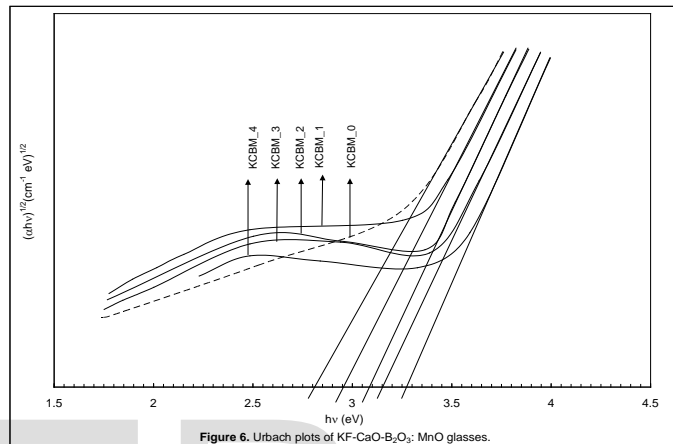


Figure 6. Urbach plots of KF-CaO-B₂O₃: MnO glasses.

The optical band gap E_{opt} can be determined from the Urbach plot $(\alpha hv)^{1/2}$ versus hv , which is related by the equation.

$$\alpha(\nu) = \alpha_0 \left[\frac{h\nu - E_{opt}}{h\nu} \right]^2 \quad (9)$$

Where, α_0 is a constant related to the extent of the band tailing, and E_{opt} is the optical band gap energy [14]. The absorption coefficient, $\alpha(\nu)$, can be determined near the absorption edge of different photon energies for all glass samples. With increase of MnO concentration from 0.1 to 0.4 wt. %, the optical band gap is observed to increase, whereas the Urbach energy is found to decrease. The gradual shifting of absorption edge with increase in the concentration of MnO towards lower wavelengths also indicate an increase in accumulation of Mn³⁺ ions that take part in the network forming positions with tetrahedral coordination. Lower the concentration of the Mn²⁺ ions that act as modifiers (with octahedral coordination), lower is the concentration of NBO's in the glass matrix. This leads to a decrease in the degree of localization of the electrons there by decreasing the donor centres in the glass matrix. The presence of lesser concentration of the donor centres raises the optical band gap and shifts the absorption edge towards lower wavelength sides. Table 5 presents data on various band positions and optical band gap energies of KF-CaO-B₂O₃: MnO glasses.

TABLE 5
DATA ON VARIOUS BAND POSITIONS AND OPTICAL BAND GAP ENERGIES OF KF-CaO-B₂O₃: MnO GLASSES

Glass	Band edge λ (nm)	Band position λ (nm) due to Mn ²⁺ transitions ⁶ A _{1g} (S)→ ⁴ T _{1g} (G)	Band position λ (nm) due to Mn ³⁺ transition ⁵ E _g → ⁵ T _{2g}	Optical band gap energy E_{opt}	Urbach energy ΔE (eV)
KCBM_0	328	-	-	2.81	0.97
KCBM_1	325	500.0	-	2.95	0.89
KCBM_2	323	496.0	-	3.09	0.73
KCBM_3	318	-	492.0	3.15	0.66
KCBM_4	315	-	490.2	3.27	0.55

4 CONCLUSIONS

Main conclusions drawn from various on KF-CaO-B₂O₃: MnO glasses are summarized as follows:

- (i) From DTA analysis, the glass forming ability parameters are found to increase with increase in concentration of MnO from 0.1 to 0.4 wt. % in the glass matrix; such an increase in values attribute to an improved stability in glass network with dominant Mn³⁺ ion states.
- (ii) IR spectral studies of these glasses exhibited two fundamental bands, band 1 (due to BO₃ units) and band 2 (due to BO₄ units). With increase in MnO concentration, the intensity of band 1 is found to decrease on the contrary of band 2; such an observation indicates an increased stability of glass network in the dominant Mn³⁺ ions states.
- (iii) Optical absorption spectral studies showed that, an increased optical bandgap and accumulation of more number of Mn³⁺ ion states with increase in MnO concentration from 0.1 to 0.4 wt. %; the observed trends recommend the improved glass stability.

Finally, various studies on KF-CaO-B₂O₃: MnO glasses confirm that with an increase of MnO concentration from 0.1 to 0.4 wt. %, there is an observed improvement in glass stability in the presence of dominant Mn³⁺ ion states.

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