J Electroceram (2006) 17:65–69
DOI 10.1007/s10832-006-9938-5

Thermal and dielectric properties of ZnO-B_2O_3-MO_3 glasses ($M = W$, Mo)

Jeong-Ryeol Kim · Geun-Kyu Choi · Dong Kyun Yim · Jong-Sung Park · Kug Sun Hong

Abstract Glasses in the ZnO-B_2O_3-MO_3 ($M = W$, Mo) ternary were examined as potential replacements to PbO-B_2O_3-SiO_2-ZnO glass frits with the low firing temperature (500–600°C) for the dielectric layer of a plasma display panels (PDPs). Glasses were melted in air at 950–1150°C in a narrow region of the ternary using standard reagent grade materials. The glasses were evaluated for glass transition temperature (T_g), softening temperature (T_d), the coefficient of thermal expansion (*CTE*), dielectric constant (ε_r), and optical property. The glass transition temperature of the glasses varied between 470 and 560°C. The coefficient of thermal expansion and the dielectric constant of the glasses were in the range of 5–8 × 10^{-6}/°C and 8–10, respectively. The addition of MO_3 to ZnO-B_2O_3 binary could induce the expansion of glass forming region, the reduction of T_g and the increase in the *CTE* and the dielectric constant of the glasses. Also, the effect of the addition of MO_3 to ZnO-B_2O_3 binary on the transmittance in the visible-light region (350–700 nm) was investigated.

Keywords Plasma display panel · ZnO-B_2O_3-MO_3 · Glass transition temperature · Dielectric properties · Optical properties

1 Introduction

Recently, the market of plasma display panels (PDPs) has been grown rapidly, as PDPs are recognized to be the most promising technologies for wall-hanging wide TV and high-definition TV (HDTV). In PDPs, a dielectric layer is formed on a front glass substrate so as to cover the display electrodes. It is necessary for the dielectric layer to maintain discharge, to have a low firing temperature, to have high transparency after firing, to have a high break down voltage, and to have a reasonable coefficient of thermal expansion (*CTE*) similar to that of glass substrates [1]. Pb-based glasses, such as PbO-B_2O_3-SiO_2-ZnO glasses have been used commercially as the dielectric layers. Although Pb-based glasses are employed commercially, there are a number of problems associated with their use. The most obvious problem is that these glasses contain PbO, a component with deleterious healthy and environmental effects. Fortunately, many researches have been conducted for glass compositions with lower glass transition temperature (T_g) as possible alternatives to Pb-based glasses, such as SnO-ZnO-P_2O_5 [2], BaO-B_2O_3-ZnO [1, 3], ZnO-B_2O_3-SiO_2 [4], and MoO_3-V_2O_5-P_2O_5-FeO_3 system [5].

Glasses containing transition metal ions, such as WO_3 and MoO_3, have attracted the researchers because of their potential uses in the electrochemical, electronic and electro-optic devices. WO_3 and MoO_3 can belong to the intermediate class of glass forming oxides; they are the incipient glass network formers and as such do not readily form the glasses but do so in the presence of the modifier oxides like CaO or PbO, and they may also act as a modifier [6, 7]. The addition of the transition metal ions to the glasses may improve the thermal, chemical and electrical properties of the glasses because of the structural modifications in the glass network.

In the present work, we investigated a new glass composition (ZnO-B_2O_3-MO_3, $M = W$ or Mo) as a candidate for a Pb-free system. Furthermore, we examined the thermal, optical and electrical properties of ZnO-B_2O_3-MO_3 glass as a potential alternative frit composition for the transparent dielectric layer of PDPs.

J.-R. Kim · G.-K. Choi · D. K. Yim · J.-S. Park · K. S. Hong (✉)
School of Materials Science and Engineering,
College of Engineering, Seoul National University, Seoul, Korea
e-mail: kshongss@plaza.snu.ac.kr

Table 1 The thermal and dielectric properties of $ZnO-B_2O_3-MO_3$ (M = W, Mo) ternary glasses

Code	ZnO	B_2O_3	MO_3	T_g (°C)	*CTE* (10^{-6}/°C)	ε_r (at 1 MHz)
G1	30	70	–	555	5.3	7.8
G2	40	60	–	566	4.3	7.7
G3	50	50	–	565	4.9	7.4
G4	60	40	–	543	5.1	8.4
W1	40	50	10 (WO_3)	507	6.5	8.6
W2	50	40	10	512	6.0	8.1
W3	60	30	10	511	6.2	9.1
W4	65	25	10	505	6.3	9.5
W5	55	30	15	512	5.5	8.7
M1	40	50	10 (MoO_3)	507	6.2	8.4
M2	50	40	10	511	6.2	8.2
M3	60	30	10	498	6.2	8.8
M4	65	25	10	494	6.2	9.1
M5	55	30	15	470	6.4	8.9

2 Experimental procedure

The glasses of the $ZnO-B_2O_3-MO_3$ (M = W, Mo) system were prepared, as usual, by mixing and finely grinding appropriate amounts of ZnO, B_2O_3, WO_3 and MoO_3 (99.9% pure, High Purity Chemical Laboratory, Saitama, Japan), Table 1, then melting in a platinum crucible at 950–1150°C for 1 h, and being stirred several times. The melts were then poured and quenched on a stainless steel plate. For the preparation of bulk specimens, the glass melts from the furnace were poured into a stainless steel mold and reheated to a temperature of 10°C above T_g of each glass for being annealed for 1 h, and then cooled very slowly in the furnace.

The T_g of the glass frits were studied roughly by differential thermal analysis (DTA: SDT2960, TA Instrument, USA) at a heating rate of 10°C/min in air. For the measurement of thermal mechanical properties, the glass cubes with dimensions of 5 × 5 × 10 mm were cut out from the bulk samples. The T_g and *CTE* of glasses was measured on a thermal mechanical analyzer (TMA: Model DIL402C, Netzsch Instruments, Germany) at a heating rate of 5°C/min up to the softening temperature (T_d). From the obtained curves, the linear *CTE* was obtained as a mean value in the temperature range of 25–350°C. For the measurement of dielectric properties, the glass plates with the dimension of 10 × 10 × 1 mm were cut and polished. Then glass samples were prepared by applying Ag paste electrode to the polished surfaces in a uniform area. The dielectric constant (ε_r) and dielectric loss (tan δ) were measured by an impedance analyzer (Model HP4194A, Hewlett-Packard, Palo Alto, CA) and ε_r was calculated form the capacitance in the frequency range from 100 Hz to 10 MHz. The transmittance of the glass plates with the dimension of 10 × 10 × 0.5 mm well polished was measured using ultraviolet-visible spectrophotometry (Model Lamda 25, Perkin Elmer, USA).

3 Results

Figure 1 shows the approximate region for the glass formation in the $ZnO-B_2O_3-MO_3$ (M = W, Mo) system. The glass forming region is close to the $ZnO-B_2O_3$ binary and it is observed that glasses with a lower MO_3 content were formed more favorably. Glasses containing WO_3 had a narrow region for glass formation similar to those containing MoO_3. Glasses containing WO_3 or MoO_3 obtained in the ternary systems were fairly transparent. Glasses with larger amounts of MO_3 than 20 mol% could not be made because of the devitrification and the crystallization during being melted. It is noteworthy that glass forming region (B_2O_3: 40–70 mol%) in $ZnO-B_2O_3$ binary from this study is wider than that (B_2O_3: 35–50 mol%) from the previous work [1].

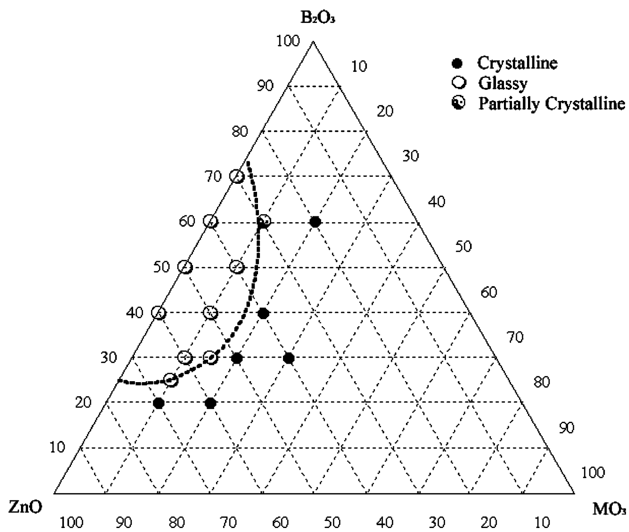

Fig. 1 Glass forming region in $ZnO-B_2O_3-MO_3$ (M = W, Mo) ternary (in mol%)

Figure 2 shows the TMA curves of $(60-x)$ZnO-40B_2O_3-$x$$MO_3$ glasses with $x=0$ and 10 as a function of temperature, as an example. In the glass with $x=0$, the glass transition of $T_g = 543°C$ and the softening temperature of $T_d = 568°C$ are observed. In contrast, in the glass with $x=10$, T_g of the glasses containing MO_3 is ∼511°C and T_d of those is lower than the former. Also, the curves of the glasses with MO_3 substitution for ZnO have the steeper slopes than that of the glass in ZnO-B_2O_3 binary. That is to say, the glasses with MO_3 substitution for ZnO have the higher *CTE* than that in ZnO-B_2O_3 binary.

In Fig. 3, the change in T_g is shown as a function of (ZnO + MO_3)/B_2O_3 ratio. T_g of the glasses containing MO_3 is lower than that of the glasses in ZnO-B_2O_3 binary. When

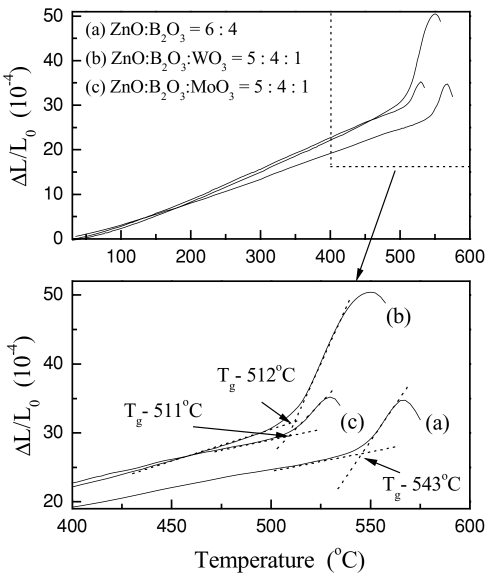

Fig. 2 TMA curves of $(60-x)$ZnO-40B_2O_3-$x$$MO_3$ glasses as a function of temperature ($x=0$ and $x=10$)

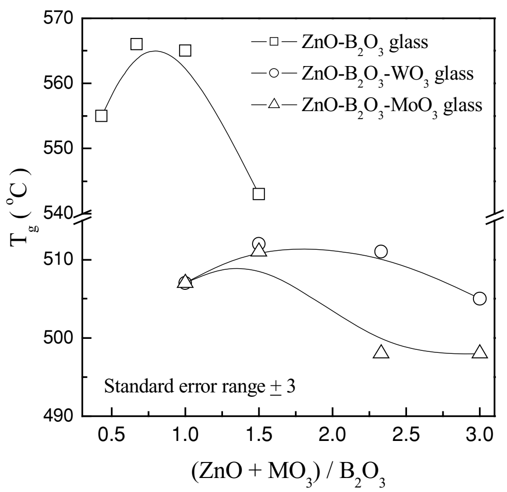

Fig. 3 Glass transition temperature (T_g) of ZnO-B_2O_3-MO_3 glasses as a function of (ZnO + MO_3)/B_2O_3 ratio (MO_3: 0 and 10 mol%)

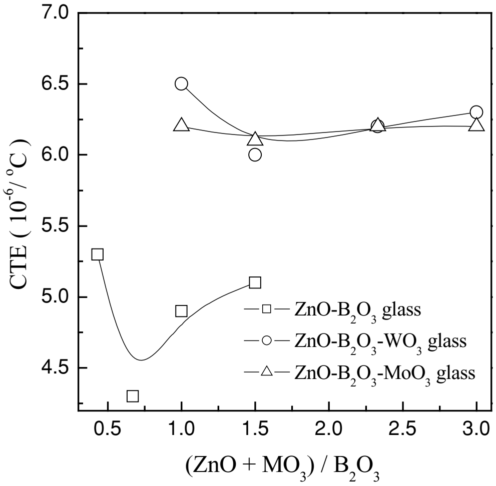

Fig. 4 The coefficient of thermal expansion (*CTE*) of ZnO-B_2O_3-MO_3 glasses as a function of (ZnO + MO_3)/B_2O_3 ratio (MO_3: 0 and 10 mol%)

the ratio of (ZnO + MO_3) to B_2O_3 is one, T_g of the glass in ZnO-B_2O_3 binary is 565°C, whereas T_g of the glass in ZnO-B_2O_3-MO_3 ternary is 507°C. Also, the compositions with MO_3 could form the transparent glasses even in the high ratio of (ZnO + MO_3) to B_2O_3. In other words, the addition of MO_3 to the compositions could induce the reduction of T_g and the expansion of glass forming region. In addition, the extremum behavior that T_g shows a marked maximum is observed, termed "the boron anomaly" [8], irrespective of the addition of MO_3.

The *CTE* of the glasses is represented as a function of (ZnO + MO_3)/B_2O_3 ratio in Fig. 4. The *CTE* of the glasses containing MO_3 is higher than that of glasses in ZnO-B_2O_3 binary, as was expected. When the ratio of (ZnO + MO_3) to B_2O_3 is one, *CTE* of the glass in ZnO-B_2O_3 binary is 4.9 ppm/°C, whereas *CTE* of the glass in ZnO-B_2O_3-MO_3 ternary is ∼6.3 ppm/°C. It is noteworthy that the *CTE* of the glasses in ZnO-B_2O_3 binary changes largely according to the ratio of ZnO to B_2O_3, whereas *CTE* of the glasses in ZnO-B_2O_3-MO_3 ternary changes slightly.

Figure 5 shows the dielectric constant (ε_r) of $(60-x)$ ZnO-40B_2O_3-xMO_3 glasses with $x=0$ and 10 as a function of frequency, as an example. In ZnO-B_2O_3-MO_3 glasses, the dielectric constants remain relatively constant over the range from 1 kHz to 10 MHz. Unfortunately, ε_r of all the glasses in the lower range of less than 1 kHz was not clean because of the large mechanical error in the determination. The ε_r of the glass with WO_3 or MoO_3 substitution for ZnO is lower than that of glass in ZnO-B_2O_3 binary. Also, typical dielectric loss (tanδ) values, measured at 1 MHz, of all the glasses were in the range of 10^{-3} (not shown). In addition, the thermal (T_g, *CTE*) and dielectric (ε_r) properties of ZnO-B_2O_3-MO_3 (M = W, Mo) glasses is summarized in Table 1.

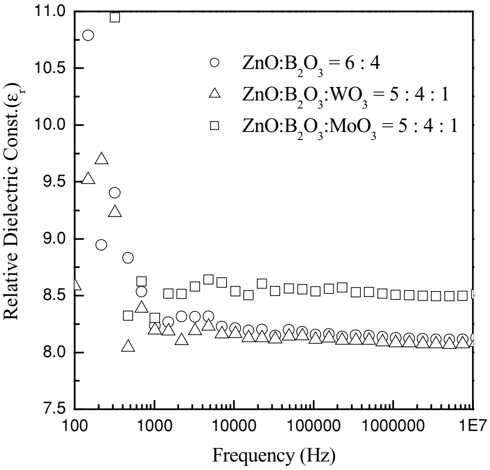

Fig. 5 The dielectric constant (ε_r) of $(60 - x)$ZnO-40B_2O_3-$x$$MO_3$ glasses as a function of frequency ($x = 0$ and $x = 10$)

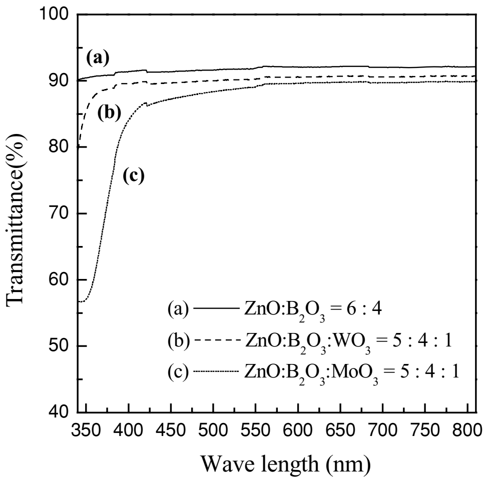

Fig. 6 The transmittance of $(60 - x)$ZnO-40B_2O_3-$x$$MO_3$ glasses in the visible-light region ($x = 0$ and $x = 10$)

Figure 6 shows the transmittance of $(60 - x)$ZnO-40B_2O_3-$x$$MO_3$ glasses with $x = 0$ and 10 as a wave length, as an example. Bulk glass having 0.5 mm thickness was used for the photospectrometry after polishing with diamond pastes (1 μm). As shown in Fig. 6, the 60ZnO-40B_2O_3 glass showed above 90 % transmittance in the visible light region. Though the transmittance of the glasses with MO_3 addition was slightly lower than that of 60ZnO-40B_2O_3, that of the glasses showed near 90% transmittance. It is noteworthy that the transmittance of the glasses with MO_3 addition in the near ultraviolet region decreased drastically. It could be explained at the outset that the absorption of light in the ultraviolet region is determined by its interaction with the oxygen ions of the glass [10]. The more weakly the O^{2-} ions are bound, the more easily this can occur. The introduction of network modifiers (i.e. W, Mo ions) can bring about the formation of non-bridging oxygens with simply bound O^{2-} ions. These can be more easily excited so that absorption takes place even with light of less energy and the absorption edge can be shifted in to longer wave region.

4 Discussion

The merits of glasses containing transition metal oxides (WO_3, MoO_3, etc.) have already attracted many glass scientists due to their electrochemical and electro-optic properties. In this work, T_g, *CTE* and ε_r of ZnO-B_2O_3-MO_3 glasses presented here can help to define potential compositions for low-firing temperature applications, such as the dielectric layers for PDPs technologies. The incorporation of MO_3 into ZnO-B_2O_3 binary could enhance the glass formation, although devitrification limited the glass forming range. When B_2O_3 as a network former was even in 25 mol%, the transparent glasses were obtained. Warren reported that the incorporation of a third component in the binary glasses could increase glass formation because of the change of glass structure [9]. WO_3 and MoO_3 in the intermediate class of glass forming oxides could enhance the glass formation even in the less range of B_2O_3.

The incorporation of MO_3 into ZnO-B_2O_3 binary could lower T_g of all the glasses. As seen in Table 1, the substitution of MO_3 for B_2O_3, a network former, gives a rapid decrease in T_g. The substitution of MO_3 for ZnO gives a slight decrease in T_g, too. These results suggest that both WO_3 and MoO_3 act mostly as the network modifiers and break the network structure more largely than ZnO. Recently, Prasad et al. reported the structure and the electric properties of PbO-MoO_3-B_2O_3 glass system [6]. According to them, with the increase in the concentration of MoO_3 in the glass matrix, the positions of the vibration modes of MoO_4 groups in the infrared (IR) transmission spectra were shifted towards higher wavenumber with the decreasing intensity indicating the decrease in the concentration of Mo ions that take part in network forming positions in the glass network. The electron spin resonance (ESR) and IR spectra suggested that the Mo ions existed in Mo^{5+} state with $Mo^{5+}O_3^-$ complexes that act as modifiers in addition to Mo^{6+} state with MoO_4 and MoO_6 structural groups in PbO-MoO_3-B_2O_3 glass system. These facts suggest that M ions (W, Mo) can exist mostly in M^{5+} state with $M^{5+}O_3^-$ complexes in ZnO-B_2O_3-MO_3 glass system. Further studies are needed to assess the exact states of W and Mo ions. These glasses with a low T_g in ZnO-B_2O_3-MO_3 glass system can be sintered at a low temperature (normally at 550–580°C [1]) for a dielectric layer in PDPs.

The incorporation of MO_3 into ZnO-B_2O_3 binary could increase *CTE* of all the glasses close to that of a glass substrate (∼8 ppm/°C). The primary reason for this is probably related to the addition of MO_3 as a modifier. By adding MO_3 to substitute MO_3 for B_2O_3 or ZnO, as seen in Table 1, the glasses containing MO_3 probably could form more non-bridging oxygen, which is known to increase *CTE*.

All the glasses in ZnO-B_2O_3-MO_3 glass system have the moderate ε_r (normally below 15 [1]) for a dielectric layer in PDPs. The ε_r of the glass with WO_3 or MoO_3 substitution for ZnO is lower than that of glass in ZnO-B_2O_3 binary. Appen and Bresker [9] have provided the equation calculating the ε_r of glasses theoretically. The equation for calculation of ε_r is given as $\varepsilon_r = 1/100\ \Sigma \varepsilon_{ri} p_i$, where p_i represents the portion of the individual oxides in mol% and ε_{ri} is the dielectric constant factor for each oxide: ZnO is 14.4 and B_2O_3 is 3–8. Unfortunately, the factor of WO_3 or MoO_3 is not yet known. Therefore, the dielectric constant factor of MO_3 on the glasses was calculated based on the current results, in order to assist future research in the area. The calculated dielectric constant factor of MO_3 on the glass of M2 composition in Table 1, was found to be approximately 10. This value is fairly reasonable less than ZnO.

5 Conclusion

We suggested ZnO-B_2O_3-MO_3 (M = W, Mo) as a potential replacement for Pb-based glasses for the dielectric layer in PDPs. Although there are several requirements such as the transparency after firing (above 80%) and break down voltage (above 9 kV at 20 μm), we examined the thermal, optical and dielectric properties fundamentally before applying them commercially. The addition of MO_3 to ZnO-B_2O_3 binary could induce the expansion of glass forming region, the reduction of T_g, the increase in the *CTE* close to that of the glass substrate and the moderate dielectric constant of the glasses. The preferred composition in ZnO-B_2O_3-MO_3 ternary is 55ZnO-30B_2O_3-15MoO_3: ($T_g = 470$°C, $CTE = 6.4$ ppm/°C, $\varepsilon_r = 8.9$ at 1 MHz). This developed glass composition has the lower T_g and the more moderate ε_r than the previously reported non-Pb glasses (i.e. BaO-B_2O_3-ZnO [1]). Though *CTE* of that has rather low value, the addition of the other modifiers (i.e. Bi ion) [11] can induced moderate *CTE* and the lower T_g, and that study is in progress. These developed glasses may be used not only as a material for Pb-free dielectric layers for PDPs but also as a material for the sealing glass in the display devices and a sintering aid for low temperature co-fired ceramic (LTCC) technologies.

Acknowledgments This research was supported by a grant from the Center for Advanced Materials Processing (CAMP) of the 21st Century Frontier R&D Program funded by the Ministry of Science and Technology, Republic of Korea.

References

1. D.N. Kim, J.Y. Lee, J.S. Huh, and H.S. Kim, *J. Non-Cryst. Solids*, **306**, 70 (2002).
2. R. Morena, *J. Non-Cryst. Solids*, **263 & 264**, 382 (2000).
3. H. Masuda, R. Kimura, N. Sakamoto, and K. Morinaga, *J. Jpn. Inst. Met.*, **63**(3), 284 (1999).
4. M.L. Cha, J.S. Jeon, and H.S. Kim, *Eco-Mater. Processing & Design VI Mater. Sci. Forum*, **486–487**, 325 (2005).
5. H.S. Zhao, Y.Q. Li, W.C. Zhou, F. LuO, and C.H. Tang, *J. Inor. Mat.*, **20**(3), 563 (2005).
6. P. Subbalakshmi and N. Veeraiah, *J. Non-Cryst. Solids*, **298**, 89 (2002).
7. P.S. Prasad, B.V. Raghavaiah, R.B. Rao, C. Lamikanth, and N. Veeraiah, *Solid State Comm.*, **132**, 235 (2004).
8. A.K. Varshneya, *Fundamentals of Inorganic Glasses* (Academic Press, San Diego, 1994), p. 107.
9. B.E. Warren, *J. Am. Ceram. Soc.*, **17**, 249 (1934).
10. H. Scholze, *Glass, Nature, Structure, and Properties* (Springer, New York, 1991), pp. 232, 318.
11. I. Dyamant, D. Itzhak, and J. Hormadaly, *J. Non-Cryst. Solids*, **351**, 3503 (2005).