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Mixed alkali effect on the luminescence characteristics of color conversion glasses

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The influence of K_2O/R_2O ($R_2O = Na_2O + K_2O$) on some characteristics of color conversion glass were studied using a BaO-ZnO-B_2O_3-SiO_2 glass. One reference glass, comprised of 40 mol% of BaO and 20 mol% of the other three components, was used, and 5 wt% of an alkali oxide was added to the other five glass samples. The ratio of the alkali oxides used were K_2O/R_2O (where $R_2O = Na_2O + K_2O$) 0, 0.25, 0.5, 0.75, and 1. Six color conversion glass samples were prepared by sintering a mixture of glass frits and a YAG phosphor. The content of the YAG phosphor was maintained at 5 wt%. The characteristics of the color conversion glasses, with respect to luminous efficacy, CIE (Commission International de I'Eclairage) chromaticity, CCT (Correlated Color Temperature), and CRI (Color Rendering Index) were analyzed based on PL spectra. The luminescence properties of the color conversion glass with $K_2O/R_2O = 0.5$ were nearly identical to those for the reference glass even though it contained 5 wt% alkali oxides.

Key words: Mixed alkali effect, Color conversion glass, Glass composition, YAG phosphor.

Introduction

The white light-emitting diodes (WLEDs), a potentially new light source, have the potential to replace the conventional fluorescence lamp. In general, WLEDs consist of yellow phosphor (YAG:Ce^{3+}) and a blue LED chip. The blue light emitted from blue LED chip excites the YAG phosphor, and then blue light is mixed with the yellow light to generate white light. In the quality of white LEDs, the homogeneity of the phosphor layer is a key determinant. Color conversion glasses containing a dispersed yellow phosphor are promising materials because of their thermal durability, chemical stability, and anti-ultraviolet properties [1, 2]. When glass materials are used as a host for a phosphor, the thermal and chemical stabilities are enhanced. In addition, such glasses show less deformation at high temperature. Optical characteristics, such as transparency and reflection, are relatively constant at any temperature. To improve the color rendering of white LED, the phosphor in the red light region needs to be reinforced [3]. However, red phosphors have poor heat-resistance, so, in such a situation, the glass that is used as a host for the phosphor must have a low glass transition temperature.

It is well known that mixed glass that contains an alkali oxide has interesting characteristics called the mixed alkali effect, particularly the nonlinear dependence of their properties on the relative concentration of the two alkali oxides. Among the properties, chemical durability also showed a maximum value at a typical K_2O/R_2O value ($R_2O = Na_2O + K_2O$) [4]. As a result, we adapted the mixed alkali effect to BaO-ZnO-B_2O_3-SiO_2 color conversion glass to minimize the degradation of the phosphor in the glass matrix.

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Experimental

Table 1 contains the composition of the six experimental glasses. The raw materials used were $BaCO_3$ (98%, Junsei, Japan), ZnO (99%, Junsei, Japan), B_2O_3 (95%,

Table 1. The composition of glass samples in the BaO-ZnO-B_2O_3-SiO_2 system.

Code	Glass Code	Base composition (mol%)	Total (wt%)	K_2O/R_2O	Total (wt%)
KPG-023	KFP-023	40BaO-20ZnO-20B_2O_3-20SiO_2	100	–	0
KPG-041	KFP-041		95	0	5
KPG-042	KFP-042			0.25	
KPG-043	KFP-043			0.5	
KPG-044	KFP-044			0.75	
KPG-045	KFP-045			1	

Junsei, Japan), SiO_2 (extra pure, Daejung, Korea), K_2CO_3 (extra pure, Daejung, Korea), and Na_2CO_3 (extra pure, Daejung, Korea). KFP-023, which contains 40 mol% of BaO and 20 mol% of the other three components, was used as a reference. In cases of KFP-041 to 045, the content of the mixed alkali was kept at 5 wt% and the molar ratio of Na_2O and K_2O was changed from a K_2O/R_2O value of 0 to 1.

To produce the glass frit, each glass batch was blended for 12 hours in a milling machine. One batch, not containing mixed alkali, was melted for 2 hours at 1400 °C, while the others were melted at 1300 °C in a alumina crucible. Each melt was passed through two stainless rolls to produce a ribbon cullet. Each ribbon cullet was then ground in an alumina mill for 2 hours to produce a glass frit and was then sieved to produce 270 mesh particles. In the next step, 5 wt% YAG ($Y_3Al_5O_{12}:Ce^{3+}$, DLP-Y60-15, Daejoo Electronic Materials Co., Ltd, Korea) phosphors were mixed with each glass frit, and a 4g sample of the mixed powder was placed in a 30Φ mold and was pressed under a pressure of 2-3 tons for 1 minute. The final product was a yellow-green-colored material. The sintering temperature of this yellow material was set at 100 °C higher than the T_g of each glass frit. The yellow material was heated at this sintering temperature for 30 minutes to produce a sintered product. The sintered material was then processed to produce a color conversion glass sample with a thickness of 1 mm.

For the characterization of glass samples, the glass transition temperature (T_g, DTG-60H, Shimadzu, Japan) was measured. To evaluate of the distribution of the phosphor in a color conversion glass, composition mapping was performed by XRF (XGT-5000, Jasco, Japan). Structural changes in the YAG phosphor after sintering were observed by X-ray diffraction analysis (X-ray diffractometer, Rigaku, Japan).

The photonic characteristics of the color conversion glasses such as luminous efficacy, CIE (Commission International de I'Eclairage) coordinates, CCT (Correlated Color Temperature), and CRI (Color Rendering Index) were measured by an integrating sphere (LMS-400IPT, J&C, Korea).

Results and Discussion

Fig. 1 shows the dependence of transition temperature (T_g) on the K_2O/R_2O ratio of the matrix glasses. The T_g values decreased with the addition of alkali oxides and then increased again with increasing K_2O/R_2O. The departure of glass viscosity from linearity is a typical characteristic of mixed alkali glasses, but the departure of glass viscosity from linearity was found to be small compared to the previously reported values, with only one little inflection point at $K_2O/R_2O = 0.75$ [5]. The addition of alkali oxides is an effective method for reducing the sintering temperature of color conversion glasses for maintaining the luminous properties of the phosphor itself. Fig. 2 shows XRF mapping images for each sample. Through the XRF mapping of yttrium in the color conversion glass, it is possible to determine that the YAG phosphors were evenly dispersed in the color conversion glasses.

Fig. 3 shows a PL emission spectrum of color conversion glasses excited at a blue wavelength (λ_{ex} = 448 nm). A peak at around 548 nm (yellow light) in the emission spectrum is due to the 5d-4f transition of Ce^{3+} ion, i.e., from the 5d states back to the 4f states [6, 7]. Color conversion glasses containing a mixed alkali oxide showed excellent luminescence properties compared to those containing only one kind of alkali, such as Na_2O or K_2O. The intensity of the PL emission spectra of $K_2O/R_2O = 0.5$ was the highest among the mixed alkali oxide glasses, the value of which was similar to that of the reference glass sample. Fig. 4 shows the luminous efficacy of the six color conversion glasses. The luminous efficacy and luminance showed the same tendency as the intensity of the PL spectrum. The luminous efficacy showed a maximum value of $K_2O/R_2O = 0.5$ and showed a minimum value of $K_2O/R_2O = 0$ and 1, respectively. In general, a glass containing an alkali oxide shows poor chemical durability, but the mixed alkali glasses prepared in this study showed the maximum chemical resistivity between the range of $K_2O/R_2O = 0.25 \sim 0.75$ [4]. The high luminous efficacy of $K_2O/R_2O = 0.5$ can be attributed to the inertness of the mixed alkali glass, caused by its high chemical durability. Phosphor degradation during the sintering process might be minimized by the inertness resulting from the high chemical resistivity.

Fig. 5 shows a CIE chromaticity diagram of the color conversion glasses under excitation by a 448 nm LED. The color coordinate for the color conversion glasses was found to be a balance of 465 nm excitation light and the excited luminescence. The variation in the CIE color coordinate did not show any typical trend, but a

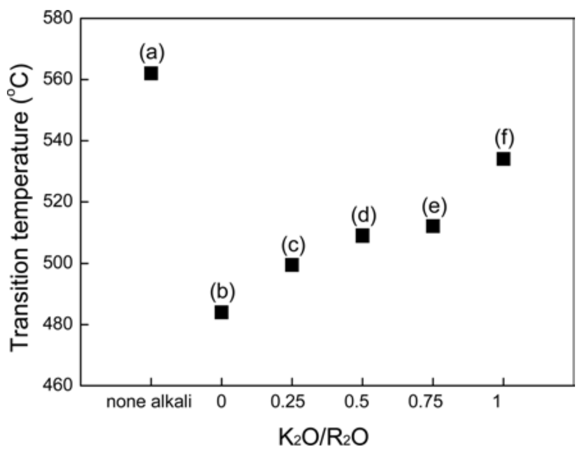

Fig. 1. Change in glass transition temperature (T_g) as a function of K_2O/R_2O: (a) KFP-023, (b) KFP-041, (c) KFP-042, (d) KFP-043, (e) KFP-044 and (f) KFP-045.

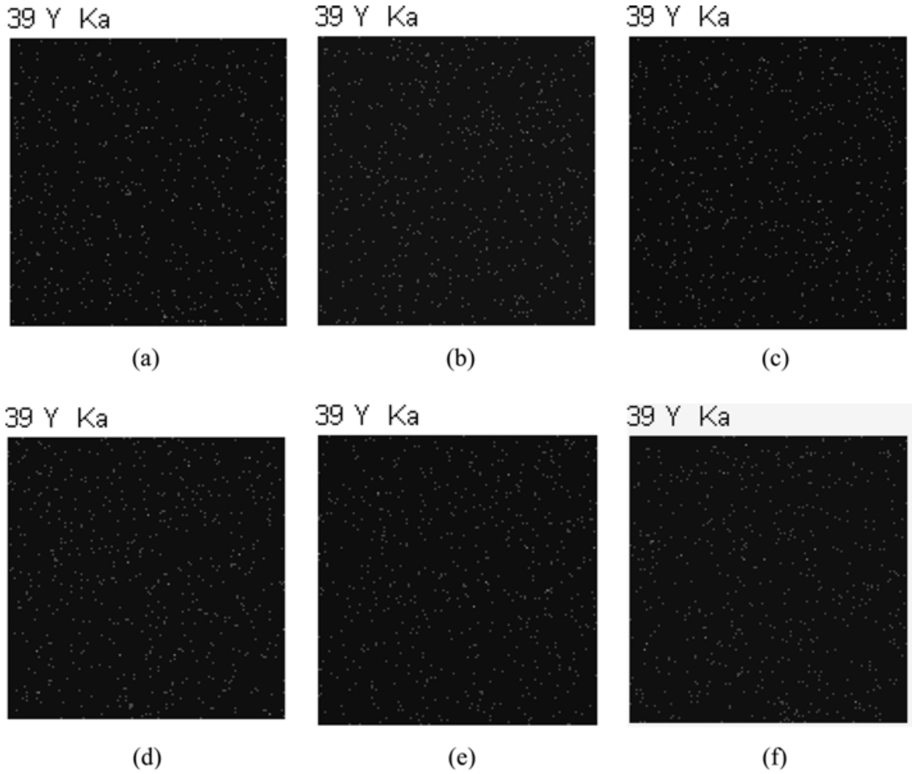

Fig. 2. XRF mapping photographs of color conversion glasses: (a) KPG-023, (b) KPG-041, (c) KPG-042, (d) KPG-043, (e) KPG-044 and (f) KPG-045.

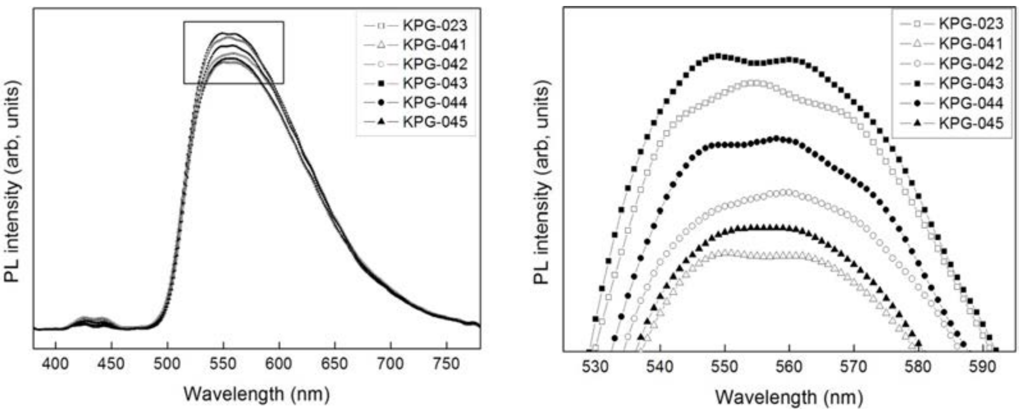

Fig. 3. PL emission spectrum of color conversion glasses (λ_{ex} = 448nm).

shift to the up-right direction with increasing K_2O/R_2O was observed. However, the color coordinates they showed were closest to that of yellow light, with a high PL intensity peak at 530 nm, far from the theoretical white point of (0.33, 0.33). It should be noted, however, that color coordination can be controlled by adjusting the concentration of the phosphor and the thickness of the sample [7]. Therefore, the KPG-043 color coordinates can be easily shifted to a white color by controlling either the YAG and red phosphor concentration or the sample thickness. Fig. 6 shows the CCT and CRI for the six color conversion glasses. Light sources have two important color specifications: Correlated Color Temperature (CCT) and Color Rendering Index (CRI). Generally, the lighting has

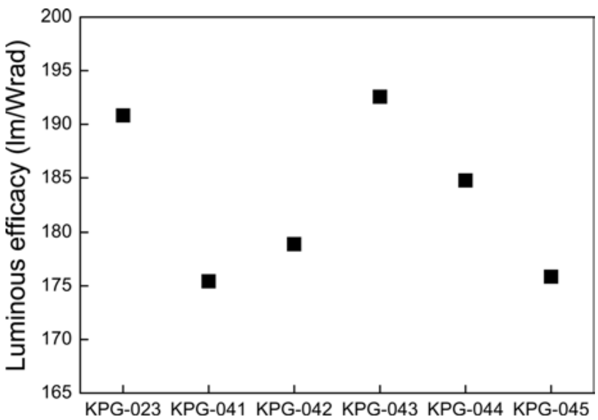

Fig. 4. Luminous efficacy of color conversion glasses.

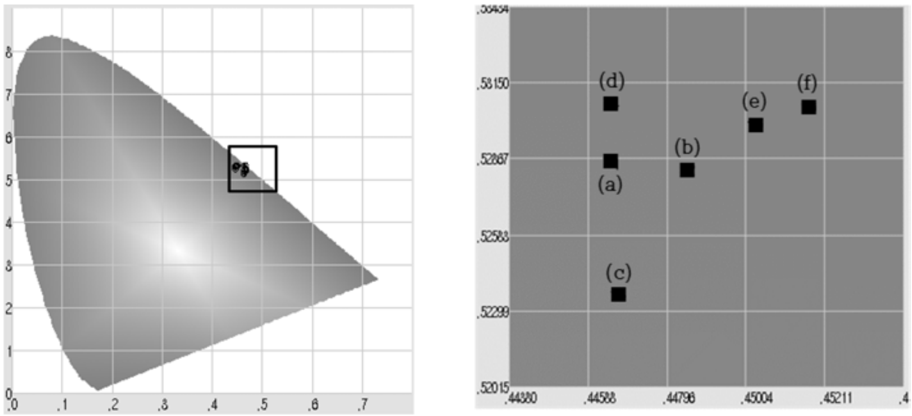

Fig. 5. CIE chromaticity coordinates of color conversion glasses: (a) KPG-023, (b) KPG-041, (c) KPG-042, (d) KPG-043, (e) KPG-044 and (f) KPG-045.

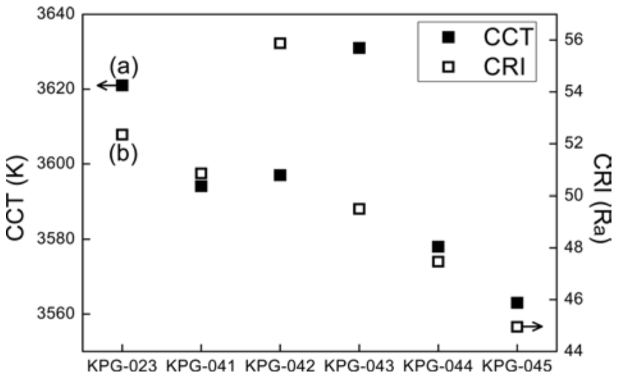

Fig. 6. Optic properties of color conversion glasses: (a) CCT and (b) CRI.

CCTs ranging from 5,000 to 5,500K and all CCTs in this range appear to be quite close to neutral white [8].

The CCT was found to be consistent with the CIE chromaticity diagram. The CCT values of all of the color conversion glasses were somewhat lower than that of neutral white, with a yellow color. The CCT values decreased with the addition of alkali components and with an increase in the K_2O/R_2O ratio, except for KPG-043. All the color conversion glasses showed a warm color in the 3554 ~ 3630 range. The CRI is a number, expressed as a percentage, which indicates the ability of a light source to show different colors accurately compared with a standard source. The higher the CRI, the better the colors look under the light. If the CRI is poor, the light source would not be useful for general lighting [8, 9]. The CRI values were decreased with the addition of alkali components and with an increase in the K_2O/R_2O values. The reference sample KPG-023 was found to have the highest value. It should be noted that the CRI can be improved by the addition of a red phosphor having poor thermal durability [10] because a mixed alkali oxide glass can be sintered at a lower temperature.

Fig. 7 shows the results of the XRD analyses of the six color conversion glasses. All of the samples showed peaks for the YAG phosphor. All the alkali-oxide-containing samples showed additional peaks, corresponding to $BaZnSiO_4$, for example. In the case of $K_2O/R_2O = 1$, a new peak assigned to $KAlSiO_4$ was found. Alkali oxides showed a trend toward crystallization of color conversion glasses. Because of this, the glass composition should be designed so as to prevent such crystallization.

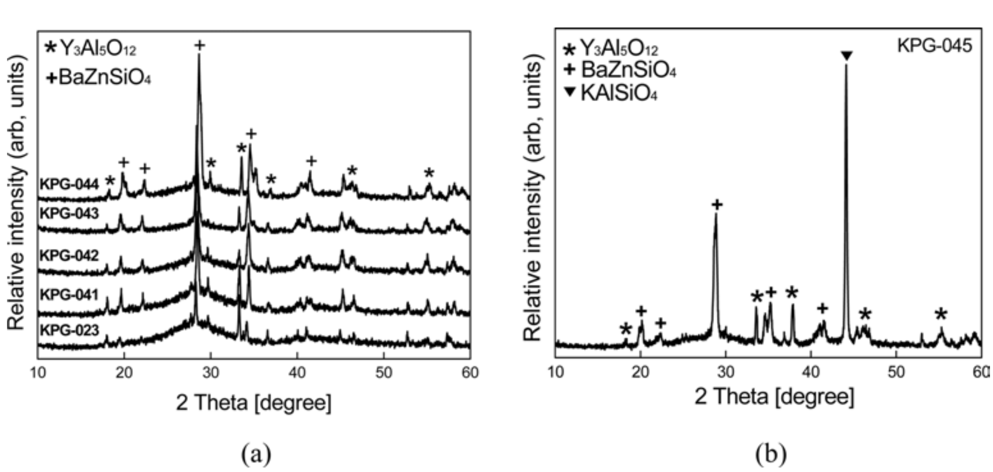

Fig. 7. XRD patterns of color conversion glasses: (a) KPG-023 and KPG-041~044, (b) KPG-045.

Conclusions

The impact of the mixed alkali effect on the luminescence characteristics of color conversion glasses was studied using BaO-ZnO-B_2O_3-SiO_2 glass as a glass matrix. The addition of an alkali oxide has the merit of lowering the T_g value of glass but also lowers the luminescence characteristics of color conversion glasses. The mixed alkali containing color conversion glasses, however, showed superior characteristics to other types of alkali containing glasses. Among the mixed alkali glass samples, the $K_2O/R_2O = 0.5$ color conversion glass showed almost the same luminous efficacy as the reference glass, even though it can be sintered at a lower temperature with the help of an alkali oxide. Such a mixed alkali effect can be used effectively in a color conversion glass when a red phosphor, which has a low thermal stability, is used to control the CRI.

Acknowledgments

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