The Effect of Cerium Reduction on Light Emission in Cerium-containing 20Y₂O₃-25Al₂O₃-55SiO₂ Glass

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The effect of cerium concentration and the addition of Sb₂O₃ on the light emission of cerium-contained glass were investigated. The glass matrix composition was 20Y₂O₃-25Al₂O₃-55SiO₂, the CeO₂ concentration ranged from 0.05 to 0.5 mol%, and Sb₂O₃ was added at concentrations of 0.02 to 0.1 mol%. The Ce³⁺ and Ce⁴⁺ absorption bands were observed at approximately 330 nm and 240 nm, respectively. A broad emission band at 400 nm, due to the 4f-5d transition of the Ce³⁺ ion, was observed under illumination by a UV light at 330 nm. The photoluminescence intensity of Ce³⁺ had a maximum value at a CeO₂ concentration of 0.1 mol%. Adding Sb₂O₃ decreased the Ce⁴⁺ absorption intensity and enhanced the light emission intensity of Ce³⁺ by about 45%.

Keywords : Photoluminescence, Glass phosphors, Cerium, Reduction

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I. INTRODUCTION

High power LEDs have undergone rapid development in recent years. The heat produced by high power LEDs induces deterioration of the transparent resin used for wrapping and fixing the powder phosphors onto the power chip [1]. As an alternative to resin, Tanabe et al. investigated the use of glass-ceramics for a novel durable phosphor for use in LED systems [1-2]. Glass phosphors for use in LEDs have also been investigated by several other research groups [3-5]. In spite of their good thermal durability, applying glass phosphors to LED products is quite difficult, because the light emission intensity and efficiency are relatively lower than those of the crystalline phosphors.

Glass does not have homogeneous site symmetry, therefore, the activator ion experiences a random distribution of local fields and, as a consequence, the light emission intensity is low [6-7]. Several activators also tend to build multivalent ion states in the glass [8-9]. In particular, cerium has two types of ions, viz. Ce³⁺ and Ce⁴⁺ [9]. However, only the Ce³⁺ ion has light emission properties. Therefore, if the Ce³⁺ proportion is increased in the glass, it is expected that the light emission efficiency of the glass phosphor

could be enhanced, and potentially be applied to LED lamps.

The final goal of this study is to enhance the light emission intensity in the cerium-containing glass, by increasing the Ce³⁺ proportion. This study reports the effects of: 1) cerium concentration; and 2) addition of Sb₂O₃ as a reduction agent in cerium-containing 20Y₂O₃-25Al₂O₃-55SiO₂ glass. To verify such effects, the light emission properties were characterized with various concentrations of CeO₂ and Sb₂O₃.

II. EXPERIMENTS

20Y₂O₃-25Al₂O₃-55SiO₂ glass samples were prepared using a conventional quenching method under oxidizing conditions. Commercial Y₂O₃, Al(OH)₃ and SiO₂ reagent grade powders were mixed by a 3D-turbulent mixer. The mixture was placed in an alumina crucible and melted at 1550°C for 4 h in an electric furnace. CeO₂ was added to the host glass in the concentration range of 0.05 to 0.5 mol% and Sb₂O₃ was added from 0.02 to 0.1 mol%. The prepared glasses were annealed at the glass transition temperature, and thereafter, lapped and polished to 2 mm thickness and

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mirror surface. The light absorption spectra were measured by UV-visible (JASCO V-570) and the photoluminescence spectra were measured by PL-spectroscopy (PSI, DARSA Pro-5200, Xe light source) in the reflection mode.

III. RESULTS AND DISCUSSION

3.1. Light Absorption Spectra

Figure 1 shows the optical absorption spectra of the cerium-containing $20\text{Y}_2\text{O}_3\text{-}25\text{Al}_2\text{O}_3\text{-}55\text{SiO}_2$ glasses. Two broad, strong absorption bands were observed in the UV region. Ce^{3+} exhibited an absorption band at around 330 nm and a broad absorption spectrum with a maximum value at 240 nm due to a charge transfer band of Ce^{4+} .

FIG. 1. The optical absorption spectra of cerium-containing $20\text{Y}_2\text{O}_3\text{-}25\text{Al}_2\text{O}_3\text{-}55\text{SiO}_2$ glasses. The concentration of cerium oxide ranged from 0.05 to 0.5 mol%.

FIG. 2. The Ce^{3+} photoluminescence spectra of cerium-containing $20\text{Y}_2\text{O}_3\text{-}25\text{Al}_2\text{O}_3\text{-}55\text{SiO}_2$ glasses. The wavelength of the excitation light is 300 nm. The concentration of cerium oxide ranged from 0.05 to 0.5 mol%.

The entire absorption intensity was increased and the Ce^{3+} absorption peak shifted to longer wavelengths as the cerium concentration increased.

Stroud reported a Ce^{3+} absorption band at 320 nm and a Ce^{4+} charge transfer band in the ultraviolet range in sodium-silicate glass [11]. Absorption spectra in this study showed good agreement with previous results (Fig. 1) [7, 10].

Figure 2 shows the Ce^{3+} emission spectra for different CeO_2 amounts. There is a maximum value at approximately 400 nm upon 330 nm excitation. The emission intensity increased remarkably at a cerium concentration of 0.1 mol%. However, the emission intensity gradually decreased at cerium concentrations greater than 0.1 mol%. The decrease can be attributed to the concentration quenching due to the reduced ion-ion distance and the increased excited state interactions between Ce^{3+} ions.

Possible modification of the local structure due to increased CeO_2 content may be responsible for the red-shift of the absorption and emission band of Ce^{3+} ions as the additional CeO_2 can change the glass structure, producing non-bridging oxygen atoms and altering the covalency and optical basicity of nearby Ce^{3+} ions [14]. As covalency increases, the interaction between the electrons is reduced, so they spread out over wider orbitals [15]. Consequently, an increase in the covalency will reduce the energy difference between the ground and the excited states. This increase in covalency may lead to a shifting of the emission band and absorption band to a longer wavelength. A similar shift due to optical basicity has been observed in 6s-6p transition of Pb^{2+} [12]. The study has shown that the increase of optical basicity resulted from an increase of the degree of Pb-O covalency and led to the shifting of the absorption band to a longer wavelength. Thus, although the nephelauxetic effect [16] is a plausible cause of the red-shift, further study is required to investigate the changes within the local structure to fully understand the observed behavior.

3.2. The Effect of Cerium Ion Reduction by Sb_2O_3

Figure 3(a) shows the optical absorption spectra for different amounts of Sb_2O_3 in 0.1 mol% CeO_2 glass. The curves exhibited the typical spectra of Ce^{3+} ions and Ce^{4+} ions. The entire absorption intensity was radically decreased by introducing Sb_2O_3 . A Ce^{3+} band shift due to changing the amount of Sb_2O_3 was not observed.

The addition of Sb_2O_3 has a proven reduction effect in the glass, similar to As_2O_3 [9]. Kim *et al.* investigated the effect of Sb_2O_3 in cerium-containing lithium-silicate glass and found that, Sb_2O_3 is the most effective to reduce the cerium ion, among the various adopted materials in the applied glass system [13]. The cerium is reduced via the following reaction at high temperatures [9]:

The Ce^{3+} absorption spectra of Sb_2O_3 -containing glasses

FIG. 3. The optical absorption spectra of Sb_2O_3 -containing glasses. The cerium oxide concentration is 0.1 mol%, the Sb_2O_3 concentration ranged from 0.02 to 0.1 mol%. (a) the change of the absorption spectra (b) the fraction of the Ce^{3+} peak value and the Ce^{4+} peak value.

showed a similar line shape and distribution and there was no noticeable shift. The overall absorption intensity decreased upon introduction of Sb_2O_3 . The reduced oscillation strength of the Ce-ions, which was induced by the local environmental change, may be responsible for the change. However, the origin of the overall decrease needs further study. It should be mentioned that the absorption peak due to Ce^{4+} decreased markedly compared to that of Ce^{3+} . This clearly indicates the role of Sb_2O_3 reducing Ce^{4+} as suggested in equation (1).

Figure 3(b) indicates the value of the $\text{Ce}^{3+}/\text{Ce}^{4+}$ ratio for different Sb_2O_3 amounts. This ratio is simply expressed by the fraction of the Ce^{3+} peak value and the Ce^{4+} peak value. This calculation method suggested by Kim *et al.* [13], is useful for estimating the slope of the Ce^{3+} proportion variation. In this work, the proportion of Ce^{3+} increased linearly with Sb_2O_3 content.

Figures 4(a) and (b) show the excitation and the

FIG. 4. The photoluminescence spectra of Sb_2O_3 -containing glasses. The cerium oxide concentration was 0.1 mol%, Sb_2O_3 concentration ranged from 0.02 to 0.1 mol%. (a) the excitation spectra (b) the emission spectra upon 330 nm excitation.

emission spectra, respectively, of Sb_2O_3 -containing glasses. A strong excitation band was observed at 330 nm, regardless of the Sb_2O_3 amount. This value corresponded to the Ce^{3+} band of the absorption spectrum (Fig. 3(a)). The emission spectra exhibited the luminescence of Ce^{3+} ions with a maximum at 400 nm upon 330 nm excitation. Both the excitation and the emission intensity were enhanced by approximately 45 % compared to Sb-free glass. This enhancement is related to the increase of the Ce^{3+} activator concentration due to the Sb_2O_3 effect. As a result, the introduction of Sb_2O_3 to cerium-containing glass increased the proportion of Ce^{3+} ions and enhanced the intensity of the photoluminescence without atmospheric control.

IV. CONCLUSIONS

Intrinsic light absorption and photoluminescence of cerium-

contained 20Y₂O₃-25Al₂O₃-55SiO₂ glass were investigated. The resulting effect of cerium concentration and reduction with Sb₂O₃ was then studied.

The Ce³⁺ absorption band and emission band shifted to longer wavelengths according to an increase of the cerium oxide content due to the nephelauxetic effect. The light absorption intensity of the Ce⁴⁺ charge transfer band radically decreased as a result of the cerium ion reduction reaction with the introduction of Sb₂O₃. The proportion of Ce³⁺ was increased gradually and the ratio of Ce³⁺/Ce⁴⁺ increased linearly by increasing the amount of Sb₂O₃. Consequently, photoluminescence intensity was enhanced by approximately 45 % compared to that of Sb-free glass. Therefore, Sb₂O₃ is considered an effective reduction additive in the preparation of a glass phosphor that does not require atmospheric control.

This fundamental study is the basis for further investigations with regard to a YAG:Ce glass-ceramic phosphor.

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