Journal of the Korean Ceramic Society
Vol. 52, No. 2, pp. 119~122, 2015.

http://dx.doi.org/10.4191/kcers.2015.52.2.119

Laser-Heating Characteristics of CuO-Incorporating Glasses

Jungki Lee, Jongwoo Kim*, and Hyungsun Kim†

School of Material science and Engineering, Inha University, Incheon 402-751, Korea
**Current address: LG CHEM LTD, Daejeon 305-738, Korea*

(Received January 16, 2015; Revised March 16, 2015; Accepted March 17, 2015)

ABSTRACT

Laser sealing with glass frits appears a promising technology for sealing various electronic devices (e.g., solar cells, displays) due to its several advantages. The purpose of this study is to understand the relationship between the composition of glasses and their laser-heating conditions. To allow glass to be sealed using laser heating, CuO was added to two different glass systems, in different amounts. The optical absorptivity of the glass samples was related directly to their CuO content. The laser-heating temperature and the CuO content exhibited a proportional relationship. Furthermore, the heating temperature increased linearly with the laser power used. From these results, we could determine the appropriate laser-heating conditions and CuO content for sealing electronic devices using laser-sealing technology.

Key words : Optical absorptivity, Laser-heating, Glass, CuO, Laser sealing

1. Introduction

Glass frits can be used as sealing materials for air tightening and protecting the insides of electronic devices from gases and moisture,[1-2] preventing device failure caused by water vapor. Furthermore, glass frits are chemically, thermally, and mechanically very stable. Therefore, glass frits have been studied extensively for use in sealing various electronic and electrical devices, such as plasma display panels, organic light-emitting diodes, and dye-sensitized solar cells.[3] Nevertheless, the conventional thermal sealing process causes significant damage to the rest of the device, as the temperatures involved are very high. Therefore, alternative laser-based sealing techniques, in which only the target area is heated, are being explored.[4] Laser sealing using low-glass-transition-temperature glass frits can potentially be used to form seals in electronic and electrical devices that are both durable and hermetic.[5]

To ensure the densification of the sealing material to the proper degree without causing thermal damage during the laser-heating process, the laser-heating temperature should be controlled. Before glass can be sealed using laser heating, it is necessary to increase the optical absorptivity of the glass at the wavelength corresponding to the laser used. It is well known that the optical absorptivity of many glass systems in the visible-light spectrum increases with the addition of *d*- and *f*-elements, such as iron, copper, chromium, and manganese.[6-8] Copper (II) oxide has been added as a constituent to various glass systems to allow them to be heated using a laser.[6] It has been reported that the Cu^{2+} ions partially fill the d-orbitals and create color centers in the glass, owing to the existence of an absorption band in the visible spectrum. Energy from the irradiated laser beam is absorbed by the transition metal ions (such as those of Cu^{2+} through d-d transitions) and the absorbed energy is converted into thermal energy through a non-radiative relaxation process.[8] Recently, transition-metal atom-heating processes have been studied extensively for the laser-induced treatment of glasses, including for controlling their degree of crystallization, and their morphology.[9,10]

The purpose of this study was to develop glass systems that can be sealed using laser heating, by understanding the relationship between the optical absorptivity of glasses and their characteristics when heated by a laser. We investigated two different glass systems (Bi_2O_3-B_2O_3-ZnO and SiO_2-B_2O_3-Na_2O). Their optical absorptivity was controlled by adding CuO to the systems. Two different homogeneously melted CuO-containing glass systems were produced, and the characteristics of the glasses when heated by a laser, were investigated in relation to different CuO content.

2. Experimental Procedure

2.1. Glass fabrication

The raw materials for the 35Bi_2O_3-25B_2O_3-40ZnO (BBZ glass) and 66SiO_2-17B_2O_3-17Na_2O (SBN glass) mother glass systems (in mol%) were prepared from high-purity chemical reagents (Bi_2O_3, H_3BO_3, ZnO, SiO_2, and Na_2O; purity > 99.9%; Sigma Aldrich, USA). CuO (> 99.9%; Sigma Aldrich, USA) was added to the mother glasses in amounts of up to 4.4 mol% to control the optical absorptivity of the

†Corresponding author : Hyungsun Kim
E-mail : kimhs@inha.ac.kr
Tel : +82-32-860-7545 Fax : +82-32-862-5546

glasses. The batches were homogeneously mixed by ball milling for 24 h and melted in an alumina crucible at 1100°C (BBZ glass) and 1300°C (SBN glass) for 30 min using an electric furnace. To form the frits, the glass melts were poured quickly on a ribbon roller and quenched. The cullets were pulverized using a planetary mono mill for 7 h. All the prepared bulk glass samples were bubble free and were machined to have the same thickness and surface roughness.

2.2 Characterization of glass and laser firing temperature

The optical absorptivity of the glasses was measured using an ultraviolet (UV)-visible spectrometer, by making five sets of measurements for wavelengths of 340–1100 nm. The glass transition temperature (T_g) was determined using a thermogravimetry-differential thermal analysis (TG-DTA) system (Rigaku, Japan). The measurements were performed at a heating rate of 10°C/min, and the samples were heated to 1200°C. The emissivity of the glasses was measured using a Fourier transform infrared spectrometry (FTIR) system (MIDAC M2410, MIDAC Corp., USA). A fiber laser (LC-aIII-Amada) with a wavelength (λ) of 1064 nm was used to irradiate the surfaces of the glass samples using an objective lens (20´ magnification) with increasing laser power. The laser irradiation conditions were power: 0.4 - 4 W, scan rate: 50 mm/s, laser frequency: 100 kHz, laser wavelength: 1064 nm, and spot size: 50 mm. The temperature of the glass surface after laser heating was measured with an infrared (IR) camera (FLIR SC325, FLIR Systems Inc., UK).

3. Results and Discussion

The ability of a material to be heated by a laser is directly related to the optical properties of the material. The optical absorptivity of glass can be varied significantly by adding CuO to BBZ glass (Fig. 1(a)), and SBN glass (Fig. 1(b)). We found that the addition of CuO to the tested glass systems increased their absorption coefficients over the entire range of wavelengths. This phenomenon is related directly to the laser-heating characteristics of the glasses. To evaluate accurately the effect of the addition of CuO on the absorption coefficients of the glasses at 1064 nm, the absorption coefficients at 1064 nm were measured (displayed in Fig. 2). The absorption coefficient of the BBZ-CuO glass sample increased from 2.59 to 38.68 cm^{-1} while that of the SBN-CuO glass sample increased from 82.67 to 98.77 cm^{-1}. From these results, optical absorptivity at 1064 nm was easily induced in the glasses by the addition of CuO, regardless of the chemical composition of the mother glass. Furthermore, the degree of increase in the absorption coefficient at 1064 nm was proportional to the amount of CuO added.

The heating and cooling of the laser-irradiated surfaces of the glasses occurred rapidly (within 0.5 s; see Fig. 3). This is an advantage because it prevents thermal damage to the

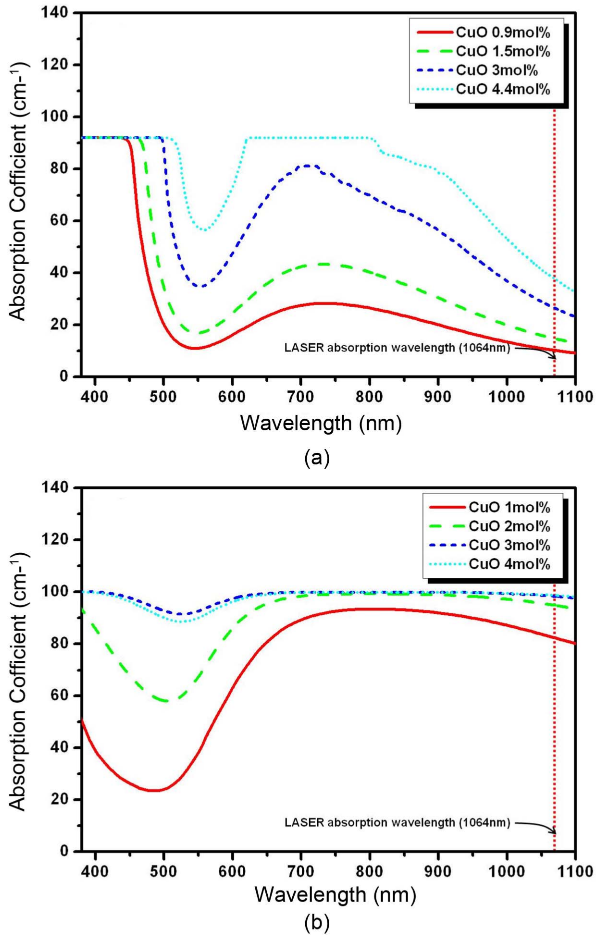

Fig. 1. Optical absorption coefficients of (a) BBZ glass and (b) SBN glass samples containing CuO.

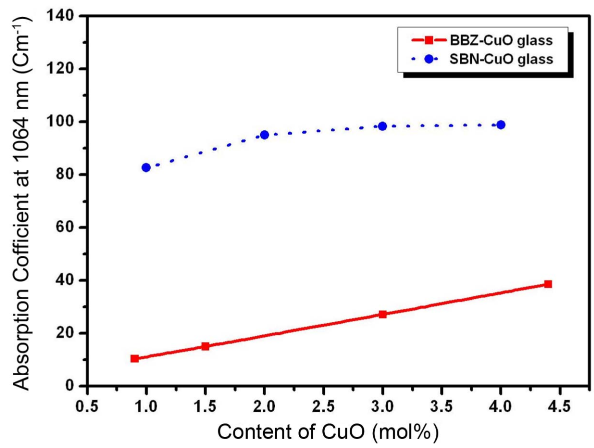

Fig. 2. Effects of CuO content of BBZ and SBN glasses on their absorption coefficients at 1064 nm.

substrate caused by the diffusion of heat from the sealing material. The maximum laser-heating temperature was approximately 850°C, while the minimum temperature was 130°C. The maximum heating temperature varied with the CuO content, which directly affected the optical absorption

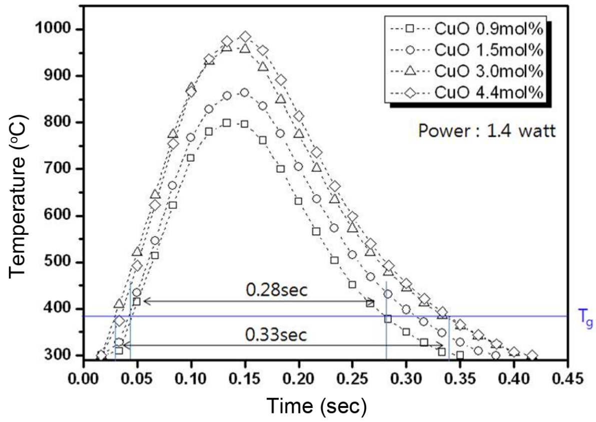

Fig. 3. Laser heating profile of BBZ-CuO glass.

coefficient at 1064 nm.

As mentioned previously, the laser-heating temperature was proportional to the CuO content and the laser power used. The variations in the laser-heating temperatures of the BBZ and SBN glasses are displayed in Fig. 4. The laser-heating temperature of BBZ-CuO glass varied from 151°C to 850°C (laser power: 0.4 - 1.4 W) while that of SBN-CuO glass varied from 166°C to 1500°C (laser power: 0.8 - 5 W). The increase in the absorption coefficient at 1064 nm with the increase in the CuO content may be related directly to the laser-heating temperature. The laser-heating temperatures of SBN glass samples containing 4 and 5 mol% CuO were similar. This was probably because the absorption coefficients of the two samples were similar.

Considering the range of glass-transition temperatures (BBZ-CuO glass: 376.1 - 386.8°C; SBN-CuO glass: 601.4 - 751.3°C), the laser-firing temperatures of the two glasses were well within the range for sintering. If the temperature is too low, the heat energy available will not be enough for necking and densification to occur. On the other hand, if the temperature is too high, thermal shock can occur after laser irradiation.[5] The ability to be heated by a laser can be induced in glasses by adding CuO to them, while their laser-heating temperature can be controlled by varying their CuO content, and the power of the laser used. Thus, several factors determine the laser-heating temperature, including those related to the materials and to the apparatus used.[4-5]

Optical parameters such as the absorption coefficient and thermal properties are the main factors determining whether a glass can be sealed by laser irradiation, and these factors are related to the chemical composition of the glass.[7] The factors depending on the apparatus used, are the type of laser used (i.e., its wavelength), as well as its power, scan rate, spot size, and irradiation time. To develop an appropriate laser-sealing technology for glass, the relationship between the laser-irradiation parameters and the laser-heating characteristics of the glass should be elucidated.

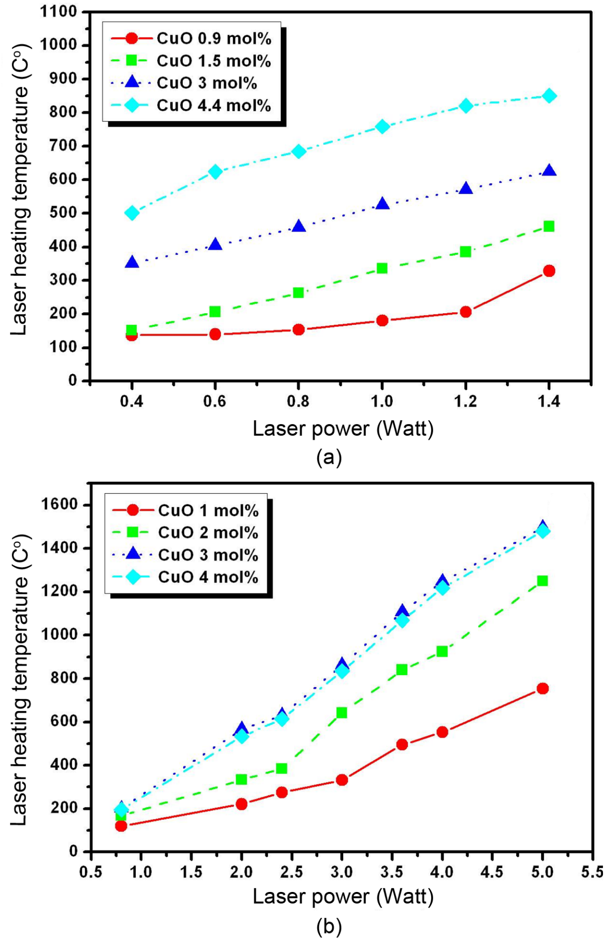

Fig. 4. Effects of CuO content and laser power used, on the laser-heating temperature of (a) BBZ-CuO glass and (b) SBN glass-CuO glass.

4. Conclusion

The optical absorptivity values of the glasses were significantly affected by the addition of CuO, with the absorptivity being proportional to the amount of CuO added. The ability to be heated by a laser could readily be induced in the glasses by adding CuO to them; this was regardless of the chemical compositions of the mother glass. The glasses underwent heating and cooling rapidly when irradiated with a laser. This is a major advantage from the viewpoint of preventing thermal defects in the seals formed after the heating process. The laser-heating temperatures of the glasses were related to their optical absorptivity at 1064 nm, and to the laser power used. Considering the thermal properties of the glasses, it may be possible to deliver sufficient heat energy to them to cause sintering. However, to develop state-of-the-art laser sealing technology, the effects of various laser irradiation parameters and the inherent properties of the glass being sealed, should be studied.

Acknowledgments

This research was supported by the Pioneer Research Center Program through the National Research Foundation of Korea, funded by the Ministry of Science, ICT & Future Planning (Grant no. NRF-2010-0019471).

REFERENCES

1. J. Choi, D. W. Shin, and W. T. Bae, "Effect of an Additive on the Physical and Electrical Properties of the B_2O_3-ZnO-Bi_2O Glass System for a Sheath Heater Module*(in Korean)*," *J. Korean Ceram. Soc.,* **50** [1] 57-62 (2013).
2. I. B. Lee, S. J. Hwang, and H. S. Kim, "Reaction between Oxide Sealant and Liquid Electrolyte in Dye-Sensitized Solar Cells," *Sol. Energy Mater. Sol. Cells,* **95** 315-17 (2011).
3. R. Sastrawan, J. Beier, U. Belledin, S. Hemming, A. Hinsch, R. Kern, C. Vetter, F. M. Petrat, A. Prodi-Schwab, P. Lechner, and W. Hoffmann, "New Interdigital Design for Large Area Dye Solar Modules Using a Lead-free Glass Frit Sealing," *Prog. Photovolt: Res. Appl.,* **14** 697-709 (2006).
4. F. Börner, W. Lippmann, A. Hurtado, and B. Schön, "Glasses for Laser Joining of Zirconia Ceramics," *J. Eur. Ceram. Soc.,* **34** 765–72 (2014).
5. R. Cruz, J. A. C. Ranita, J. Maçaira, F. Ribeiro, A. M. B. Silva, J. M. Oliveira, M. H. F. V. Fernandes, H. A. Ribeiro, J. G. Mendes, and A. Mendes, "Glass-Glass Laser-Assisted Glass Frit Bonding," *IEEE Trans. Comp. Packag. Technol.,* **2** [12] 1949-56 (2012).
6. K. Koshiba, T. Honma, Y. Benino, and T. Komatsu, "Patterning and Morphology of Nonlinear Optical $Gd_xBi_{1-x}BO_3$ Crystals in CuO-doped Glass by YAG Laser Irradiation," *Appl. Phys. A,* **89** 981-86 (2007).
7. B. S. Bae and M. C. Weinberg, "Optical Absorption of Copper Phosphate Glasses in the Visible Spectrum," *J. Non-Crys. Solids,* **168** 223-31 (1994).
8. T. Honma, P. T. Nguyen, and T. Komatsu, "Crystal Growth Behavior in CuO-doped Lithium Disilicate Glasses by Continuous-wave Fiber Laser Irradiation," *J. Ceram. Soc. Jpn.,* **116** [12] 1314-18 (2008).
9. A. Streltsov, J. Dickinson, R. Grzybowski, D. Harvey, S. Logunov, A. Ozturk, J. Surtherland, and M. Potuzak, "Laser Texturing of Doped Borosilicate Glasses," Proc. SPIE, **7584** 75840S-1-12 (2010).
10. H. Sugita, T, Honma, Y. Benino, and T. Komatsu, "Formation of $LiNbO_3$ Crystals at the Surface of TeO_2-based Glass by YAG Laser-induced Crystallization," *Solid State Commun.*, **143** 280-84 (2007).