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# Effects of $Na_2O$ additions on the thermal and optical properties of $BaO-ZnO-B_2O_3-SiO_2$ glass powders prepared by spray pyrolysis

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**Fine-sized $BaO-ZnO-B_2O_3-SiO_2$ (BZBS) glass powders doped with various amount of $Na_2O$ were directly prepared by spray pyrolysis at a temperature of 1400 °C. The BZBS glass powders prepared with low amounts of $Na_2O$ below 5.7 wt.% of the product had a glass structure with amorphous phases. The glass transition temperature ($T_g$) of the BZBS glass powders was changed from 517.3 to 468 °C when the amount of $Na_2O$ added to the product was changed from 0 to 5.7 wt.%. Melting of the glass powders with 1.9 wt.% $Na_2O$ occurred at a temperature of 560 °C. On the other hand, melting of the glass powders with 3.8 and 5.7 wt.% $Na_2O$ occurred at temperatures of 540 and 520 °C, respectively. The dielectric layers formed from the glass powders with an amount of $Na_2O$ added below 5.7 wt.% of the product had high transparencies, above 80%, at a firing temperature of 580 °C. The addition of $Na_2O$ to the glass powders improved the transparencies of the dielectric layers at low firing temperatures.**

**Key words: Glass powder, Spray pyrolysis, Gas phase reaction.**

## Introduction

For the development of a reasonable dielectric layer for a plasma display panel (PDP), several properties are required such as high transparency (above 80% after firing), high break down voltage (above 9 kV at 20 μm), a dielectric constant below 15, a reasonable coefficient of thermal expansion ($8\text{-}9 \times 10^{-6}$/K) to match the glass substrate, and a low firing temperature of about 550-600 °C, for price competitiveness [1, 2].

Pb and Bi-based glass powders are commercially used as transparent dielectric layers in PDPs. However, the Pb and Bi components are materials which involve environmental regulations [3, 4]. The $BaO-ZnO-B_2O_3-SiO_2$ (BZBS) system has been reported as an alternative to Pb or Bi-based systems [5]. The as-quenched BZBS glass frits have a dilatometric softening temperature of about 575 °C with no evidence of crystallization when heated up to 600 °C [6]. A BZBS transparent dielectric layer has adequate thermal and electrical properties for a PDP application, but indicates the glass transition temperature ($T_g$) is as high as 515 °C. Therefore, the softening and glass transition temperatures of BZBS glass powders should be lowered.

The thermal properties of glass powders could be controlled by changing the mean size and the composition of the powders. Recently, improved thermal properties of fine-sized glass powders prepared by spray pyrolysis have been reported [7-9]. Therefore, the dielectric layers formed from the glass powders obtained by spray pyrolysis had good morphological and optical properties even at low firing temperatures. $Li_2O$, $Na_2O$, and $K_2O$ are well known as important additives for improving the softening capability as well as the melting property of glass powders at low firing temperatures. However, the effects of alkali metal oxides on the characteristics of glass powders prepared by spray pyrolysis have not been investigated. In this study, fine-sized BZBS glass powders doped with various amounts of a Na component were directly prepared by spray pyrolysis. The effects of the Na component on the thermal and firing properties of the BZBS glass powders obtained by spray pyrolysis were investigated. The morphological and optical properties of the dielectric layers formed from the prepared glass powders were also investigated.

## Experimental Procedure

The compositions of the prepared $BaO-ZnO-B_2O_3-SiO_2-Na_2O$ glass powders are shown in Table 1. The amount of $Na_2O$ added was altered from 0 to 12.6 wt.% of the product. The spray pyrolysis equipment used consisted of six ultrasonic spray generators that operated at 1.7 MHz, a 1000-mm-long tubular alumina reactor of 50-mm internal diameter, and a tefron bag filter. The preparation temperature was fixed at 1400 °C. The spray solutions were obtained by adding $Ba(NO_3)_2$ (99%, Junsei, Japan), ZnO (99%, Kanto, Japan), $H_3BO_3$ (99.5%, Kanto, Japan), tetraethyl orthosilicate (98% TEOS, Aldrich, Germany),

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**Table 1.** Compositions of $BaO$-$ZnO$-$B_2O_3$-$SiO_2$-$Na_2O$ glass powders

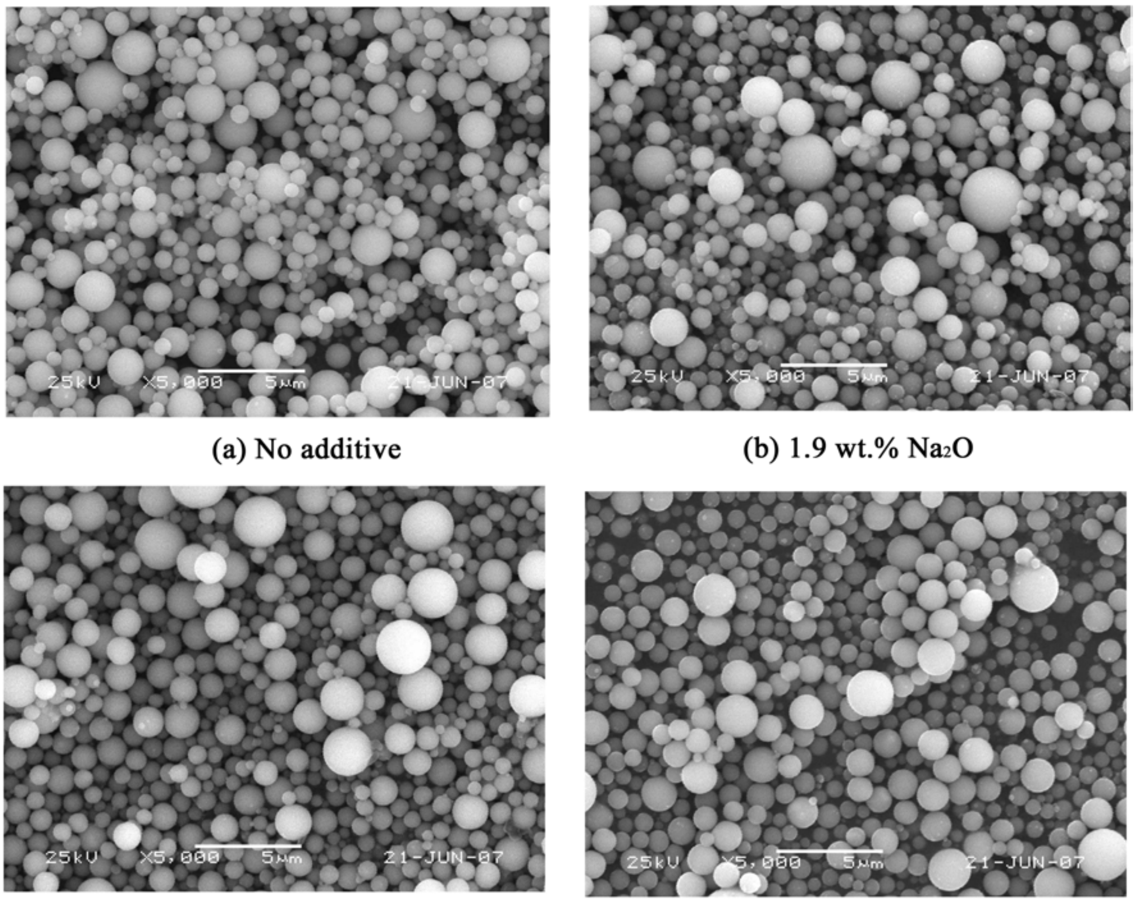
| Composition | | | (mol %) | additive | |
|---|---|---|---|---|---|
| BaO | ZnO | $B_2O_3$ | $SiO_3$ | $Na_2CO_3 \rightarrow Na_2O$ (wt.% of product) | |
| 28 | 41 | 28 | 10 | - | - |
| 28 | 41 | 28 | 10 | 3 | 1.9 |
| 28 | 41 | 28 | 10 | 6 | 3.8 |
| 28 | 41 | 28 | 10 | 9 | 5.7 |
| 28 | 41 | 28 | 10 | 12 | 7.6 |
| 28 | 41 | 28 | 10 | 15 | 9.5 |
| 28 | 41 | 28 | 10 | 20 | 12.6 |

$Na_2CO_3$ (99%, Kanto, Japan) and nitric acid to distilled water. The overall solution concentration was 0.5 M. The spray solution was atomized with ultrasonic spray generators and introduced into a hot reaction column. The flow rate of air used as a carrier gas was 20 l minute$^{-1}$.

The glass transition temperature ($T_g$) of the prepared glass powders was studied using differential scanning calorimetry(DSC). The crystal structures of the powders and dielectric layers were studied using X-ray diffraction (XRD) with Cu K$\alpha$ radiation ($\lambda$ = 1.5418 Å). The morphologies of the powders and dielectric layers were investigated using scanning electron microscopy(SEM). The glass powders were mixed with an organic vehicle that consisted of ethyl cellulose, $\alpha$-terpineol, and butyl carbitol acetate (BCA). The glass paste was screen-printed onto soda-lime glass substrates. The printed glass substrate was dried at 120 °C for 30 minutes in order to remove the solvent. The dried glass substrate was fired in 2 steps. In the first step, the glass was fired at 400 °C for 10 minutes with a heating rate of 5 K minute$^{-1}$ and in the second step, the glass substrate was fired at temperatures between 520 and 580 °C for 7 minutes under the same conditions. Optical transmittances of the dielectric layers formed from the prepared glass powders were studied using a UV-Visible spectrophotometer.

## Results and Discussion

Fig. 1 shows SEM micrographs of the $BaO$-$ZnO$-$B_2O_3$-$SiO_2$-$Na_2O$ glass powders with various amounts of $Na_2O$. The prepared glass powders had a spherical shape and non-aggregation characteristics irrespective of the amount of $Na_2O$ added. Each glass powder particle was formed from one droplet by drying, decomposition, melting and quenching processes. The detailed formation mechanism



(a) No additive

(b) 1.9 wt.% $Na_2O$

(c) 5.7 wt.% $Na_2O$

(d) 9.5 wt.% $Na_2O$

**Fig. 1.** SEM micrographs of the BZBS glass powders.

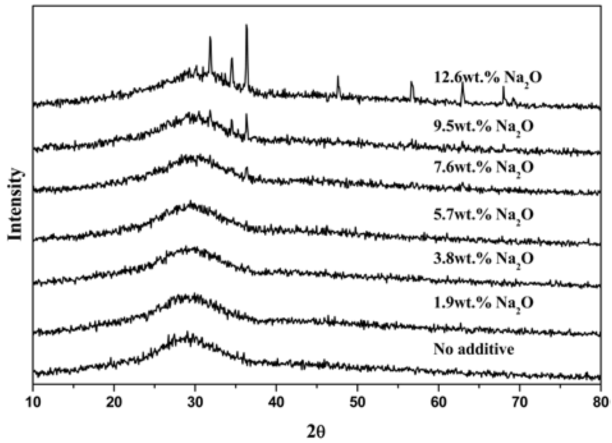



**Fig. 2.** XRD spectra of the BZBS glass powders.

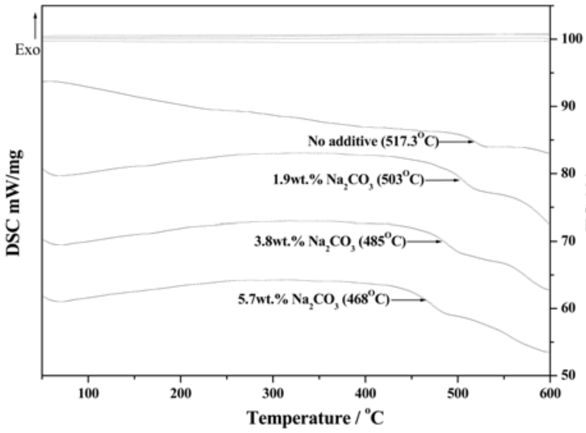
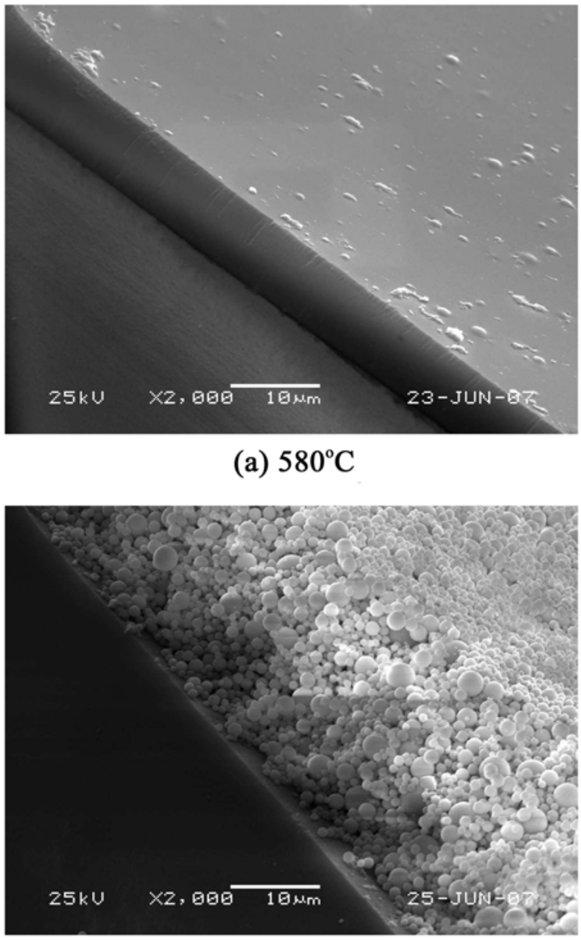



**Fig. 3.** TG/DSC curves of BZBS glass powders.




(a) 580°C

(b) 560°C

**Fig. 4.** Cross sections of dielectric layers formed from the BZBS glass powders prepared from a spray solution without a $Na_2O$ addition.

of the glass powders in the spray pyrolysis process was described in the previous paper [10].

The XRD patterns of the prepared glass powders with various amounts of $Na_2O$ are shown in Fig. 2. The prepared BZBS glass powders with a low amount of $Na_2O$, below 5.7 wt.% of the product, had broad peaks at around 28°. The broad peak at around 28° in the XRD pattern represents the character of these glass materials. On the other hand, peaks from crystalline phases appeared in the patterns of glass powders with large amounts of $Na_2O$ and the crystallinity of the powders increased with an increase in the amount of $Na_2O$ added to the product.

The thermal properties of the BaO-ZnO-$B_2O_3$-$SiO_2$-$Na_2O$ glass powders are shown in Fig. 3. Fig. 3 shows the TG/DSC curves of the glass powders with various amounts of $Na_2O$ prepared by spray pyrolysis. In the TG curves, weight losses from the BZBS glass powders did not occur irrespective of the amount of $Na_2O$ added to the product. Complete decomposition of the precursors occurred inside the hot wall reactor maintained at 1400 °C even with the short residence time of the powders of 0.7 s. The glass transition temperatures ($T_g$) of the glass powders prepared by spray pyrolysis were measured from the DSC curves and represented in the curves. The $T_g$ of the glass powders decreased with an increase in the amount of $Na_2O$ added to the glass product. The $T_g$ of the BZBS glass powders was changed from 517.3 to 468 °C when the amount of $Na_2O$ added to the product was changed from 0 to 5.7 wt.%.

The characteristics of the dielectric layers formed from the BZBS glass powders with no amount of $Na_2O$ added are shown in Fig. 4. The screen printed layers were fired at temperatures of 560 and 580 °C. The dielectric layer fired at a temperature of 580°C had a clean surface and a dense inner structure. On the other hand, the melting of the glass powders did not occur at a firing temperature of 560 °C. The spherical shape and micrometre size of the glass powders was maintained after firing at a temperature of 560 °C.

The effects of $Na_2O$ additions on the firing characteristics of the BZBS glass powders prepared by spray pyrolysis are shown in Fig. 5. The screen printed layers of the glass powders with various amounts of $Na_2O$ were fired at temperatures between 520 and 580 °C. The softening

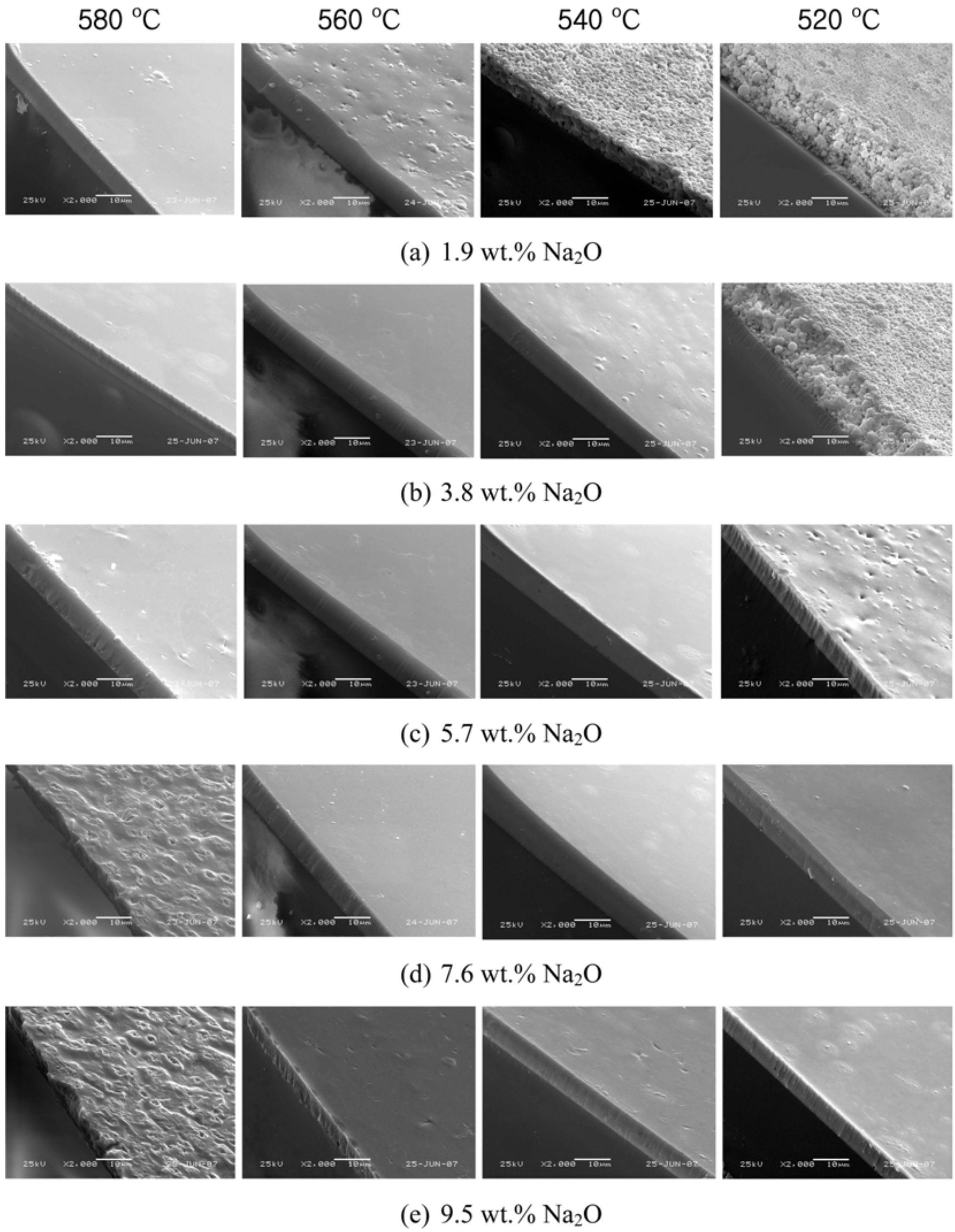



**Fig. 5.** Cross sections of dielectric layers formed from the BZBS glass powders prepared from spray solutions with $Na_2O$ addititions.

temperature of the glass powders without crystalline phases decreased with an increase in the amount of $Na_2O$ added to the product. Melting of the glass powders with 1.9 wt.% $Na_2O$ occurred at a temperature of 560 °C. On the other hand, melting of the glass powders with 3.8 and 5.7 wt.% $Na_2O$ occurred at temperature of 540 and 520 °C, respectively. Melting of the glass powders with 7.6 and 9.5 wt.% $Na_2O$ occurred even at a low temperature of 520 °C. Therefore, the dielectric layers formed from the glass powders with 7.6 and 9.5 wt.% $Na_2O$ had clean surfaces and dense inner structures at a firing temperature of 520 °C. On the other hand, the dielectric layers fired at a high temperature of 580 °C had rough surfaces and porous inner structures. Fig. 6 shows the XRD spectra of the dielectric layers fired at a temperature of 580 °C. The dielectric layers formed from the glass powders with an amount of $Na_2O$ added below 5.7 wt.% to the product had amorphous phases without crystalline phases. On the other hand, the dielectric layer formed from the glass powders with 7.6 wt.% $Na_2O$ added to the product had crystalline phases. Crystallization of the glass with a large amount of

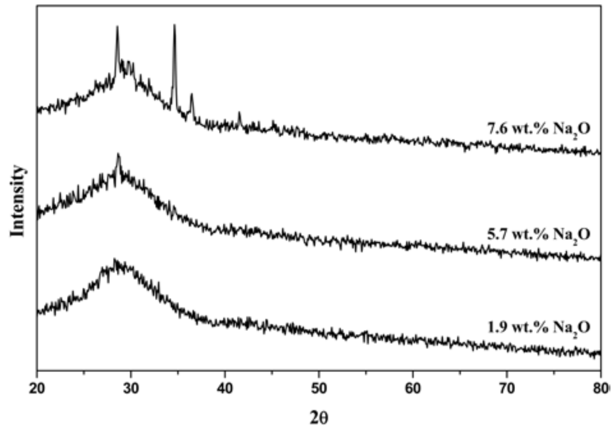



**Fig. 6.** XRD patterns of the dielectric layers formed from the BZBS glass powders.

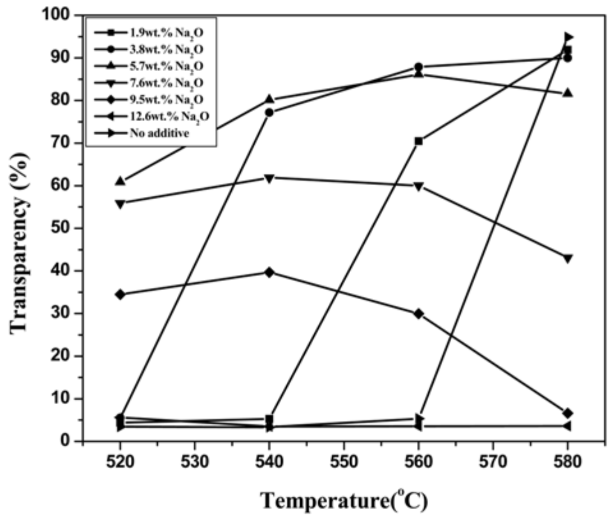



**Fig. 7.** Transparency of dielectric layers formed from the BZBS glass powders, fired at different temperatures.

$Na_2O$ added occurred at a firing temperature of 580 °C. Therefore, the dielectric layers formed from the glass powders with 7.6 and 9.5 wt.% $Na_2O$ added to the product had rough surfaces and porous inner structures at a firing temperature of 580 °C.

Fig. 7 shows the transparencies of the dielectric layers formed from the glass powders with various amounts of $Na_2O$ added to the product. The transparencies of the dielectric layers formed from the prepared glass powders were measured using a spectrophotometer in visible light with a wavelength of 550 nm. The dielectric layers formed from the glass powders with an amount $Na_2O$ added below 5.7 wt.% of the product had high transparencies above 80% at a high firing temperature of 580 °C. The transparency of the dielectric layer formed from the glass powders with no amount of $Na_2O$ added was 95%. The addition of $Na_2O$ to the glass powders decreased the transparencies of the dielectric layers at a high firing temperature of 580 °C. The addition of $Na_2O$ to the glass

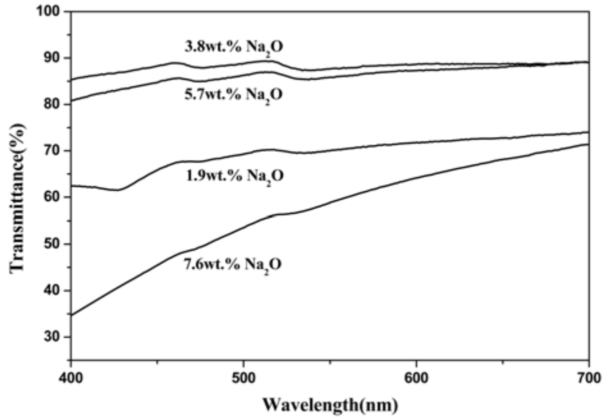



**Fig. 8.** Transmittance patterns of dielectric layers at a firing temperature of 560 °C.

powders improved the transparencies of the dielectric layers at low firing temperatures. The dielectric layers formed from the glass powders with an amount of 1.9 wt.% $Na_2O$ added had transparencies above 60% at firing temperatures above 560 °C. However, the dielectric layer formed from the glass powders with an amount of 5.7 wt.% $Na_2O$ added had a transparency of 80% even at the low firing temperature of 540 °C. The dielectric layers formed from the glass powders with an amount of 7.6 wt.% $Na_2O$ added had similar transparencies at firing temperatures between 520 and 560 °C. On the other hand, the dielectric layer formed from the glass powders had a low transparency at a high firing temperature of 580 °C because of the crystallization of the layers as shown in Fig. 6. Fig. 8 shows the transmittance of the dielectric layers formed from the BZBS glass powders with various amounts of $Na_2O$ added at a firing temperature of 560 °C. The transparencies of the dielectric layers formed from the glass powders with amounts of 3.8 and 5.7 wt.% $Na_2O$ added of the product are higher than 85% within the visible range.

## Conclusions

$BaO-ZnO-B_2O_3-SiO_2-Na_2O$ glass powders with a fine size and spherical shape were directly prepared by high temperature spray pyrolysis. The effects of $Na_2O$ additions on the properties of the BZBS glass powders and dielectric layers were investigated. The $Na_2O$ additions did not change the morphologies of the BZBS glass powders. The BZBS glass powders prepared with a low amount of $Na_2O$ below 5.7 wt.% of the product had broad peaks at around 28°. On the other hand, peaks from crystalline phases appeared from the glass powders with large amounts of $Na_2O$ and the crystallinity of the powders increased with an increase in the amount of $Na_2O$ added to the product. The $T_g$ of the glass powders decreased with an increase in the amount of the $Na_2O$ added to the glass product. Therefore, the characteristics of the dielectric layers formed from the glass powders were affected by the amounts of $Na_2O$ added. The dielectric layers formed from the glass powders with 5.7 wt.% $Na_2O$ added had clean surfaces, dense inner structures and a high transparency within the visible range even at low firing temperatures.

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