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Short communication

Effect of precursor types on the characteristics of the Pb-based glass powders prepared by spray pyrolysis

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Abstract

Lead (Pb)-based glass powders with a spherical shape and submicron size were directly prepared by spray pyrolysis using spray solutions with various types of Pb and silicon (Si) components. The glass powders formed by the spray solution with Pb chloride and tetraethyl orthosilicate (TEOS) precursors had a broad X-ray diffraction (XRD) peak at around 28° with small crystalline peaks. The powders had an impurity peak caused by chlorine in the EDX spectrum. However, the glass powder formed from the spray solutions that contained Pb nitrate and Pb acetate precursors had an amorphous phase, irrespective of the type of Si precursor. The dielectric layers formed from the glass powders obtained from the spray solutions with Pb nitrate and Pb acetate had a dense structure and high transmittance above 85%, irrespective of the type of Si precursor components. In contrast, the dielectric layer formed from the glass powders prepared from the spray solution with Pb chloride and TEOS had large voids in the layer and had low transmittance below 50% under the visible range.

Keywords: A. Powders: gas phase reaction; A. Powders: chemical preparation

1. Introduction

Various types of glass powders are used in plasma display panels (PDPs) to form barrier ribs and dielectric layers in the front and back panels [1–4]. The dielectric layer of the front panel, which is used as protective layer for the electrode, plays a key role in PDPs. These layers should have a low dielectric constant, high transparency, high breakdown voltage, low firing temperature, and a reasonable thermal expansion coefficient. Lead (Pb)-based and Bi-based glass powders are used commercially as transparent dielectric layers in PDPs [5,6].

The glass powders used in transparent dielectric layers are mainly prepared using a melting process [5,6]. In recent years, Pb-based and Bi-based glass powders for dielectric layers for PDPs have been prepared by spray pyrolysis [7–10]. The glass powders prepared by spray pyrolysis have a spherical shape and are very small (submicron). The effects of the preparation conditions on the properties of the transparent dielectric layers have been carefully studied. The layers formed from glass powders prepared by spray pyrolysis have good transparency. In spray pyrolysis, various types of ceramic and metal powders have been widely studied. The ceramic and metal powders are strongly affected by the type of precursors and the preparation conditions [11]. However, the effects of the type of precursor on the properties of the glass powders prepared by spray pyrolysis have not been studied.

In this study, Pb-based glass powders were directly prepared by spray pyrolysis. The main components of the glass powders were Pb and silicon (Si). The effects of the Pb and Si precursor components on the Pb-based glass powders prepared by spray pyrolysis were investigated.

2. Experimental

The spray pyrolysis equipment used consisted of six ultrasonic spray generators that were operated at 1.7 MHz, a tubular alumina reactor (1000 mm long, 50 mm internal diameter), and a bag filter. Glass powders with a 21 mol% PbO–50 mol% B_2O_3–16 mol% SiO_2–12 mol% BaO–0.5 mol% CuO composition were directly prepared by spray pyrolysis. The preparation temperatures were fixed at 1000 °C. The flow

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rate of the carrier gas was fixed at 15 L/min. $Pb(NO_3)_2$, $Pb(CH_3COO)_2\cdot 3H_2O$, and $PbCl_2$ were used as precursors of the Pb component. Tetraethyl orthosilicate (TEOS, 98%) and fumed silica were used as precursors of the Si component. The mean size and BET surface area of fumed silica were 12 nm and 200 m^2/g, respectively. H_3BO_3, $BaCO_3$, and $Cu(NO_3)_2\cdot 3H_2O$ were used as precursors of the B, Ba, and Cu components. The overall concentration of the solution was fixed at 0.33 M. The spray solution formed using TEOS as the precursor of the Si component was a clear solution. In contrast, the spray solution formed from the fumed Si as the precursor of the Si component was a colloidal solution, which was stable enough to generate the droplets by use of an ultrasonic nebulizer.

The crystal structures of the prepared powders were investigated by use of XRD (RIGAKU, D/MAX-RB) with Cu Kα radiation (λ = 1.5418 Å). Measurement of the thermal properties of the prepared powders was performed by use of a thermo-analyzer (TG-DSC, Netzsch, STA409C) in the range of 40–600 °C. The morphological characteristics of the prepared powders and the fired dielectric layers were investigated by scanning electron microscopy (SEM, JEOL, JSM-6060). The transmittance of the dielectric layer was investigated by use of a spectrophotometer in the visible light range (UV–vis spectrophotometer, Shimadzu, UV-2450).

3. Results and discussion

The morphological characteristics of the Pb-based glass powders prepared by spray pyrolysis from spray solutions with various Pb and Si precursors are shown in Fig. 1. The Pb-based glass powders had a spherical shape and did not aggregate, irrespective of the precursors of the Pb and Si components. The mean size of the Pb-based glass powders varied slightly from 0.75 to 0.85 μm. Therefore, the Pb-based glass powders were prepared by the same formation mechanism in the spray pyrolysis irrespective of the precursor types of Pb and Si components. The glass powders were formed by a melting and quenching process inside a hot wall reactor. Each glass particle was formed from one droplet.

Fig. 2 shows the XRD patterns of the glass powders prepared by spray pyrolysis. The glass powders from the spray solution with Pb chloride and TEOS precursors as the source of Pb and Si components, respectively, had broad a XRD peak at around 28°. Crystalline peaks with low intensities were also observed. The individual particles prepared by spray pyrolysis had the same composition, because each particle was formed from one droplet, all with the same composition. Therefore, the individual particles prepared by spray pyrolysis all had the same crystal structure. The glass particles formed from the

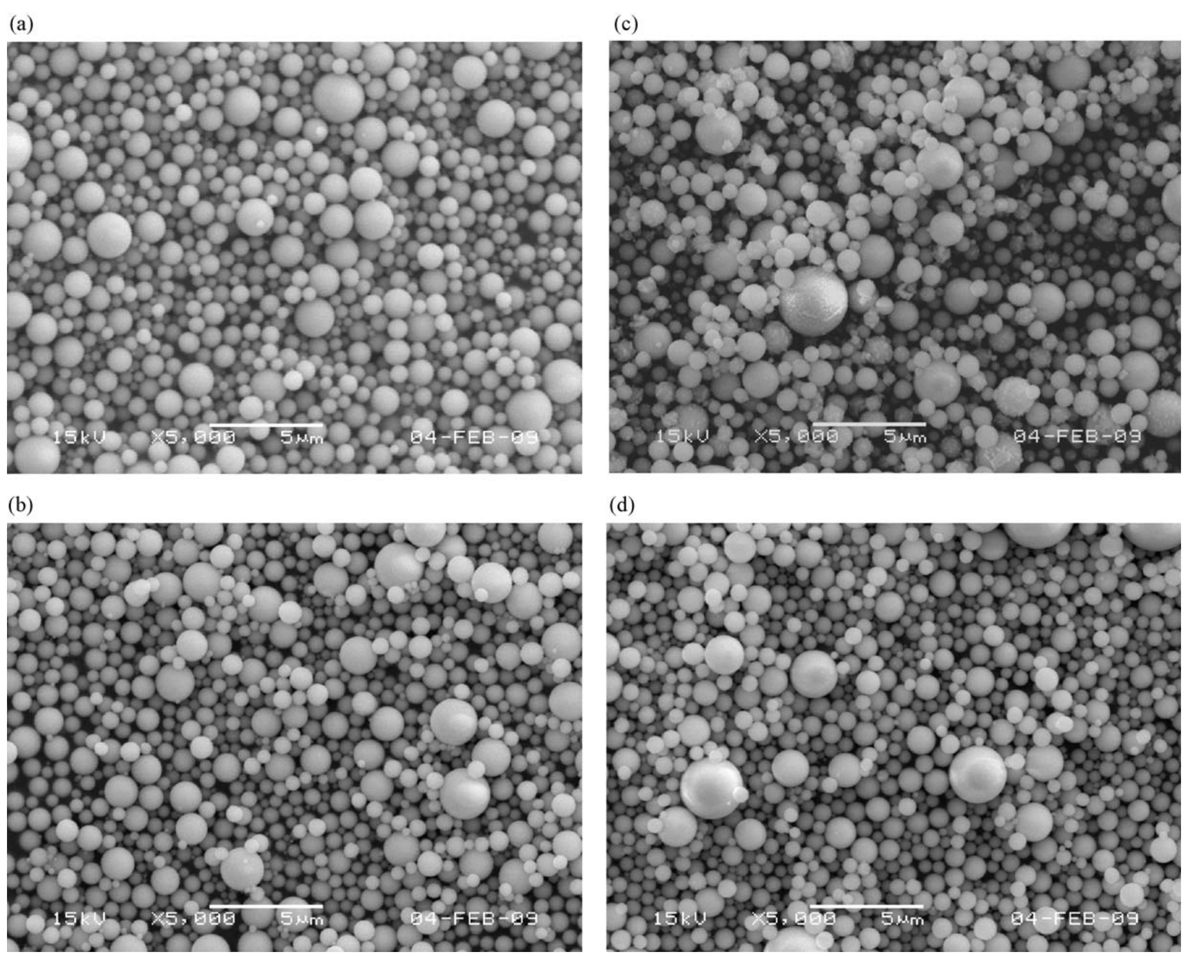

Fig. 1. SEM images of the glass powders prepared by spray pyrolysis. (a) Pb nit, TEOS; (b) Pb nit, silica; (c) Pb chl, TEOS; (d) Pb ace, TEOS.

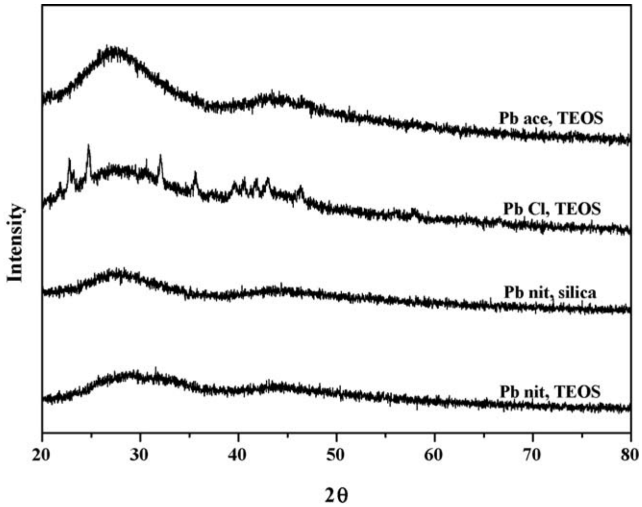

Fig. 2. XRD patterns of the glass powders prepared by spray pyrolysis.

Table 1
Compositions of the glass powders prepared by spray pyrolysis.

Element	Atomic (%)	Theoretical ratio
(a) Pb chloride		
Pb	6.69	35
Cl	5.47	18
Si	9.24	20
Ba	7.09	27
Pb/Cl/Si/Ba	0.7/0.6/1/0.8	1.3/0.7/1/0.8
(b) Pb acetate		
Pb	9.62	43
Si	8.56	33
Ba	6.63	24
Pb/Si/Ba	1.1/1/0.8	1.3/1/0.7

spray solution with Pb chloride and TEOS precursors as the source of Pb and Si components, respectively, had a mixed structure of amorphous and crystalline phases. However, the glass powders formed from the spray solutions with Pb nitrate and Pb acetate precursors had an amorphous phase, irrespective of the Si component precursor.

Fig. 3 shows the EDX spectra of the glass powder prepared by spray pyrolysis. TEOS was used as the source of the Si. The compositions of the glass powder, measured by EDX, are summarized in Table 1. The chlorine peak was observed in the EDX spectrum of the glass powder from the spray solution made with Pb chloride. Complete elimination of the chlorine component in the glass powder did not occur because of the short time spent by the powder inside the hot wall reactor (1.1 s). The composition ratios of the components of glass powder formed from the spray solution with Pb chloride were different from those of the spray solution. Therefore, chloride precursors could not be used to prepare a glass powder with a homogeneous composition and an amorphous phase. In contrast, glass powder prepared from the spray solution with Pb acetate had a similar composition to that of the spray solution.

Fig. 4 shows the TG/DSC curves of the glass powders prepared by spray pyrolysis. In the TG curves, the weight loss of the powder was as low as 1% (weight) at temperatures below 600 °C, irrespective of the Pb and Si precursors. The glass transition temperature (T_g) of the glass powder was 493 °C, irrespective of the Pb and Si precursors.

Fig. 5 shows the cross-sections of the dielectric layers formed from the prepared glass powders at a firing temperature of 580 °C. The dielectric layer formed from the glass powder made from the spray solution with Pb nitrate and TEOS had a dense structure without voids in the layers. In contrast, the dielectric layer formed by the glass powders made from the

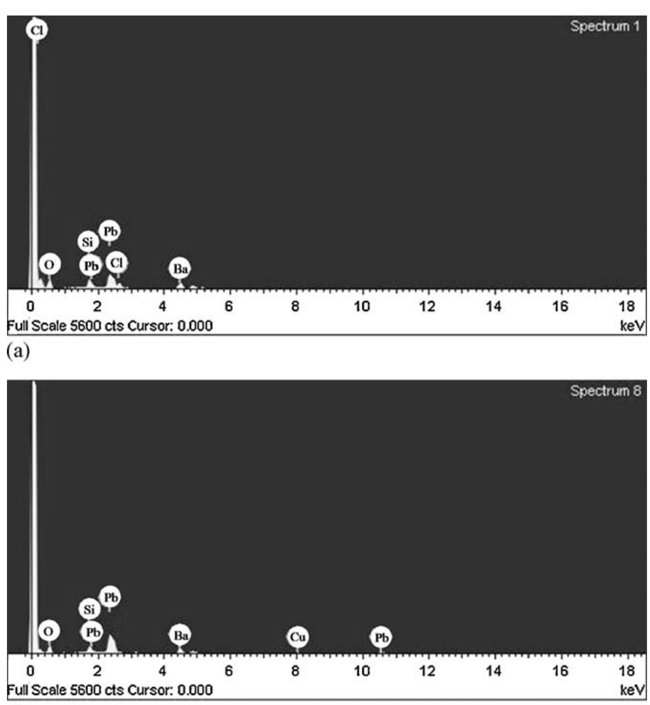

Fig. 3. EDX spectra of the glass powders prepared by spray pyrolysis. (a) Pb chl, TEOS; (b) Pb ace, TEOS.

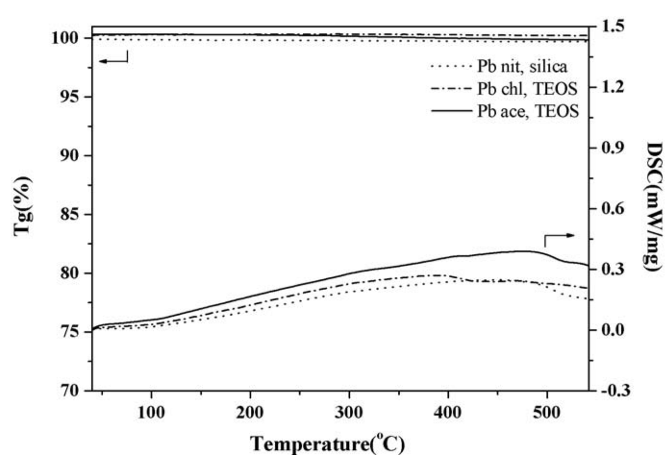

Fig. 4. TG/DSC curves of the glass powders prepared by spray pyrolysis.

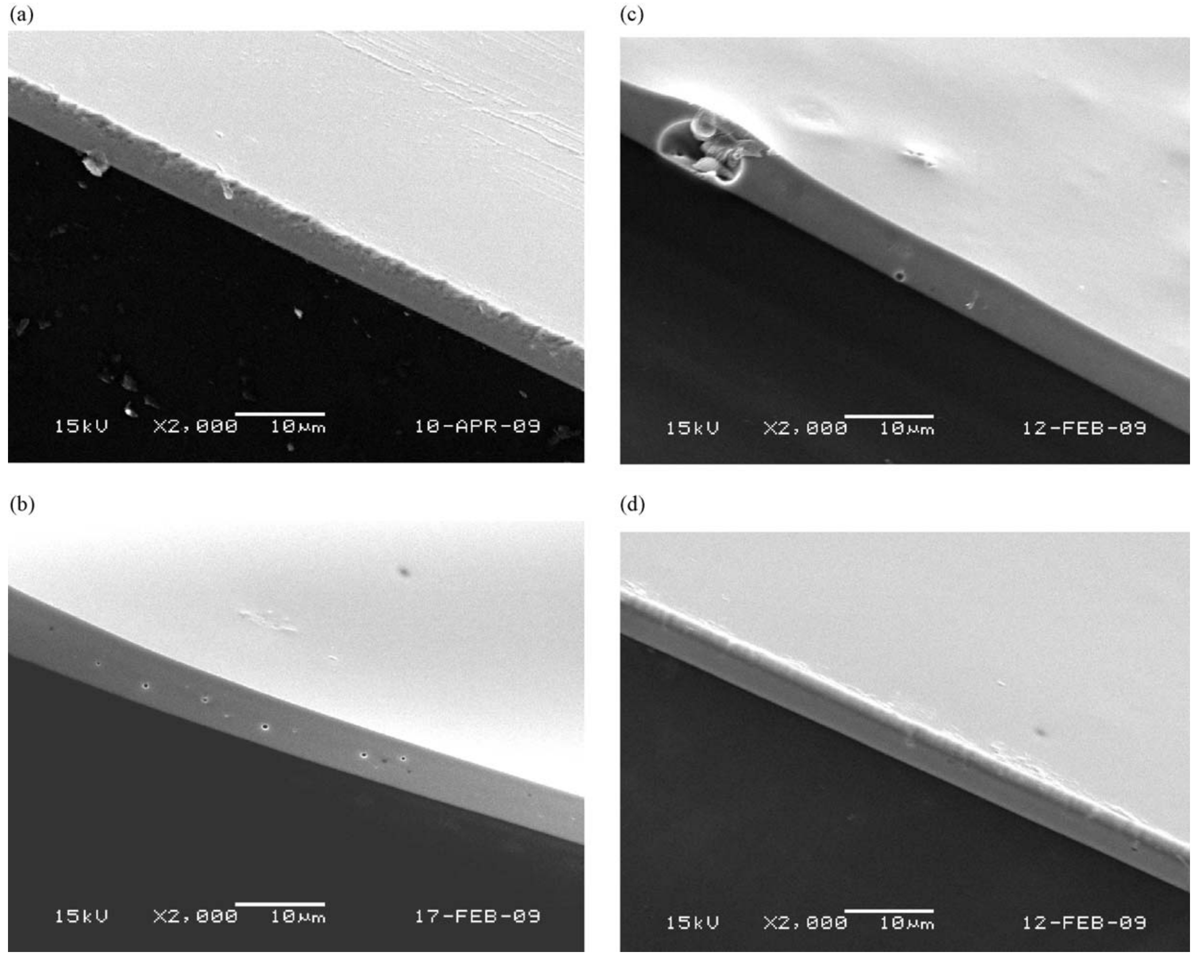

Fig. 5. SEM images of cross-sections of the dielectric layers formed from the glass powders prepared by spray pyrolysis. (a) Pb nit, TEOS; (b) Pb nit, silica; (c) Pb chl, TEOS; (d) Pb ace, TEOS.

spray solution with Pb nitrate and fumed silica had a dense structure with some small voids in the layers. Therefore, the clear spray solution obtained from TEOS as the Si precursor was appropriate to use to prepare the glass powder for transparent dielectric layer with a dense structure and no voids. The dielectric layer formed from the spray solution with Pb acetate and TEOS also had a dense structure without voids in the layers. In contrast, the dielectric layer formed from the spray solution with Pb chloride and TEOS had large voids in the layer.

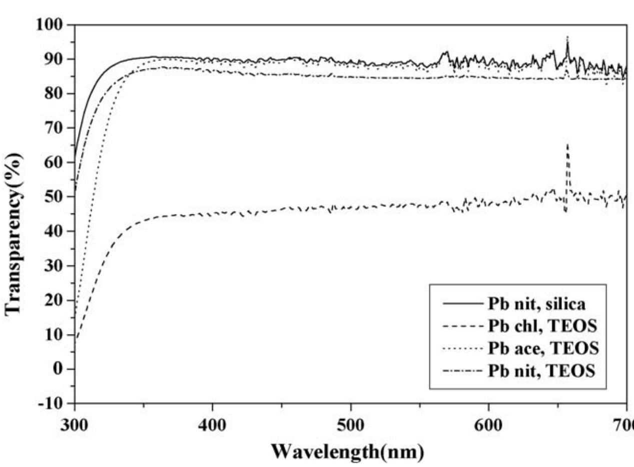

Fig. 6. Transparencies of dielectric layers formed from the glass powders prepared by spray pyrolysis.

Fig. 6 shows the transmittance of the dielectric layers formed from glass powder by spray pyrolysis. The dielectric layer with Pb chloride and TEOS had large voids in the layer and had low transmittances below 50% under the visible range. However, the dielectric layers formed from the glass powder by spray solutions with Pb nitrate and acetate had high transmittances above 85%, irrespective of the type of Si precursor.

4. Conclusions

The effects of Pb and Si precursors on Pb-based glass powder prepared by spray pyrolysis were investigated. Pb chloride was not an appropriate source material of the Pb component in the preparation of Pb-based glass powders by spray pyrolysis. Elimination of the chlorine component was not complete because of the short length of time the powders spent inside the hot wall reactor. However, Pb-based glass powders formed from spray solutions with Pb acetate and Pb nitrate had good characteristics and transparent dielectric materials, irrespective of the type of Si component.

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