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Synthesis and crystallization of solder glass for electronic package

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Abstract Low-temperature solder glass for use in electronic package was experimentally prepared and its crystallization behavior was investigated using differential thermal analysis (DTA) under nonisothermal condition. The composition of the solder glass was determined from PbO-ZnO-B_2O_3-TiO_2 glasses containing small amounts of CaO, SiO_2, Al_2O_3, and P_2O_5. The crystallization exotherm corresponding to the formation of lead titanate ($PbTiO_3$) was observed. The crystallization of $PbTiO_3$ was a three-dimensional process with the average activation energy of 223±3 kJ/mol for the crystallization from the glass matrix.

전자 Package 봉착유리의 합성과 결정화

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요 약 전자 package용 저온봉착 유리를 실험적으로 합성하고 이 유리의 결정화 거동을 비등온 조건하에서 열분석기(DTA)를 이용하여 조사하였다. 이 유리의 조성을 미량의 CaO, SiO_2, Al_2O_3 및 P_2O_5 등이 함유된 PbO-ZnO-B_2O_3-TiO_2 유리로부터 결정하였다. 연 티탄산염($PbTiO_3$) 생성에 해당되는 결정화 발열이 관찰되었다. 이 $PbTiO_3$의 결정화는 삼차원과정으로 진행되었고 유리기지(glass matrix)로부터 생성되는 이 결정의 평균 활성화에너지는 223±3 kJ/mol 이었다.

1. Introduction

Solder glass has been used for sealing television bulbs and display panels. It has also been used to seal ceramic microelectronic packages [1, 2]. One of the solder glasses, $PbTiO_3$-containing glass-ceramics have been commonly used in solder glass to reduce the high thermal expansion coefficient (TEC) of the low melting lead borate glassy phase [1, 3, 4]. The perovskite-type low-temperature $PbTiO_3$ has a strong negative TEC due to a high tetragonal distortion for temperatures below the phase transformation [3, 5]. Tummala [2] reported the development of low-expansion composites in low-temperature lead glass by the formation of perovskite lead titanate crystals of negative thermal expansion, but the crystallization kinetics of the glasses were not investigated. Accordingly, further work would be required to assess the critical parameters for sealing electronic materials. The formation process of such lead titanate crystals is of great importance both from a technological aspect as well as a fundamental point of view. In order to clarify the formation process of such materials, it is essential to study the temperature range where crystallization can occur and the crystallization kinetics.

The aim of the present study was to determine the composition for the formation of $PbTiO_3$-containing solder glass at relatively low temperature and explain the crystallization kinetics of the solder glass.

2. Experimental procedures

2.1. Glass preparation

Glasses were prepared using a conventional melt-

quenching method. Reagent-grade Pb_3O_4, ZnO, H_3BO_3, $CaCO_3$, SiO_2, Al_2O_3, TiO_2, and $NH_4H_2PO_4$ were used as starting materials. The batches were placed in platinum crucibles and melted in an electrical resistance furnace. The batches were initially kept at 700°C for 1 h in order to release volatile products coming from the starting materials. Then they were heated to 1150°C and melted at this temperature for 2 h. The melts were poured into distilled water. The as-quenched glasses were ground and screened with different sizes, and stored in an oven at 100°C to prevent moisture attack until they were required for the nonisothermal DTA measurements using a Seiko model SSC/5200, Japan. The nominal composition of the base glass in weight percent was PbO 78.8 %, ZnO 6.3 %, B_2O_3 10.0 %, CaO 1.3 %, SiO_2 1.6 %, Al_2O_3 1.0 %, and P_2O_5 1.0 %. The base glass was doped with 3, 4, 5, and 6 wt% of TiO_2, and each TiO_2-doped glass was melted together to investigate the formation of $PbTiO_3$ crystal.

2.2. Method of analysis

The crystallization behaviors can be analyzed by an isothermal or a nonisothermal method [6-8]. In this work, a nonisothermal DTA technique was used. The phase analysis and crystallization temperatures of these glasses were investigated by X-ray diffraction (XRD : Rigaku RINT 2000, Japan) and DTA, respectively. In order to determine the kinetic parameters of the glasses, DTA measurements were also performed using about 30 mg of the glass powders in an air atmosphere with different heating rates. The DTA results were further analyzed to obtain the crystallization mode and the activation energy values for crystallization of the glass powders using the Kissinger [9] and Ozawa [10] methods. The reason that all of these methods were used in the present study was to obtain more accurate kinetic parameters. A best fit for the results was calculated by the least square method. The arithmetic mean as well as the standard deviation were calculated for the activation energies.

3. Results and discussion

3.1. Crystalline phases and crystallization temperatures

Glass transition temperature (T_g), crystallization temperature (T_x), and maximum peak temperature (T_p) of the as-quenched glass powder (< 44 mm) were determined using DTA at a heating rate of 10°C/min. The DTA curves of the samples doped with different TiO_2 contents are shown in Fig. 1 and the results are summarized in Table 1. It is seen that T_g, T_x, and T_p are increased with increasing TiO_2 content. It is also interesting to note that crystallization temperatures and peak temperatures of glass samples (except glass sample, G4) are lower than 444°C and 467°C, respectively, indicating that the glasses would be used for sealing applications at temperatures in the 410°C (T_x)~468°C (T_p) range.

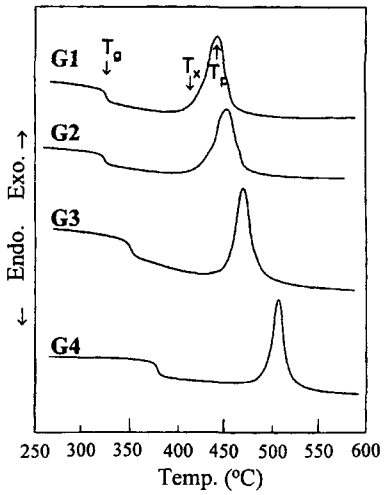

Fig. 1. DTA curves of glass samples doped with different TiO_2 contents (for sample descriptions, see Table 1).

Table 1
DTA results of glass samples doped with different TiO_2 contents

Glass sample number	Amount of TiO_2 (wt%)	T_g (°C)	T_x (°C)	T_p (°C)
G1	3	323	410	440
G2	4	327	415	453
G3	5	342	443	468
G4	6	372	469	503

T_g: transition temperature, T_x: crystallization temperature, T_p: maximum peak temperature.

Figure 2 shows XRD patterns of TiO_2-doped glass powders (< 44 μm) heated at temperatures higher than crystallization temperatures for 1.5 h. Among the samples, glass sample number G3 with 5 wt% TiO_2 shows XRD patterns in close correspondence to $PbTiO_3$ crystal phase, and has relatively low crystallization temperature as given in Table 1. Sample G3 was therefore chosen for further study.

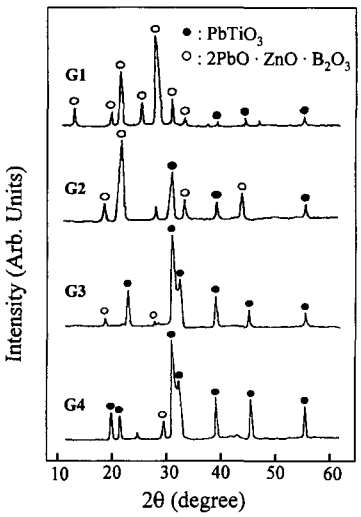

Fig. 2. XRD patterns of each sample heat treated at temperature, 20°C higher than crystallization temperature for 1.5 h.

3.2. *Kinetic parameters of crystallization*

The DTA data were analyzed primarily using the modified Ozawa equation [11, 12] :

$$\ln[-\ln(1-x)] = -n\ln\phi - 1.052(mE/RT) + \text{constant} \quad (1)$$

Where m and n are numerical factors that depend on the crystallization mechanism, x is the fraction crystallized at a given temperature, ϕ is DTA heating rate, R is the gas constant, E is the activation energy for crystallization, and T is the absolute temperature. The parameters n and m can have various values [8, 12-14], as summarized in Table 2. The values of m and n are equal for the special case where bulk crystallization is the predominant crystallization mechanism and the number of nuclei cannot appreciably change during the crystallization process.

In the present study, a sample of the glass powder (G3) with particle size < 44 μm was nucleated at temperature slightly lower than crystallization temperature for 3 h. Thus, the number of nuclei formed during the DTA run can be regarded as negligible. Therefore, value of n is believed to be the same as that of m. At a given temperature T, Equation (1) can be rewritten as

$$\ln[-\ln(1-x)_T = -n\ln\phi + \text{constant} \quad (2)$$

Thus, value of n can be determined by the equation :

$$\left[\frac{d\ln(-\ln(1-x))}{d\ln\phi}\right]_T = -n \quad (3)$$

The fraction x at given temperature T is given as

$$x = A_T/A \quad (4)$$

Where A is the total area of the exotherm between the temperature T_i at which crystallization just begins and the temperature T_f at which the crystallization is completed. A_T is the area between T_i and T. A plot from Equation (3) is presented in Fig. 3, and indicates that bulk crystallization dominates in the glass powder (n = 2.9). Thus, the m value of the glass powder becomes ~3 because n equals m, that is n = m as mentioned previously. Allowing for experimental errors, the value of n is considered to be 3. The bulk crystallization was also confirmed by thermal analysis. DTA indicated that the peak exotherm temperatures were independent of particle size (< 44 μm and 420~840 mm), suggesting crystallization by bulk mechanism [15].

Equation (1) can be rewritten to determine the activation energy :

$$\ln\phi = -1.052(mE/nRT) - \{\ln[-\ln(1-x)]\}/n + \text{constant} \quad (5)$$

Thus, the plot of lnf vs 1/T, where T is the tempera-

Table 2
Values of n and m for different crystallization mechanisms in the heating process

Crystallization mechanism	n	m
Bulk crystallization with a constant number of nuclei (i.e. the number of nuclei is independent of the heating rate)		
three-dimensional growth of crystals	3	3
two-dimensional growth of crystals	2	2
one-dimensional growth of crystals	1	1
Bulk crystallization with an increasing number of nuclei (i.e. the number of nuclei is inversely proportional to the heating rate)		
three-dimensional growth of crystals	4	3
two-dimensional growth of crystals	3	2
one-dimensional growth of crystals	2	1
Surface crystallization	1	1

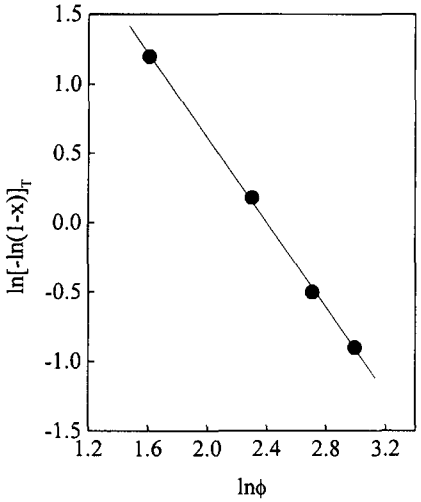

Fig. 3. Plot of $\ln[-\ln(1-x)]_T$ vs $\ln\phi$ for determining the value of n for $PbTiO_3$.

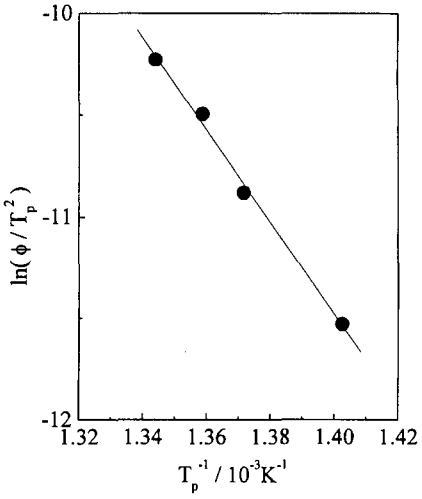

Fig. 5. Plot of $\ln(\phi/T_p^2)$ vs $1/T_p$ for the activation energy using Kissinger equation.

ture at which the crystal volume fraction reaches a specific value, gives a straight line, and the slope has the value 1.052(m/nR)E. The activation energy can be obtained when the ratio m/n is known. Because it is known that the volume fraction of crystals at the peak temperature, T_p, in DTA curves is almost independent of ϕ, Equation (5) should apply for T_p. A plot of lnf vs $1/T_p$, for DTA heating rates of 5, 10, 15, and 20°C per min, is given in Fig. 4, from which value of 1.052(m/nR)E for $PbTiO_3$ is obtained. In the present study, m = n as previously mentioned. Thus, the value of E

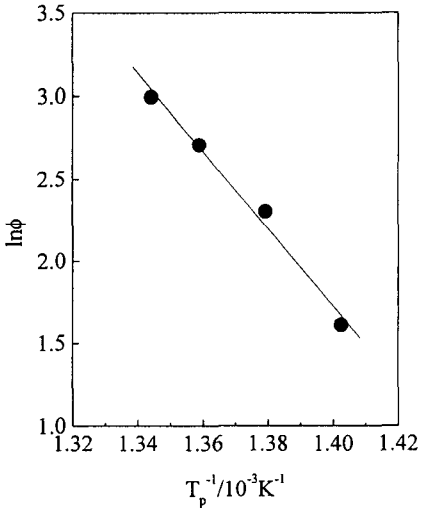

Fig. 4. Plot of $\ln\phi$ vs $1/T_p$ for determining the activation energy using modifed Ozawa equation.

is 226.2 kJ/mol. To further confirm the accuracy of the above result for activation energy value, the following Kissinger [9] equation can be applied :

$$\ln\left(\frac{\phi}{T_p^2}\right) = -E/RT_p + \text{constant} \quad (6)$$

where ϕ is the DTA heating rate, T_p is the crystallization peak temperature, E is the activation energy for crystallization estimated by the Kissinger method, and R is the gas constant. Matusita and Sakka [14] have stated that Equation (6) is valid if crystal growth occurs on a fixed number of nuclei. Because the investigated glass was nucleated to have a fixed number of nuclei during the DTA runs as mentioned previously, Equation (6) is applicable for the study. The Kissinger plot by this equation for the glass, for heating rates of 5, 10, 15, and 20°C per min, is shown in Fig. 5. The value of E determined from the slope of this plot is 224.2 kJ/mol. This value is in good agreement with that of 226.2 kJ/mol obtained by Equation (5). Thus, the average activation for the crystallization can be taken to be 223±3 kJ/mol.

4. Conclusions

From the experimental results the following conclusions could be drawn :

1) Low-temperature solder glass containing $PbTiO_3$ as major crystalline phase was prepared by adding 5 wt% TiO_2 to the base glass.

2) From the nonisothermal DTA measurement, the crystallization peak temperature for the glass powder (< 44 μm) with a DTA heating rate of 10°C/min was determined as 468°C.

3) The average activation energy of crystallization obtained from the modified Ozawa and the Kissinger equations under nonisothermal condition were 223±3 kJ/mol for $PbTiO_3$. The crystallization mechanism for lead titanate was a three-dimensional process.

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