

# Low-temperature and low-expansion glass-crystal composites by the formation of Perovskite lead titanate

R. R. TUMMALA

*Glass Development Department, IBM System Products Division, East Fishkill, Hopewell Junction, New York, USA*

The development of low-expansion and low-temperature solder glass composites by the formation of Perovskite lead titanate was studied by the use of differential thermal analysis and thermal expansion measurements techniques. The thermal expansion coefficients of these composites containing Perovskite lead titanate of highly negative thermal expansion coefficient are predictable, at least in simple systems, by the existing theories of thermoelasticity.

## 1. Introduction

Low-temperature and low-thermal expansion glasses are highly desirable for a number of applications such as sealing TV bulbs, gas discharge display panels, liquid crystal displays, and others. In all these applications, the hermeticity of the device is achieved by sealing glass substrates of thermal expansion coefficient around  $90 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$  with low temperature sealing glasses. Glasses in the system  $\text{PbO}-\text{ZnO}-\text{B}_2\text{O}_3$  with small amounts of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{BaO}$ , etc [1] are often used to seal the substrates around  $450^\circ\text{C}$ . These glasses which devitrify during sealing operations, form glass-ceramic composites [2] of lower thermal expansion coefficient than the parent vitreous glass. While much work has been reported on the formation of low-expansion crystalline materials in the high-temperature, non-lead glass systems [3,4] little work has been done on the development of low-expansion materials in very low melting solder glass systems. Martin [5,6] reported the formation of lead titanate in some lead glasses, but lead titanate in his composites being mostly of cubic type, at least at low temperatures, low expansion materials were not obtained at low temperatures. The purpose of the present paper is to report the development of low-expansion composites in low-temperature lead glasses by the formation of Perovskite lead titanate crystals of negative thermal expansion.

## 2. Experimental techniques

### 2.1. Sample preparation

The glasses used in the present investigation are given in Table I. Glass 1 is a low-temperature vitreous glass, obtained by melting reagent grade oxides in platinum crucible at  $1000^\circ\text{C}$  for 3 h. Glasses 2 and 3 are standard, commercial divitrifiable solder glasses capable of sealing at about  $450^\circ\text{C}$  to substrate materials of thermal expansion coefficient in the range  $85$  to  $95 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$ . The powders of these glasses (average particle size  $10 \mu\text{m}$ ) with the desired volume proportion of submicron size titania powders were dry mixed first, and then mixed with about 2% terpeneol binder. Samples ranging in size up to  $1 \text{ cm} \times 3 \text{ cm}$  were cold-pressed and dried at  $150^\circ\text{C}$ . Following drying, the samples were heated at the rate of  $5^\circ\text{C min}^{-1}$  to a temperature of  $370^\circ\text{C}$  and held there for 1 h, and then raised to and held at  $410$  to  $430^\circ\text{C}$  for an additional hour. This procedure

TABLE I Compositions of Glasses

	Glass I	Glass II	Glass III
PbO	66.0	74.8	75.5
$\text{B}_2\text{O}_3$	14.0	8.6	9.0
ZnO	10.0	12.0	11.0
$\text{SiO}_2$	4.0	2.0	2.0
BaO	1.0	0.7	2.0
CuO	5.0	—	—
$\text{Al}_2\text{O}_3$	—	1.7	0.5
$\text{Na}_2\text{O}$	—	0.2	—

was found necessary to ensure complete removal of organics as well as to give sufficient flow of glass prior to crystallization.

## 2.2. Thermal expansion measurements

Thermal expansion measurements were made in duplicate using a continuous heating dilatometer capable of transmitting expansion of samples through a fused silica pushrod to the plunger of a linear variable differential transformer. The samples were heated at a rate of approximately  $10^{\circ}\text{C min}^{-1}$  to  $410^{\circ}\text{C}$  and then cooled slowly to room temperature. Thermal expansion coefficients were calculated from the cooling curves.

## 2.3. DTA

Differential thermal analysis of the heat-treated composites were performed both on sintered compacts and on powders obtained from crushing the sintered compacts. DTA curves were obtained on 2 to 3 g samples at a heating rate of  $3^{\circ}\text{C min}^{-1}$ . The equipment and procedure used are described elsewhere [7].

## 3. Results and discussion

Fig. 1 shows the variation of measured thermal expansion coefficient with volume proportion of titania in glass I–titania composites after heat-treatment at  $430^{\circ}\text{C}$  for 1 h. Included in this figure

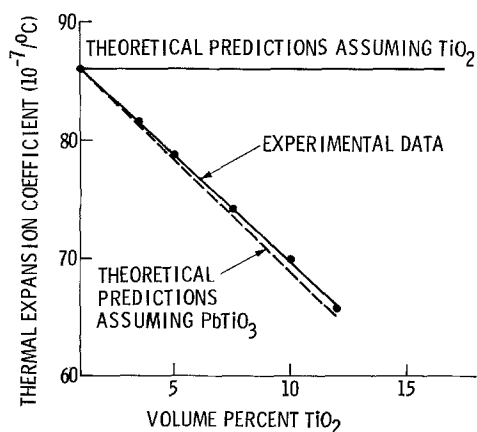


Figure 1 Thermal expansion coefficients of glass I–TiO<sub>2</sub> composites.

are the theoretical predictions based on the assumption that titania in these composites remains as titania after the heat-treatment and that the thermal expansion coefficient of polycrystalline titania is  $88 \times 10^{-7} \text{ }^{\circ}\text{C}^{-1}$  [8]. The theoretical pre-

dictions were calculated using the equation derived previously [9]:

$$\alpha_c = \alpha_m - AV_d(\alpha_m - \alpha_d)$$

$\alpha_c$  = thermal expansion coefficient of composite

$\alpha_m$  = thermal expansion coefficient of glassy matrix

$\alpha_d$  = thermal expansion coefficient of dispersed phase

$V_d$  = volume proportion of dispersed phase

$A$  = constant defined in [9],  $A = 0.87$  in the present study.

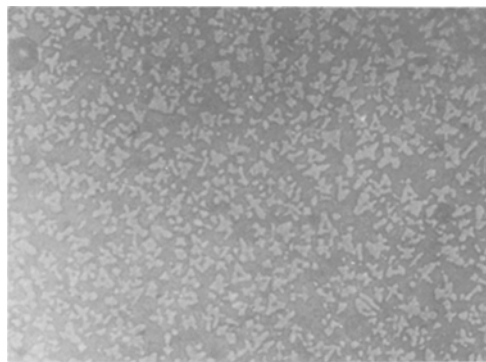
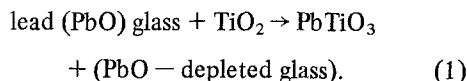


Figure 2 Microstructure of glass I–PbTiO<sub>3</sub> composite,  $\times 80$ .

The microstructure of sintered glass I–titania composites shows (Fig. 2) the presence of crystalline phases dispersed in a continuous glassy matrix. These crystalline materials were identified by X-ray diffraction to be almost completely tetragonal lead titanate and traces of titania. In these composites, which consisted originally of glass I and titania, the lead titanate seems to have formed as a result of reaction between PbO in the glass and titania dispersion, according to the reaction:



Shirane and Hoshino [10] report that Perovskite lead titanate has a negative thermal expansion coefficient up to  $490^{\circ}\text{C}$  at which temperature it undergoes transition from the tetragonal to the cubic phase with change in the thermal expansion coefficient from  $-53 \times 10^{-7} \text{ }^{\circ}\text{C}^{-1}$  to  $+83 \times 10^{-7} \text{ }^{\circ}\text{C}^{-1}$ . The dashed line shown in Fig. 1 was calculated using Equation 1, but assuming that (a) all the titania has reacted to form lead titanate, (b) the thermal expansion coefficient of Perovskite lead

titanate is  $-53 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$ , and (3) the thermal expansion coefficient of PbO-depleted glass to be lower than that of the original glass. The thermal expansion coefficients of PbO-depleted glasses were measured by melting compositions equivalent to the unreacted glassy phase compositions and found to be 83, 80, and  $79 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$  respectively corresponding to the compositions left behind after reaction with 5, 10 and 12 vol %  $\text{TiO}_2$ . The general agreement between calculated and observed thermal expansion coefficients indicates that the low thermal expansion of lead titanate-containing composites is predictable in terms of properties of individual phases. In addition, the agreement implies that no internal cracking [11] took place in these composites in spite of large differences in thermal expansion coefficient of the matrix ( $80 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$ ) and

dispersed ( $-53 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$ ) phases. The agreement between calculated and observed values could have been improved by taking into account the contribution of small amounts of residual titania (of thermal expansion coefficient  $88 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$ ) in the composites, but this was not done because the exact amount of residual titania could not be determined.

Thermal expansion coefficients of glass II– $\text{TiO}_2$  and glass III– $\text{TiO}_2$  composites are shown in Figs. 3 and 4. These composites, which contain a number of crystalline phases (Fig. 5), in addition to lead titanate, are too complex to analyse in terms of properties of individual phases, but the reduced thermal expansion coefficient coincident with the formation of Perovskite lead titanate is generally true in these composites as well. With the

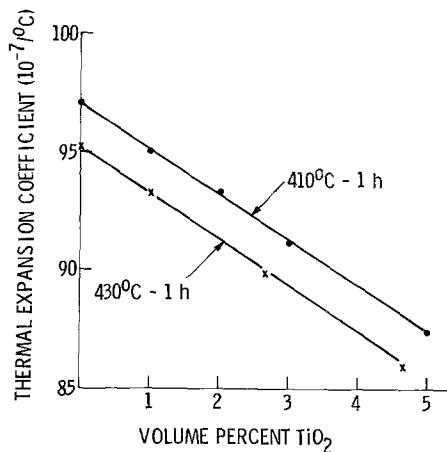


Figure 3 Thermal expansion coefficients of glass II– $\text{TiO}_2$  composites.

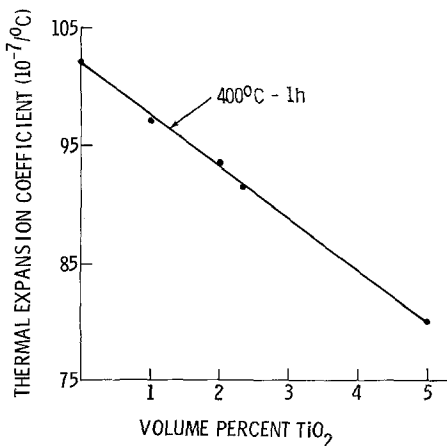


Figure 4 Thermal expansion coefficient of glass III– $\text{TiO}_2$  composites.

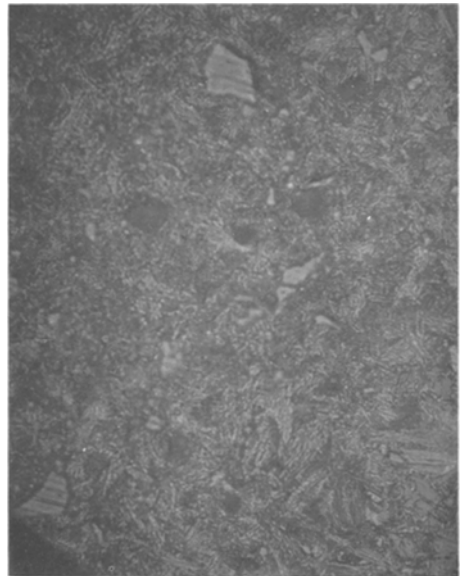


Figure 5 Microstructure of glass II +  $\text{TiO}_2$  heat-treated at  $410^\circ\text{C}$ ,  $\times 80$ .

exception of lead titanate and a trace of titania, the crystalline materials found in these composites are the same as reported by Petzoldt [12]. Whereas the solder glasses are unsuitable for sealing to substrates of a thermal expansion coefficient of  $90 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$  around  $400^\circ\text{C}$  because of their high thermal expansion coefficient in the vitreous state, the lead titanate containing composites, because of their reduced thermal expansion coefficient, are satisfactory.

The DTA of glass II without titania addition shows (Fig. 6) an endotherm at about  $350^\circ\text{C}$  corresponding to glass transition, a strong exotherm at  $477^\circ\text{C}$  corresponding to crystallization

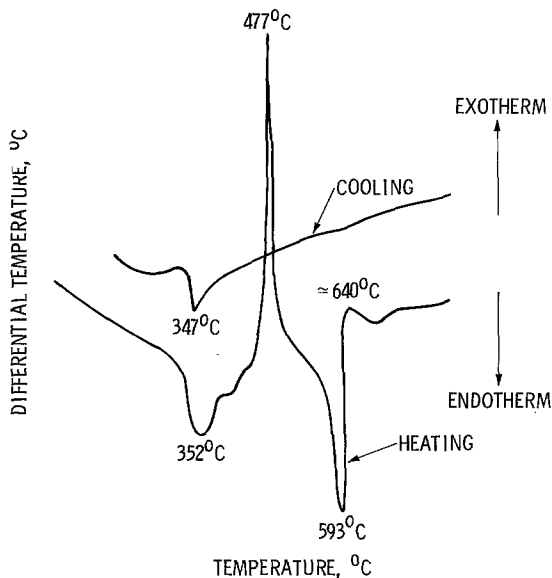


Figure 6 DTA of glass III.

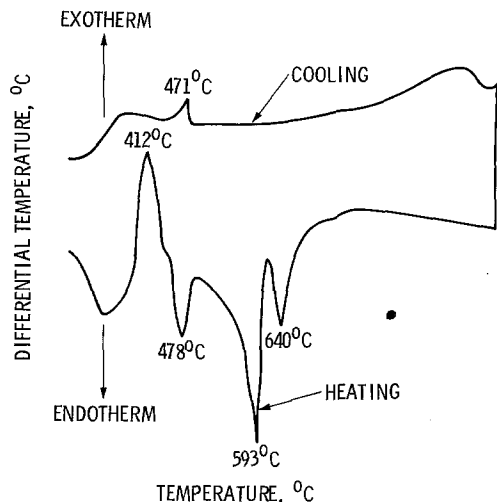


Figure 7 DTA of glass III + 5% TiO<sub>2</sub> heat-treated at 410° C for 1 h.

of one or more phases and endotherms at 539 and 640° C corresponding to the melting of crystals. The DTA curve in Fig. 7 for glass II-TiO<sub>2</sub> composite heat-treated at 410° C for 1 h prior to thermal analysis shows, in addition to the exotherm and endotherms found in glass II, an endotherm at 478° C on heating and an exotherm at 471° C on cooling. These peaks undoubtedly correspond to tetragonal to cubic transition of lead titanate, since lead titanate was the only crystalline material identified on cooling the DTA sample. The slightly lower transition temperature observed in the present composites compared to

the published value of 490° C for the tetragonal to cubic transition is attributed to the presence of residual mismatch stresses [13].

#### 4. Conclusions

It has been shown that the reaction of fine particle titania with lead glasses results in the formation of Perovskite lead titanate of negative thermal expansion coefficient. The reaction which takes place around 400° C results in the formation of composites of much lower thermal expansion than the materials presently available. The thermal expansion coefficient of composites containing lead titanate seems predictable by the existing theories of thermoelasticity. The formation of Perovskite lead titanate brings the thermal expansion coefficients and sealing temperatures to such levels as to make these composites attractive for sealing substrates of thermal expansion coefficients around  $90 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$  at about 400° C.

#### Acknowledgement

The author would like to thank Miss B. J. Foster for thermal expansion measurements, Mr W. Fedrowitz for DTA runs, and G. A. Walker and S. Lawhorne for X-ray diffraction.

#### References

1. J. DROUKAL, *Silik. Tech.* 17 (1966) 242.
2. A. E. DALE and J. E. STANWORTH, *J. Soc. Glass Tech.* 32 (1948) 147T.
3. S. D. STOOKEY, *Glastech. Ber. Fifth International Congress on Glass*, Verlag der Deutschen Glastechnischen Schen Gesellschaft, Frankfurt am Martin, (1959) pp. V/1-8.
4. P. W. McMILLAN, "Glass-Ceramics" (Academic Press, London, 1964).
5. F. W. MARTIN, *Phys. Chem. Glasses* 6 (4) (1965) 143.
6. *Idem*, U.S.P. 3 486 871 (1969).
7. A. REISMAN, M. BERKENBLIT and S. CHAN, to be published.
8. J. F. LYNCH, C. G. REUDER and W. H. DUCKWORTH, "Engineering Properties of Selected Ceramic Materials" (American Ceramic Society 1966).
9. R. R. TUMMALA, *J. Appl. Phys.* 41 (1970) 5104.
10. G. SHIRANE and S. HOSHINO, *J. Phys. Soc. Japan* 6 (1951) 265.
11. R. R. TUMMALA and A. L. FRIEDBERG, *J. Amer. Ceram. Soc.* 54 (7) (1970) 376.
12. J. PETZOLDT, *Glastech. Ber.* 39 (3) (1966) 130.
13. R. R. TUMMALA and A. L. FRIEDBERG, *J. Mater. Sci.* 6 (1971) 1421.

Received 26th March and accepted 11 June 1975.