JOURNAL OF MATERIALS SCIENCE **36** (2001) 477–483

Effect of P_2O_5, B_2O_3 and PbO on the sinterability of β.quartz solid solution and gahnite glass-ceramics

B. E. YEKTA
Ceramic Division, Materials & Energy Research Centre Tehran, Iran
V. K. MARGHUSSIAN
Ceramic Division, Department of Materials, Iran University of Science & Technology, Tehran, Iran

The effect of P_2O_5, B_2O_3 and PbO additives on the sintering and crystallization behaviour of β.quartz solid solution gahnite glass-ceramics were investigated. According to our results, only the addition of PbO to glasses produces sinterable glass-ceramics containing β.quartz solid solution and gahnite as the sole crystalline phases, respectively. The nucleation mechanism of the glasses were determined by the Ozawa equation and their activation energy for crystallization were determined by the modified form of the Kissinger, Matusita and Marotta equations. The results indicate that the better sinterability of the lead bearing β.q.$_{ss}$ glass-ceramic than the lead free one could be explained by changes of bulk to surface nucleation and increase of its activation energy for crystallization. At the other hand, it could not be observed any differences between the nucleation mechanism and the activation energy for crystallization of the lead bearing and lead free gahnite glass-ceramics. Then the differences in sinterability of the two glass-ceramics could not be explained by comparison of theirs activation energy for crystallization.

1. Introduction

While the crystallization of bulk glasses based on the $ZnO\text{-}Al_2O_3\text{-}SiO_2$ system has been investigated extensively [1–6], the sintering-crystallization route for production of glass-ceramics in this system has attracted little attention.

The aim of this investigation was preparation of β.quartz solid solution (β.q.$_{ss}$) and gahnite ($ZnAl_2O_4$) glass-ceramics with compositions located in the above system by sintering of compacted glass powders. It is known that the crystallization usually prevents the complete densification of glass powders [7–10]. According to previous claims [7], glass compositions developed for production of bulk glass-ceramics are not suitable for the sintering route. If these glasses are finely ground and compacted again, every particle will crystallize in its volume separately and its crystallization will result in an infinite increase in viscosity excluding proper sintering. On the other hand, glasses which are usually capable of surface crystallization may be successfully sintered before or simultaneously with crystallization. In this case although every particle crystallizes from its surface, the significant surface area of ground material ensures volume fine crystallization. At the other hand, phase transformation of β.q.$_{ss}$ and gahnite crystalline phases to higher temperature crystalline forms, e.g., gahnite in the case of β.q.$_{ss}$ and cristobalite in the case of gahnite glass-ceramics, limits the sintering temperature of the glasses to about the onset of their crystallization peak temperatures. Accordingly, the addition of various amounts of B_2O_3, P_2O_5 and PbO to the above-mentioned glass system was considered.

These oxides are known to lower the viscosity of silicate glasses. There are some reports about the effect of B_2O_3 [8, 9, 11–13], P_2O_5 [8, 9, 13] and PbO [11, 14] additives on the sintering of magnesium aluminosilicate and lithium aluminosilicate glass-ceramics. But to our knowledge the effect of these additives on the sintering and crystallization behaviour of $ZnO\text{-}Al_2O_3\text{-}SiO_2$ glasses has not yet been reported.

2. Experimental procedure

2.1. Glass prepartion

The glasses were prepared by fusing reagent-grade chemicals in a platinum crucible for 2 h at 1480°C in an electric furnace. The molten glasses were then quenched in cold distilled water. The chemical compositions of the glasses are displayed in Tables I and II. Glass A was prepared by addition of 2 wt% Li_2O to a composition reported as suitable for production of β.q.$_{ss}$ glass-ceramics. Glass B was also prepared by replacing ZrO_2 with TiO_2 in the original glass. The effect of individual amounts of PbO, P_2O_5 and B_2O_3 on the sintering behaviour of the glasses were examined by addition of 5, 10 and 15 wt% of these oxides as a replacement for ZnO or directly to the total composition for

TABLE I Chemical composition of glasses after addition of PbO, B_2O_3 and P_2O_3 into glass A

glass	SiO_2	Al_2O_3	ZnO	ZrO_2	Li_2O	As_2O_3	PbO	B_2O_3	P_2O_5
A	45.57	22.78	22.78	6.37	2	0.49	—	—	—
A PbO5	45.57	22.78	17.78	6.37	2	0.49	5.00	—	—
A PbO10	45.57	22.78	12.78	6.37	2	0.49	10.00	—	—
A PbO15	45.57	22.78	7.78	6.37	2	0.49	15.00	—	—
A PbO17.5	45.57	22.78	5.28	6.37	2	0.49	17.50	—	—
A $B_2O_3$5	45.57	22.78	17.78	6.37	2	0.49	—	5.00	—
A $B_2O_3$10	45.57	22.78	12.78	6.37	2	0.49	—	10.00	—
A $B_2O_3$15	45.57	22.78	7.78	6.37	2	0.49	—	15.00	—
A $P_2O_5$5	45.57	22.78	17.78	6.37	2	0.49	—	—	5.00
A $P_2O_5$10	45.57	22.78	12.78	6.37	2	0.49	—	—	10.00
A PO15	45.57	22.78	7.78	6.37	2	0.49	—	—	15.00

TABLE II Chemical composition of glasses after addition of PbO, B_2O_3 and P_2O_5 into glass B

Glass	SiO_2	Al_2O_3	ZnO	TiO_2	As_2O_3	PbO	B_2O_3	P_2O_5
B	46.50	23.25	23.25	6.50	0.50	—	—	—
B PbO5	44.17	22.09	22.09	6.17	0.47	5.00	—	—
B PbO10	41.85	20.92	20.92	5.85	0.45	10.00	—	—
B PbO15	39.52	19.76	19.76	5.52	0.42	15.00	—	—
B PbO17.5	38.36	19.18	19.18	5.36	0.41	17.50	—	—
B $B_2O_3$5	44.17	22.09	22.09	6.17	0.47	—	5.00	—
B $B_2O_3$10	41.82	20.92	20.92	5.85	0.45	—	10.00	—
B $B_2O_3$15	39.52	19.76	19.76	5.52	0.42	—	15.00	—
B $P_2O_5$5	44.17	22.09	22.09	6.17	0.47	—	—	5.00
B $P_2O_5$10	41.85	20.92	20.92	5.85	0.45	—	—	10.00
B $P_2O_5$15	39.52	19.76	19.76	5.52	0.42	—	—	15.00

glass A and B, respectively. In the case of PbO, a 17.5 wt% addition also was made in the above-mentioned manner to both glasses.

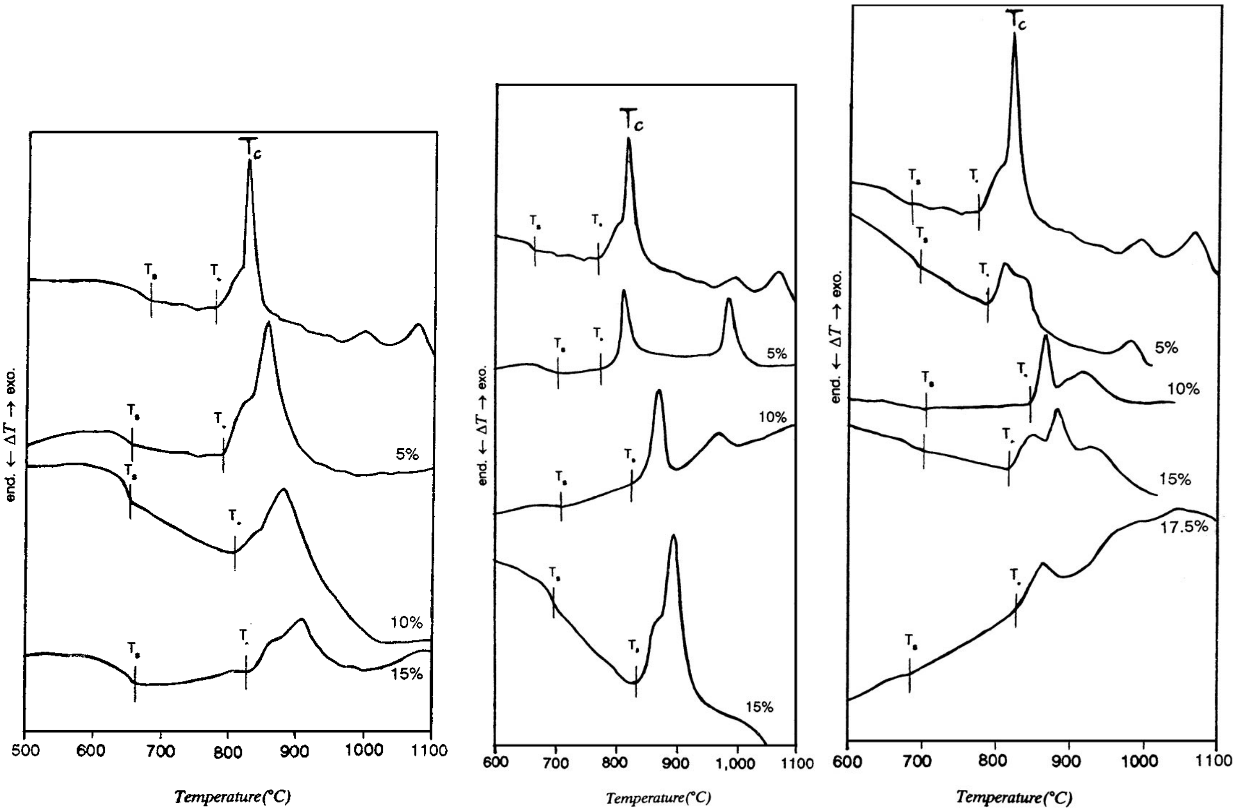
2.2. Methods of analyses

The glass frits were ground in an electric hard porcelain mortar for 4 h and then ball-milled for 18 h. The particle size measurements of the powdered glasses which were carried out by a laser particle size analyser (Fritsch, Analysete 22) showed a mean particle size of 1.5–3.0 μm . The dilatometric softening point (T_s), the onset of the crystallization peak temperature (T_o) and the maximum crystallization peak temperature (T_c) of the glass powders were determined by Differential Thermal Analysis (polymer laboratories, model 1640) using 20 mg af glass powders in a platinum crucible in an air atmosphere with a heating rate of 10°C min^{-1}. DTA was also used to obtain the nucleation mechanism and the activation energy values for crystallization of glasses by using the Ozawa [15], Marotta [16], Matusita [17] and modified Kissinger [18] methods at heating rates of 10, 20, 30 and 40°C min^{-1}. The glass powders were mixed with 0.45 wt% carboxy methyl cellulose and cold-pressed using a laboratory uniaxial hydraulic press into $57 \times 15 \times 4$ mm rectangular bars at initial and final pressures af 10 and 40 MPa, respectively.

The effect of B_2O_3, P_2O_5 and PbO on the sinterability of the glasses was investigated by sintering them for 60 min at the onset of their crystallization peak temperatures with a heating rate of 40°C min^{-1} in an electric furnace. The crystalline phases precipitated during sintering were identified by XRD (Siemens, model D-500).

3. Results and discussion

According to the experimental results, crystallization of a compacted glass powder during sintering increases its viscosity and therefore prevents the complete densification of the body. Thus it seems that the optimum temperature for sintering of a compacted glass powder, which is susceptible to crystallization, is the onset of its crystallization peak temperature at which the rate of viscous flow is higher than the rate of nucleation and growth of the crystalline phase. Figs 1a–c and 2a–c depict the DTA curves of the glasses A and B containing various amounts of B_2O_3, P_2O_5 and PbO, at a heating rate of 10°C min^{-1}, respectively. Tables III and IV show the characteristic temperatures of the glasses obtained from the above DTA results. Figs 3 and 4 depict the linear shrinkages of the two series of glasses after sintering at the onset of their crystallization peak temperatures for 60 min. According to these figures while the addition of B_2O_3, P_2O_5 and PbO improves the sinterability of glass A, the sinterability of glass B can only be improved by addition of PbO. With attention to the Figs 1 and 2 and Tables III and IV it can be concluded that the improvement of sinterability of the glasses are associated with a) the shift of the crystallization peak temperatures to higher temperatures, b) increase in the temperature interval between the dilatometric softening point and the onest of the crystallization temperature and, in the case of β.q.$_{ss}$ glass-ceramic, c) a decrease in the DTA peak intensity. It seems that the increase of crystallization temperature and widening of the temperature interval between dilatometric softening point and the onset crystallization temperature improves the sinterability via providing more opportunity for viscous flow of glasses. The increase of activation energy for



(a) (b) (c)

Figure 1 (a) DTA curves of glass A containing various amount of B_2O_3, at a heating rate of 10°C min^{-1}; (b) DTA curves of glass A containing various amount of P_2O_5, at a heating rate of 10°C min^{-1}; (c) DTA curves of glass A containing various amount of PbO, at a heating rate of 10°C min^{-1}.

TABLE III Characteristic temperatures (°C) of glass A containing various amounts of PbO, B_2O_3 and P_2O_5, respectively

glass	T_s	T_o	T_c	T_o-T_s
A	680	775	831	95
A PbO5	690	785	813	95
A PbO10	695	825	855	130
A PbO15	700	815	847	115
A PbO17.5	675	838	867	163
A $B_2O_3$5	680	785	855	105
A $B_2O_3$10	655	810	885	155
A $B_2O_3$15	655	830	915	175
A $P_2O_5$5	705	775	817	70
A $P_2O_5$10	715	830	868	115
A $P_2O_5$15	715	840	894	125

TABLE IV Characteristic temperatures (°C) of glass B containing various amounts of PbO, B_2O_3 and P_2O_5, respectively

glass	T_s	T_o	T_c	T_o-T_s
B	725	775	823	50
B PbO5	724	800	837	76
B PbO10	725	795	846	70
B PbO15	700	820	847	120
B PbO17.5	695	820	858	125
B $B_2O_3$5	710	800	846	90
B $B_2O_3$10	715	780	806	65
B $B_2O_3$15	720	760	782	40
B $P_2O_5$5	700	790	865	90
B $P_2O_5$10	670	830	790	60
B $P_2O_5$15	620	680	780	60

crystallization of the glasses which shows itself as a decrease in peak intensity in the DTA experiments, might be the other factor affecting the sinterability of the glasses.

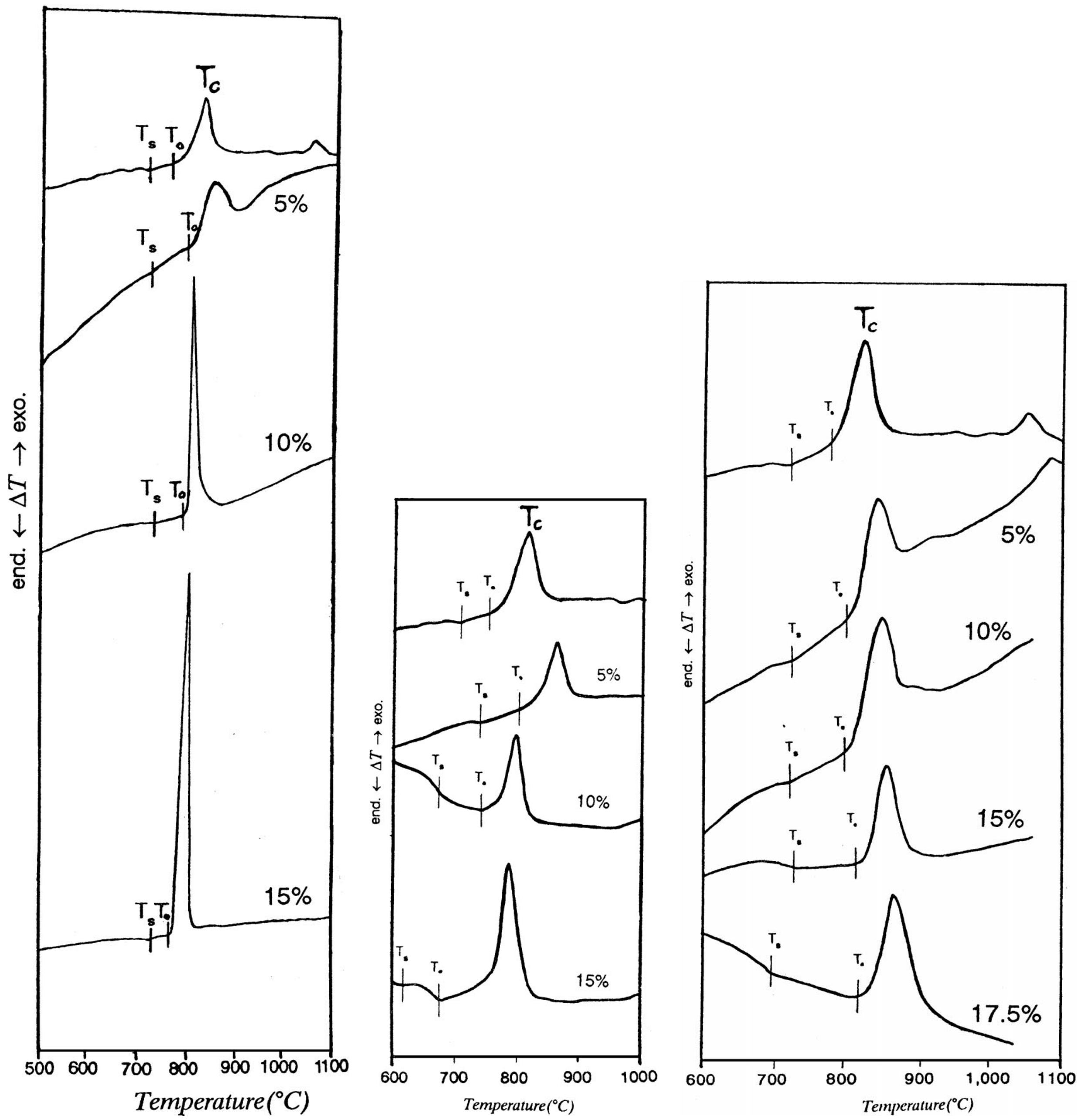
XRD results of the heat treated glasses indicate that the addition of PbO and P_2O_5 to glass A and PbO and B_2O_3 to glass B produces glass-ceramics containing β.q.$_{ss}$ and gahnite, as the sole crystalline phases, respectively. According to our results [10], the β.q.$_{ss}$ and gahnite crystallized at about 700°C in both glasses, APbO17.5 and BPbO17.5, and were thermaly stable respectibvely up to 820 and 900°C. After that a new crystalline phase appeared in each sample of lead aluminosilicate in APbO17.5 and cristobalite in BPbO17.5, respectively.

In addition, as the sintering behaviour of the glasses A and B improved similarly by the addition of PbO, the glasses APbO17.5 and BPbO17.5 adopted for subsequent calculations.

Accordingly, the nucleation mechanism and the activation energy for crystallization of the glasses A, APbO17.5, B and BPbO17.5 were calculated and compared with each other. The nucleation mechanism (n) was determined by the Ozawa equation:

$$[\mathrm{d}\ \ln(-\ln(1-x))/\mathrm{d}\ \ln\alpha]_T = -n$$

Where x is the volume fraction crystallized at a fixed temperature (T) when heated at a heating rate of α and is determined through the ratio of the partial area at a certain temperature to the total area of a DTA



(a) (b) (c)

Figure 2 (a) DTA curves of glass B containing various amount of B_2O_3, at a heating rate of 10°C min^{-1}; (b) DTA curves of glass B containing various amount of P_2O_5, at a heating rate of 10°C min^{-1}; (c) DTA curves of glass B containing various amount of PbO, at a heating rate of 10°C min^{-1}.

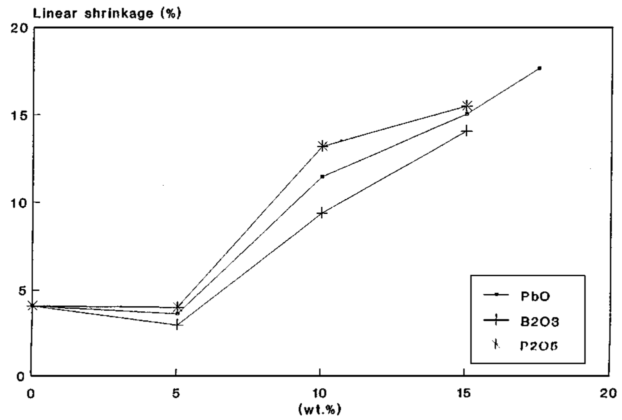


Figure 3 The linear shrinkage of glass A containing various amount of PbO, B_2O_3 and P_2O_5.

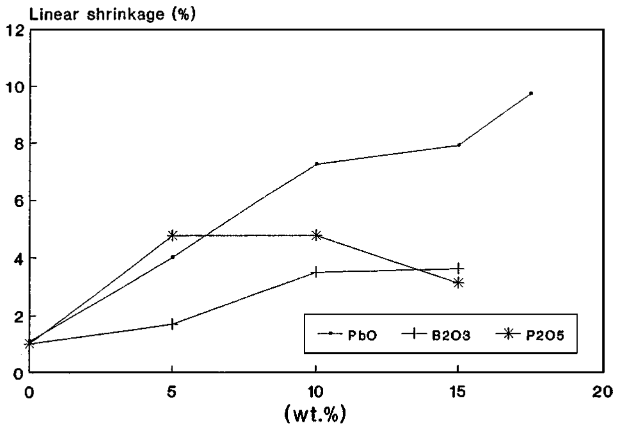


Figure 4 The linear shrinkage of glass B containing various amount of PbO, B_2O_3 and P_2O_5.

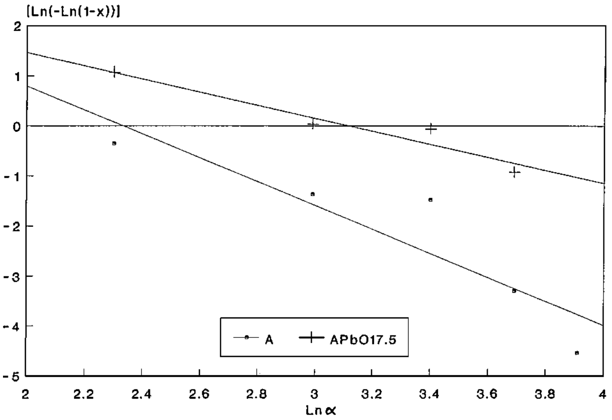


Figure 5 The Ozawa plot for the A and APbO17.5 glasses.

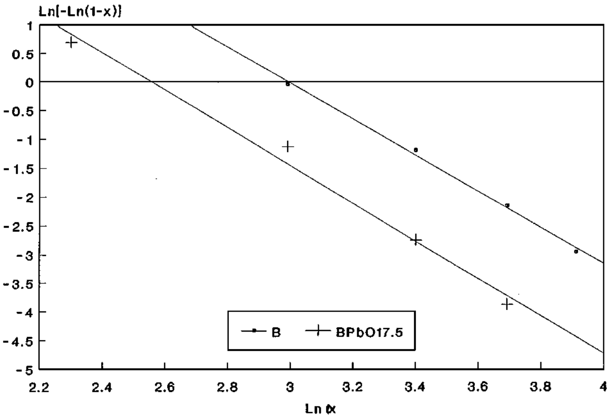


Figure 6 The Ozawa plot for the B and BPbO17.5 glasses.

crystallization exotherm. When surface crystallization dominates, $n = 1$, and when crystallization occurs dominantly in the bulk, $n = 3$. Figs 5 and 6 show the Ozawa plot for the A, APbO17.5, B and BPbO17.5 glasses, respectively. The n values determined according to this procedure were 3, 1, 3 and 3 for the glasses A, APbO17.5, B and BPbO17.5, respectively. Thus it can be concluded that the crystallization in the glasses A, B and BPbO17.5 occur dominantly in the bulk, wheares in the glass APbO17.5 surface crystallization dominates. These results are not consistent with Rabinovich results [7] and indicates that the sinterability of glass-ceramic powder does not depend on the crystallization mechanisms.

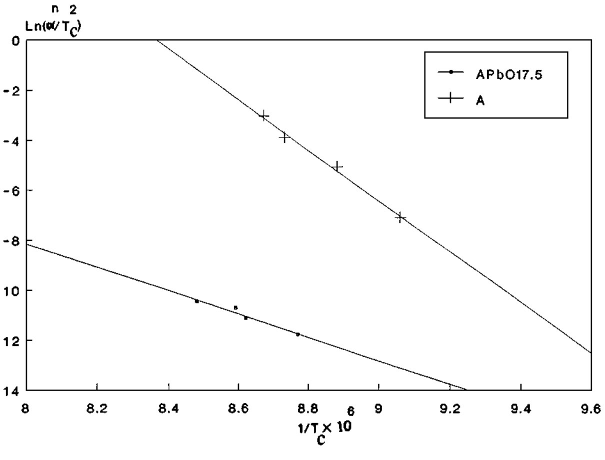


Figure 7 The modified Kissinger plots for the A and APbO17.5 glasses.

Activation energy for crystallization of the glasses were determined by the modified form of the Kissinger, Matusita and Marotta equations:

$$\mathrm{Ln}\left(\alpha n/T_c^{2}\right) = -mEc/RT_c + \mathrm{const.}$$

(modified Kissinger)

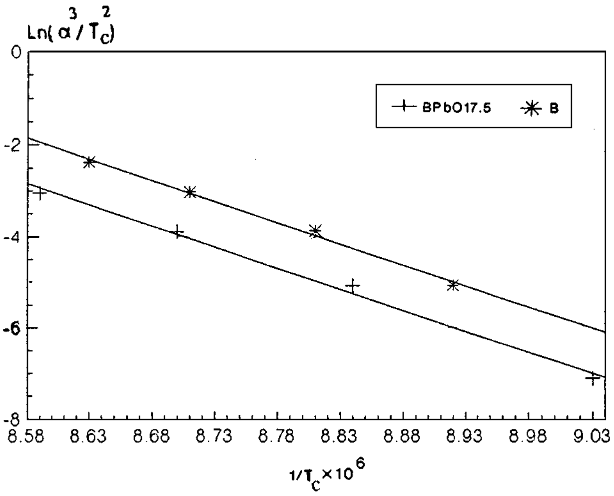
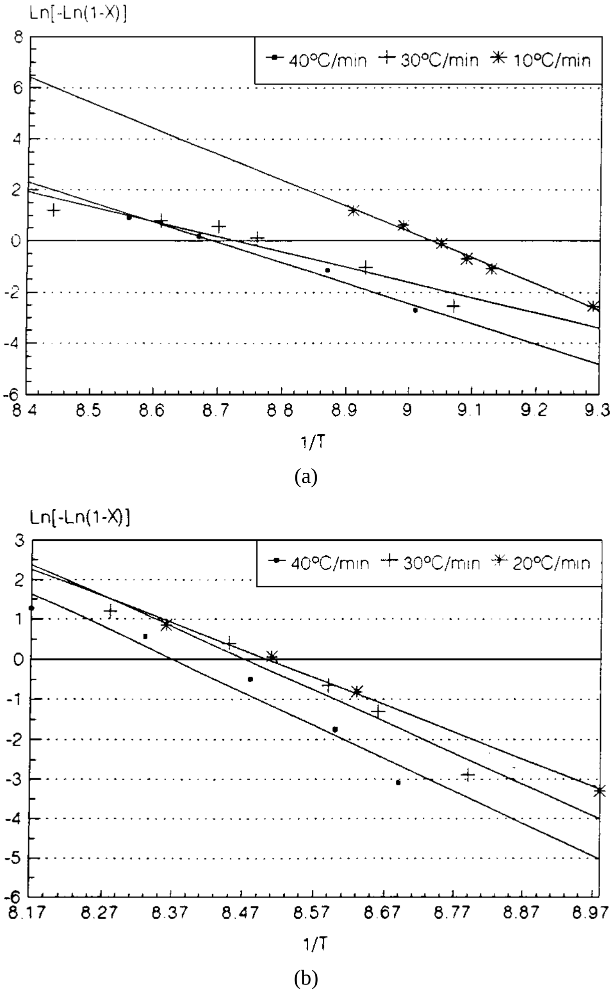


Figure 8 The modified Kissinger plots for the B and BPbO17.5 glasses.



(a)

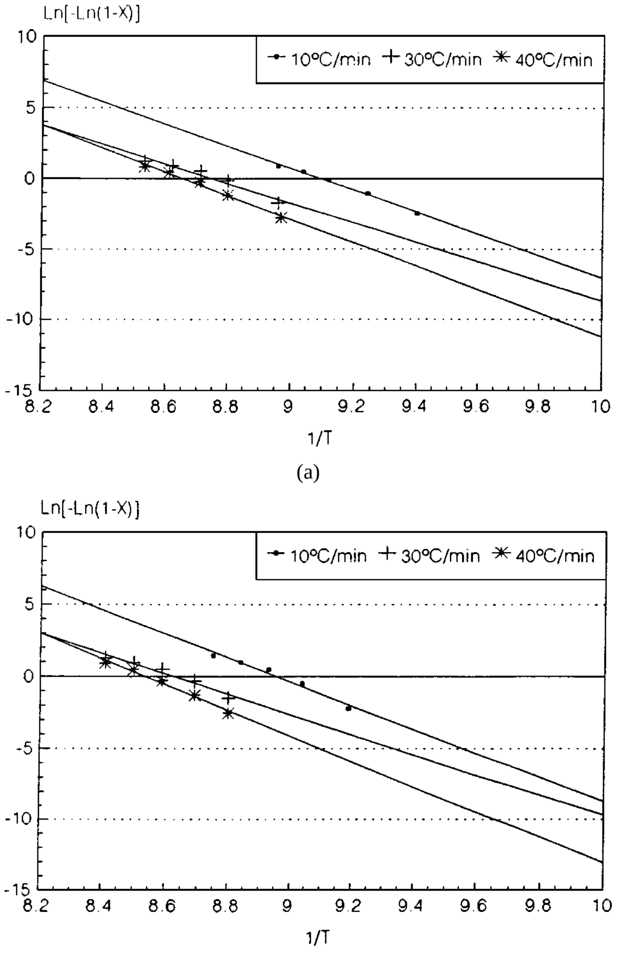
(b)

Figure 9 (a) The Matusita plots for the A glass; (b) The Matusita plots for the APbO17.5 glass.

$$\mathrm{Ln}[-\mathrm{Ln}(1-x)] = -n\,\mathrm{Ln}\,\alpha - \frac{1.052mE_c}{RT} + \text{const.}$$
(Matusita)

$$\mathrm{Ln}\,\alpha = -\frac{E}{RT_c} + \text{const.} \quad \text{(Marotta)}$$

Where E_c, T_c, R, and m indicate the activation energy for crystallization, crystallization peak temperature at a heating rate of α, the gas constant and the dimensionality of crystal growth, respectively. The value of m is related to n as: $m = n$ when crystallization at different heating rates occurs on a fixed number of nuclei (in other words the number of nuclei is constant during the DTA runs at different values of α) and $m = n - 1$ when nucleation occurs during the DTA runs [17]. In this work, as we did not consider any nucleation step before DTA runs and sintering experiments, m should be equal to $n - 1$. Figs 7–12 depict the modified Kissinger, Matusita and Marotta plots for the A, APbO17.5, B and BPbO17.5 glasses, respectively. The activation energy for crystallization of the glasses determined from above-mentioned methods are summerized in Table V. It can be seen that while there are no difference between the activation energies for crystallization of the two gahnite glass-ceramics, the activation energy for crystallization of glass APbO17.5 is higher than glass A (as determined by different methods).



(a)

(b)

Figure 10 (a) The Matusita plots for the B glass; (b) The Matusita plots for the BPbO17.5 glass.

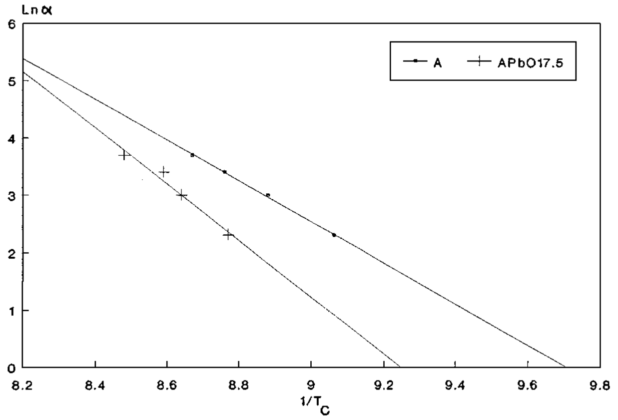


Figure 11 The Marotta plots for the A and APbO17.5 glasses.

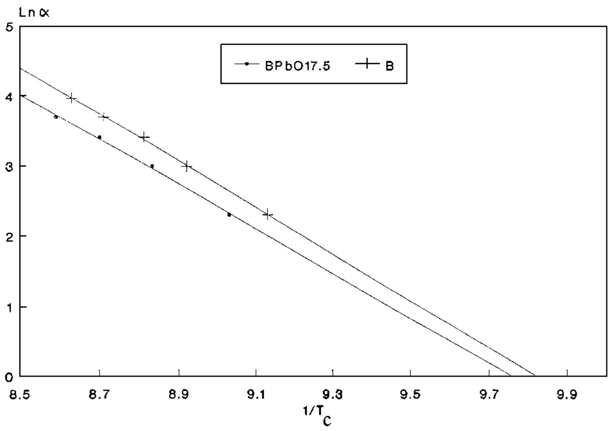


Figure 12 The Marotta plots for the B and BPbO17.5 glasses.

TABLE V The activation energy for crystallization of the glasses

			E (kj/mol)		
glass	n	m	Marrota	Matusita	modified Kissinger
A	3	2	301.6	303.5	370.5
A PbO17.5	1	1	373.7	309.5	392.0
B	3	2	259.6	323.0	381.0
B PbO17.5	3	2	260.0	359.0	381.0

Therefore the better sinterability of lead bearing β.q.$_{\text{ss}}$ and gahnite glass-ceramics as compared with the lead free glass-ceramics can be explained by increase in peak temperature for the crystallization exothermic effect and peak broadening, indicating suppression of devitrification propensity.

4. Conclusions

1. Addition of B_2O_3, P_2O_5 and PbO improves the sinterability of β.q.$_{\text{ss}}$ glass-ceramics. The sinterability of gahnite glass-ceramic can only improve by addition of PbO.

2. The improvement of sinterability of the glasses by additives are associated with a) the shift of the crystallization peak temperatures to higher temperatures, b) increase in the temperature interval between the dilatometric softening point and the onset of the

crystallization temperature and, in the case of β.q.$_{ss}$ glass-ceramics, c) a decreased in the DTA peak intensity.

3. Whereas the improvement of sinterability of β.q.$_{ss}$ glass-ceramic by addition of PbO were associated by an increase in the activation energy for crystallization and a decrease in the crystallization mode, the addition of PbO into the gahnite glass-ceramic does not changes the above mentioned parameters.

4. The activation energies for crystallization of the sinterable β.q.$_{ss}$ glass-ceramic calculated by Morotta, Matusita and modified Kissinger methods were 373.7, 309.5 and 392.0 kJ/mol, respectively. The activation energies for crystallization of the sinterable gahnite glass-ceramic calculated by the above-mentioned methods were 260.0, 359.0 and 381.0, respectively.

References

1. Z. STRNAD, "Glass-Ceramic Materials, Glass Science and Thechnology" (Elsevier, New York, 1986) p. 104.
2. P. W. MCMILLAN, "Glass-Ceramics" (Academic Press, New York, 1979) p. 147.
3. P. W. MCMILLAN, G. PARTRIDGE and J. G. DARRANT, *Phys. Chem. Glass* **10** (1969) 153.
4. G. H. BEAL and D. A. DUKE, *J. Mater. Sci.* **4** (1969) 340.
5. E. TKALCEC, H. IVANKOVIC and B. GRZETA, *J. Non-Cryst. Solids* **129** (1991) 174.
6. A. J. STRYJAK and P. W. MCMILLAN, *J. Mat. Sci.* **13** (1978) 1275.
7. E. M. RABINOVICH, in "Advances in Ceramics, Vol. 4: Nucleation and Crystallization in Glasses," edited by J. H. Simmons, D. R. Uhlmann's and G. H. Beall (Am. Ceram. Soc., Ohio, 1982) p. 327.
8. S. KNICKERBOCKER, M. R. TUZZOLO and S. LAWHORNE, *J. Amer. Ceram. Soc.* **72** (1989) 1873.
9. S. H. KNICKERBOCKER, A. H. KUMAR and L. W. HERRON, *Am. Ceram. Soc. Bull.* **72** (1993) 90.
10. B. EFTEKHARI YEKTA and V. K. MARGHUSSIAN, *J. Eur. Ceram.* **19** (1999) 2963.
11. L. F. SHEN, S. C. LIH and H. C. JUNG, *Ceramic Int.* **20** (1994) 67.
12. J. JYH SHYU and C. TANG WANG, *J. Mater. Sci.* **31** (1996) 3603.
13. J.J. SHYU and H.H. LEE, *J. Amer. Ceram. Soc.* **78** (1995) 2161.
14. C. LEONELLI, T. MANFREDINI, M. PAGANELLI and G.C. PELLACANI, *ibid.* **74** (1991) 983.
15. T. OZAWA, *Polymer* **12** (1971) 150.
16. A. MAROTTA, A. BURI and P.PERNICE, *Phys. Chemis. Glasses* **12** (1980) 94.
17. K. MATUSITA, T. KOMATSU and R. YOKOTA, *J. Mater. Sci.* **19** (1984) 291.
18. K. MATUSITA and S.SAKKA, *J. Non Cryst. Solids* **38/39** (1980) 741.

Received 25 August 1999
and accepted 22 May 2000