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CRYSTALLIZATION KINETICS OF BaO-Al₂O₃-SiO₂ GLASSES

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SUMMARY

Barium aluminosilicate glasses are being investigated as matrix materials in high-temperature ceramic composites for structural applications. Kinetics of crystallization of two refractory glass compositions in the barium aluminosilicate system have been studied by differential thermal analysis (DTA), X-ray diffraction (XRD), and scanning electron microscopy (SEM). From variable heating rate DTA, the crystallization activation energies for glass compositions (wt.%) 10BaO-38Al₂O₃-51SiO₂-1MoO₃ (glass A) and 39BaO-25Al₂O₃-35SiO₂-1MoO₃ (glass B) were determined to be 553 and 558 kJ/mol, respectively. On thermal treatment, the crystalline phases in glasses A and B were identified as mullite (3Al₂O₃-2SiO₂) and hexacelsian (BaO.Al₂O₃.2SiO₂), respectively. Hexacelsian is a high-temperature polymorph which is metastable below 1590°C. It undergoes structural transformation into the orthorhombic form at ~300°C accompanied by a large volume change which is undesirable for structural applications. A process needs to be developed where stable monoclinic celsian, rather than hexacelsian, precipitates out as the crystal phase in glass B.

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INTRODUCTION

Refractory glass compositions in the barium aluminosilicate system are being considered as matrix material in the fabrication of ceramic-fiber reinforced ceramic-matrix composites for high temperature structural applications in the high efficiency, high performance aerospace propulsion and power systems of the future. Information on the crystallization behavior of these glasses is needed for converting them into more refractory glass ceramics. The objective of this study was to investigate the crystallization kinetics and other properties pertinent to the use in composite processing of two glass compositions belonging to the highly refractory $\text{BaO-Al}_2\text{O}_3\text{-SiO}_2$ system. The kinetics of crystallization have been evaluated using differential thermal analysis. The crystalline phases in the heat treated glasses were identified by X-ray diffraction and the morphologies of crystal growth were observed in the scanning electron microscope.

EXPERIMENTAL PROCEDURE

Barium aluminosilicate (BAS) glasses, of the compositions listed in Table I, were melted in a continuous electric arc furnace. The glass samples were fabricated in the form of bars, rods, and flakes. Thermal expansion coefficient(α), glass transition temperature (T_g), and softening point(T_s) were measured using an Orton automatic recording dilatometer. Glass rods of ~1cm diameter were annealed for 2h at 800°C. The rods were cut to 2.54cm lengths and run at a rate of

3°C/min in static air. Densities of annealed glass samples were measured by the immersion method in water. Measurements were made on several samples of each glass.

Crystallization kinetics of the glasses was studied by differential thermal analysis (DTA) using a Perkin-Elmer DTA-1700 system interfaced with a computerized data acquisition and manipulation system. Glass flakes were crushed and sieved into various size fractions. The crystallization peak temperatures of the glasses were measured in the DTA at various scan rates from 2.5 to 40°C/min in flowing argon. Samples of glass B in the form of bulk pieces (~2mm) and powder (<60 mesh) were run in the DTA whereas a 20 to 60 mesh powder sample of glass A was used. Glass transition temperatures were also obtained from DTA, and compared with the values derived from dilatometry.

To study the crystallization of the glasses, rods of each glass were sliced into discs (~2mm thick by ~1cm diameter) and heat treated in air in an electric furnace. The samples were held isothermally for 1 or 10 hours at various temperatures from below the glass transition to above the highest crystallization peak temperature at 50°C intervals. Phases crystallizing in the heat treated glasses were identified by x-ray diffraction (XRD) using a Phillips ADP-3600 diffractometer equipped with a crystal monochromator and copper K α radiation. Several samples were analyzed before and after being crushed.

The morphology of the crystalline phases developed by heat treatment of bulk glass samples was examined in a Cambridge Stereoscan

200 scanning electron microscope (SEM). Duplicate heat treated samples were mounted in epoxy, ground and polished to a 0.5 μm finish. After polishing, the samples were lightly etched with HF to reveal the crystalline microstructure. A thin layer of gold was evaporated onto the sample surface before viewing in the SEM.

RESULTS AND DISCUSSION

Positions of the glass compositions used in the present study in the $\text{BaO-Al}_2\text{O}_3\text{-SiO}_2$ phase diagram¹ are shown in Fig. 1. Values of density, thermal expansion coefficient, glass transition temperature (T_g), and softening point (T_s) as obtained from dilatometry for the BAS glasses are given in Table II. Note that the viscosity corresponding to the dilatometric softening point, T_s , is about $10^{11.5}$ Pa.s in contrast with a value of $10^{6.6}$ Pa.s at the ASTM or "Littleton" softening point of glass. Glass B has higher values of density, thermal expansion coefficient, transition temperature and softening point than glass A probably due to the higher baria and lower silica contents of glass B. The knowledge of these physical properties will be useful in determining the processing parameters for the fiber reinforced glass composites.

Typical DTA traces for the crystallization of glass compositions A and B are shown in Fig. 2. The effect of heating rate on the DTA crystallization peak is illustrated in Figs. 3 through 5. The crystallization exotherm shifts to higher temperature with increase in heating rate. The powder sample of glass A shows a sharp, symmetrical exothermic peak whereas the powder sample of glass B showed a very

broad crystallization peak. This could have been caused by crystallization of a second phase in the bulk of the glass B. In order to investigate this further, samples of glass B with different surface areas were run in the DTA. A significant difference in peak temperature was seen for the samples of different sizes. The powder samples crystallized at lower temperatures than the bulk samples. Also, the crystallization peaks of the powder samples are sharper and more distinct. This is probably due to the higher surface area of the powder samples which results in a greater number of nucleation sites for the crystals to form and grow from. Values of the crystallization peak temperature at various scan rates for the different glass samples are given in Table III. The T_g values obtained from the DTA traces are also shown. The T_g values obtained from DTA are higher than those from dilatometry probably due to the fact that unannealed samples were used in the DTA scans.

A variable heating rate DTA method was used to evaluate the kinetic parameters for crystallization of the glasses. The kinetic model of Bansal et al². was used which is expressed as:

$$\ln[T_p^2/\Theta] = \ln(E/R\nu) + E/(RT_p) \quad (1)$$

where T_p is the peak maximum temperature, Θ the heating rate, E the activation energy, R the gas constant, and ν the frequency factor. The crystallization kinetic parameters (E and ν) are related to the reaction rate constant (k) through the Arrhenius-type expression:

$$k = \nu \exp[-E/RT] \quad (2)$$

Equation (1) is an extension of the Johnson-Mehl-Avrami^{3,4} isothermal kinetic model for use in non-isothermal methods. It has been demonstrated in earlier studies⁵⁻⁷ that the crystallization kinetic parameters obtained from the isothermal method and the non-isothermal technique using eq.(1) are in excellent agreement. In the derivation of eq.(1) it has been assumed that the rate of reaction is maximum at the peak which is a valid assumption for power-compensated differential scanning calorimetry (DSC) but not for DTA. However, the DTA peak corresponds to the point at which the heat balance at the sample thermocouple is zero. The maximum rate of reaction normally occurs at a point prior to the DTA peak temperature. So long as a consistent point is chosen, e.g., peak temperature, onset temperature, etc., to represent a given process in a series of DTA traces recorded at different scan rates, activation energies in agreement with the DSC results would be obtained. However, the attempt frequency, ν , would depend on the choice of that representative temperature. Hammett and Loehman⁸ obtained quite similar results from DSC and DTA techniques for the crystallization of a complex lithium silicate glass composition. This implies that DTA can be used to evaluate crystallization activation energy at temperatures beyond the range of DSC. The plots of $\ln(T_p^2/\theta)$ vs. $1/T_p$ for the crystallization of glasses A and B are shown in Fig. 6. The plots are linear indicating the applicability of the kinetic model of Bansal et al². The values of the crystallization kinetic parameters for the two glasses evaluated

from linear least squares fitting of the experimental data from eq.(1) are presented in Table IV. Surprisingly, the values of the crystallization activation energy for the two glasses are about the same even though the compositions and the structures of the phases crystallizing out in the two glasses are quite different as seen from the XRD results presented below.

The results of XRD analysis of the heat treated glasses are summarized in Table V. Selected powder XRD patterns of the heat treated samples are shown in Figs. 7 and 8. Both glasses remain amorphous up to 950°C. After 1h at this temperature, glass A exhibits a trace of mullite and glass B contains hexacelsian. Mullite is the only phase detected in samples of glass A. It occurs in increasing amounts as the treatment temperature and time increase. Substantial amounts of amorphous phase remain in glass A even after heating for 10h at 1150°C. After 1h at 950°C, hexacelsian is detected in glass B and the amount of this phase increases with treatment temperature and time. After 1h at 1050°C, a second phase (celsian) is seen in the powder XRD pattern. Celsian is present in small amounts in all samples heat treated above this temperature. Only small amounts of amorphous phase remain above 1000°C. Bahat⁹ has also reported the presence of hexacelsian as the crystalline phase in BaO-Al₂O₃-SiO₂ glass ceramic containing 1wt% of MoO₃ as the nucleating agent.

Figure 9 shows the difference in surface versus bulk crystallization in glass B. The XRD pattern obtained from the surface of the heat treated specimen shows only hexacelsian phase. The difference in relative peak intensities is probably due to orientation

of the surface crystals. The XRD powder pattern of the same sample exhibits the peaks for hexacelsian at the correct positions and expected relative intensities and also reveals the presence of a small amount of monoclinic celsian phase. These results correlate well with the DTA results obtained for different particle sizes of glass B.

Figures 10 and 11 show SEM photomicrographs of polished and etched samples of each glass after different heat treatments. In glass A heated at 1150°C for 1 and 10h, clusters of mullite crystals are seen. The clusters are larger and more numerous in the 10h sample. Samples of glass B heated at 1000 and 1150°C for 1h show a different morphology. At 1000°C, the sample is not completely crystallized. Large dark areas of glassy material remain. In the crystallized regions, crystals of ~5 to 10µm sizes are present. At 1150°C, the sample is almost fully crystallized and the crystal size has increased to ~20 to 30µm. From electron microscopy and energy dispersive spectroscopy (Fig. 12), hexacelsian was found¹⁸ to be the main crystalline phase in glass B heated for 1h at 800°C and for 48h at 1000°C. A small amount of mullite is also present along the grain boundaries of the hexacelsian crystals.

Celsian, $\text{BaAl}_2\text{Si}_2\text{O}_8$, exists in two polymorphs. Hexacelsian is the high temperature phase and celsian the low temperature form. Hexacelsian has a hexagonal structure and celsian is monoclinic. The average linear thermal expansion coefficients¹⁰ of hexacelsian (300 - 1000°C) and celsian (20 - 1000°C) are $\sim 8.0 \times 10^{-6}$ and $2.29 \times 10^{-6}/^\circ\text{C}$, respectively. The celsian to hexacelsian phase change occurs at $\sim 1590^\circ\text{C}$. At temperatures below $\sim 1590^\circ\text{C}$, hexacelsian is metastable.

Bahat¹¹ has studied the heterogeneous nucleation of alkaline earth feldspar ($\text{RO-Al}_2\text{O}_3\text{-SiO}_2$ where $\text{R} = \text{Ba, Sr, or Ca}$) glasses by a wide variety of nucleating agents. It is generally believed^{12,13} that for heterogeneous nucleation, a close similarity between the lattice parameters of the nucleating agent and the nucleated crystal is an important parameter in determining the effectiveness of the agent. However, Bahat¹¹ observed that the nucleation by various nucleating agents in the $\text{RO-Al}_2\text{O}_3\text{-SiO}_2$ glasses had no correlation with the crystal structure of the catalyst, thus questioning the importance of close structural geometric fit between the catalyst and the nucleated crystal in these glasses. The metastable forms (hexagonal and orthorhombic) of the alkaline earth feldspars nucleated more readily from the glasses than the stable forms (monoclinic and triclinic). This was ascribed to the simpler structures of the high symmetry modifications. The hexagonal forms are roughly built¹⁴ of alternate double sheets of tetrahedra and a single layer of R^{2+} cations normal to the c-axis. In contrast, the low symmetry forms¹⁵ are made of three-dimensional networks in which the Al and Si are at least partially ordered in a special distribution. Due to these structural differences, the high symmetry forms have lower kinetic barriers for nucleation.

Unfortunately, the hexacelsian to celsian transformation is very sluggish. Bahat¹⁶ has investigated the kinetics of hexacelsian to celsian transformation. The activation energy of crystal growth of celsian from hexacelsian was found to be quite low (20.1 ± 20 % kcal/mol) suggesting that the transformation does not involve the

breaking of Si-O or Al-O bonds. The solid solubilities¹⁰ of silica in the hexagonal and monoclinic modifications of celsian are about 4 and 2 wt%, respectively. During the transformation of hexacelsian into the monoclinic form, the excess silica must precipitate out. The kinetics of exsolution of silica may control the rate of the overall transformation. The transformation of hexacelsian into the monoclinic modification is very sluggish probably due to the slow rate of diffusion of silica. Also, at $\sim 300^{\circ}\text{C}$ hexacelsian undergoes a rapid, reversible displacive transformation¹⁷ into the orthorhombic form accompanied by a large volume change of 3% or more. On thermal cycling this would lead to microcracking of composites with glass B as the matrix which is unacceptable. Celsian does not undergo any phase change and is the desired phase for structural glass-ceramic composites. It is, therefore, necessary to create the necessary conditions for the crystallization of celsian rather than hexacelsian in the glass upon heat treatment if the BAS glass is to be used as the matrix material for high temperature composites. This is the subject of research currently in progress¹⁸.

SUMMARY AND CONCLUSIONS

Crystallization kinetics of two refractory barium aluminosilicate glasses has been investigated by variable heating rate differential thermal analysis. The crystallization activation energies of the glass compositions (wt%) 10BaO-39Al₂O₃-49SiO₂-1MoO₃ (glass A) and 37BaO-26Al₂O₃-34SiO₂-1MoO₃ (glass B) are evaluated to be 553 and 558 kJ/mol, respectively. On thermal treatment, mullite (3Al₂O₃-2SiO₂) and

hexacelsian ($\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) crystallized out in glasses A and B, respectively. Hexacelsian is stable above $\sim 1590^\circ\text{C}$ and metastable below this temperature. At $\sim 300^\circ\text{C}$ hexacelsian undergoes a rapid, reversible displacive transformation into orthorhombic form accompanied by a large volume change of $\sim 3\%$ which is undesirable as a matrix material for structural composites. Monoclinic celsian is the stable phase below $\sim 1590^\circ\text{C}$ and is the desired phase. Processing conditions need to be developed so that celsian, rather than hexacelsian, precipitates out in glass B on heat treatment.

ACKNOWLEDGMENTS

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TABLE I. - COMPOSITIONS (WEIGHT %) OF THE BARIUM ALUMINOSILICATE GLASSES INVESTIGATED

Component	Glass A		Glass B	
	Batch	Analyzed	Batch	Analyzed
BaO	10	10.3	39	36.7
Al ₂ O ₃	38	39.3	25	26.2
SiO ₂	51	49.4	35	34.0
MoO ₃	1	1.0	1	1.0

TABLE II. - VALUES OF DENSITY, AVERAGE THERMAL EXPANSION COEFFICIENT, GLASS TRANSITION TEMPERATURE, AND DILATOMETRIC SOFTENING POINT OF THE BARIUM ALUMINOSILICATE GLASSES

Glass composition	Density, g/cm ³	$\alpha \times 10^6, ^\circ\text{C}^{-1}$	T _g , [*] °C	T _s , [*] °C
A	2.797±0.003	3.66	850	922
B	3.220±0.003	5.95	877	926

*From dilatometry.
†25-800 °C.

TABLE III. - DTA GLASS TRANSITION AND CRYSTALLIZATION PEAK TEMPERATURES AT VARIOUS SCAN RATES FOR THE BARIUM ALUMINOSILICATE GLASSES

Glass composition	Scan rate, θ °C/min	T _p , °C	T _g [*] , °C
A (powder)	2.5	994	-----
	5	1008	-----
	10	1023	-----
	20	1039	887
	30	1053	893
	40	1062	898
B (powder)	2.5	1002	-----
	5	1024	-----
	10	1037	-----
	20	1064	-----
	30	1074	878
	40	1082	888
B (bulk)	2.5	1083	-----
	5	1100	-----
	10	1121	882
	20	1144	885
	30	1161	888
	40	1168	892

*From DTA.

TABLE IV. - KINETIC PARAMETERS FOR THE CRYSTALLIZATION OF BARIUM ALUMINOSILICATE GLASSES

Glass	E, kJ/mol	v , s ⁻¹
A (Powder)	553	1.2x10 ²⁰
B (Powder)	543	2.2x10 ¹⁹
B (Bulk)	558	3.7x10 ¹⁸

TABLE V. - CRYSTALLINE PHASES AND PHYSICAL APPEARANCE OF THE BARIUM ALUMINOSILICATE GLASSES AFTER VARIOUS HEAT TREATMENTS

Treatment		Glass A		Glass B	
Temperature, °C	Time, hr	Crystal phase*	Appearance	Crystal phase*	Appearance
850	1	Amorphous	Tan-clear	Amorphous	Tan-clear with streaks
900	1	Amorphous	Tan-clear	Amorphous	Tan-clear with streaks
950	1	Mullite tr	Red-brown clear	BaAl ₂ Si ₂ O ₈ hc	Mottle-brown translucent
1000	1	Mullite	Red-brown clear	BaAl ₂ Si ₂ O ₈ hc	Mottle brown opaque
1050	1	Mullite	Red-brown	BaAl ₂ Si ₂ O ₈ hc, c	Mottle brown opaque
1100	1			BaAl ₂ Si ₂ O ₈ hc, c	Mottle brown opaque
1150	1	Mullite	Red-brown clear	BaAl ₂ Si ₂ O ₈ hc, c	Mottle brown opaque
1150	10	Mullite	Gray-brown translucent	BaAl ₂ Si ₂ O ₈ hc, c	Mottle brown opaque

*From XRD.
hc - hexacelsion
c - celsian

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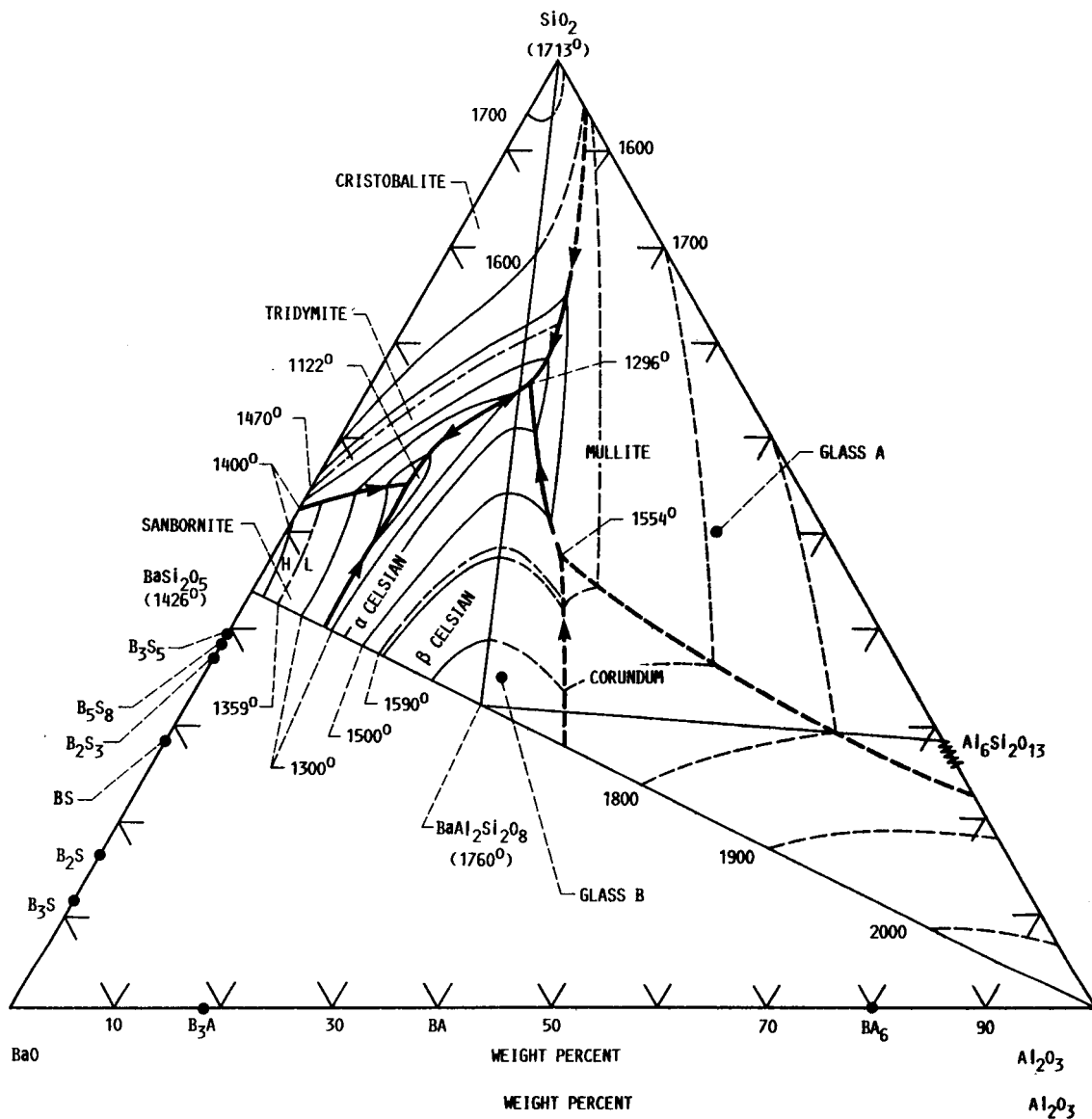


FIGURE 1. - PHASE DIAGRAM OF THE BaO-Al₂O₃-SiO₂ SYSTEM SHOWING THE POSITIONS OF THE GLASS COMPOSITIONS USED IN THE PRESENT STUDY. (TAKEN FROM FIGURE 4544 PHASE DIAGRAMS FOR CERAMISTS-1975 SUPPLEMENT BY E.M. LEVIN AND H.F. McMURDIE, EDITED BY M.K. RESER, THE AMER. CERAM. SOC., COLUMBUS, OH, P. 220.)

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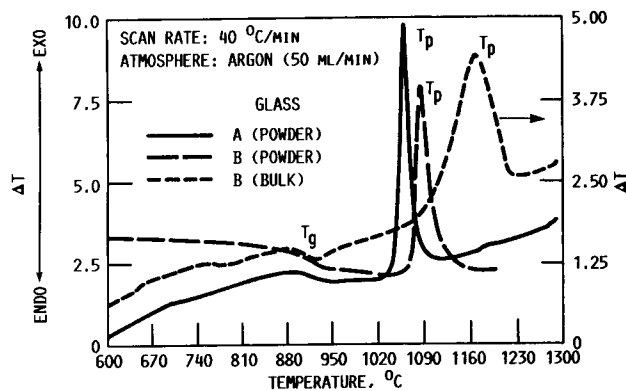


FIGURE 2. - TYPICAL DTA TRACES OF BARIUM ALUMINO-SILICATE GLASSES OF COMPOSITIONS A (POWDER) AND B (BULK AND POWDER) USING SCAN RATE OF 40 °C/MIN UNDER ARGON FLOW; T_g IS THE GLASS TRANSITION PEAK AND T_p IS THE CRYSTALLIZATION PEAK TEMPERATURE.

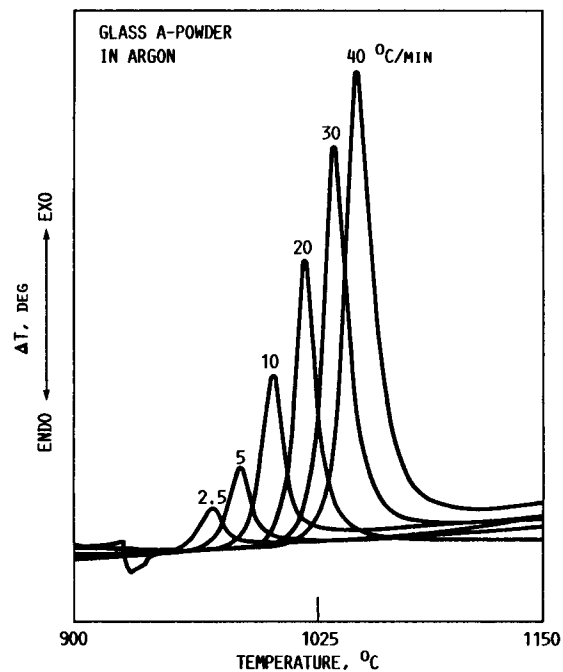


FIGURE 3. - INFLUENCE OF HEATING RATE ON THE DTA EXOTHERM FOR THE CRYSTALLIZATION OF BARIUM ALUMINOSILICATE GLASS (POWDER) OF COMPOSITION A IN ARGON.

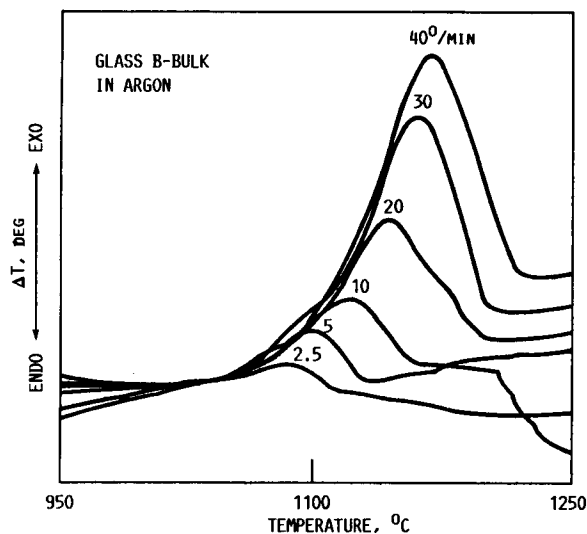


FIGURE 4. - EFFECT OF HEATING RATE ON THE DTA CRYSTALLIZATION PEAK FOR THE BARIUM ALUMINOSILICATE GLASS (BULK) OF COMPOSITION B UNDER ARGON FLOW.

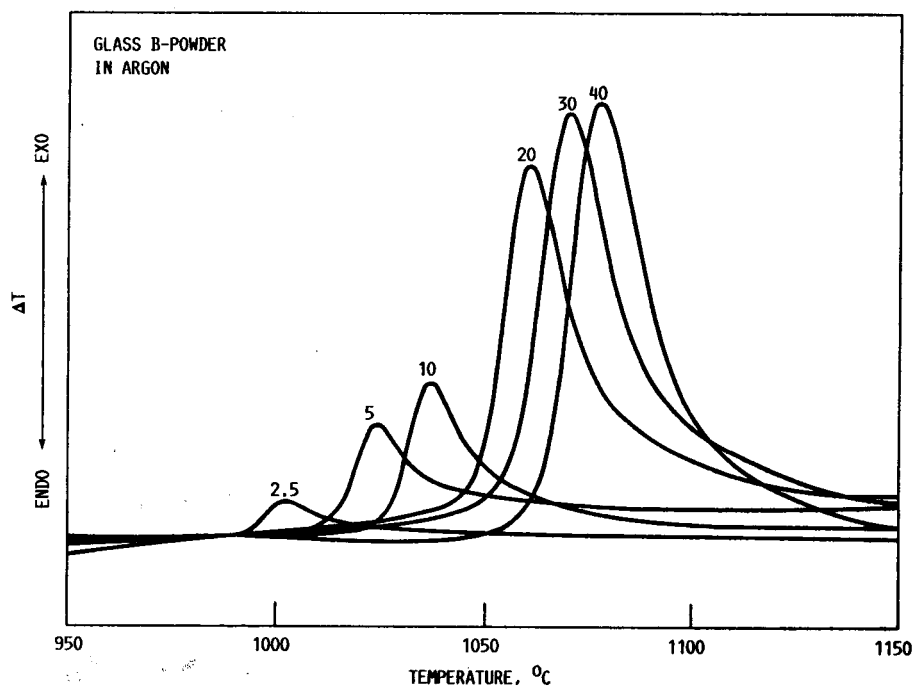


FIGURE 5. - EFFECT OF HEATING RATE ON THE DTA CRYSTALLIZATION EXOTHERM OF BARIUM ALUMINO-SILICATE GLASS (POWDER) OF COMPOSITION B IN ARGON.

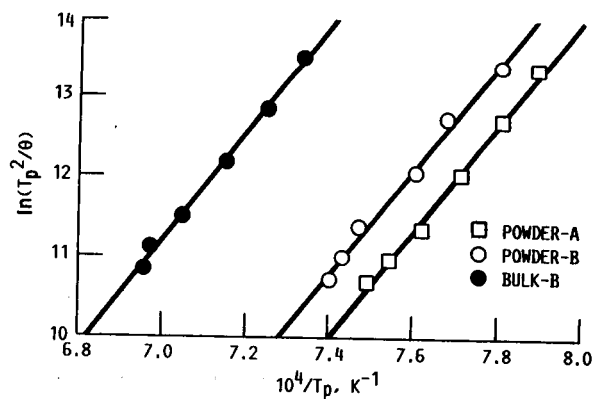


FIGURE 6. - PLOTS OF $\ln(T_p^2/\theta)$ AGAINST RECIPROCAL OF PEAK TEMPERATURE FOR THE CRYSTALLIZATION OF BARIUM ALUMINOSILICATE GLASSES OF COMPOSITIONS A AND B.

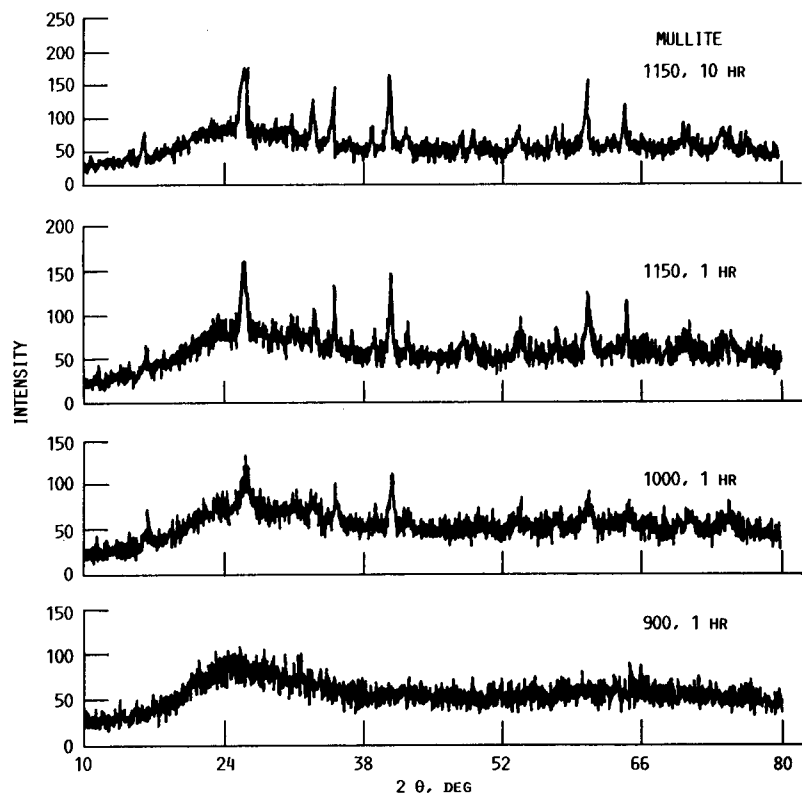


FIGURE 7. - POWDER X-RAY DIFFRACTION PATTERNS OF BARIUM ALUMINOSILICATE GLASS OF COMPOSITION A AFTER VARIOUS HEAT TREATMENTS AS INDICATED.

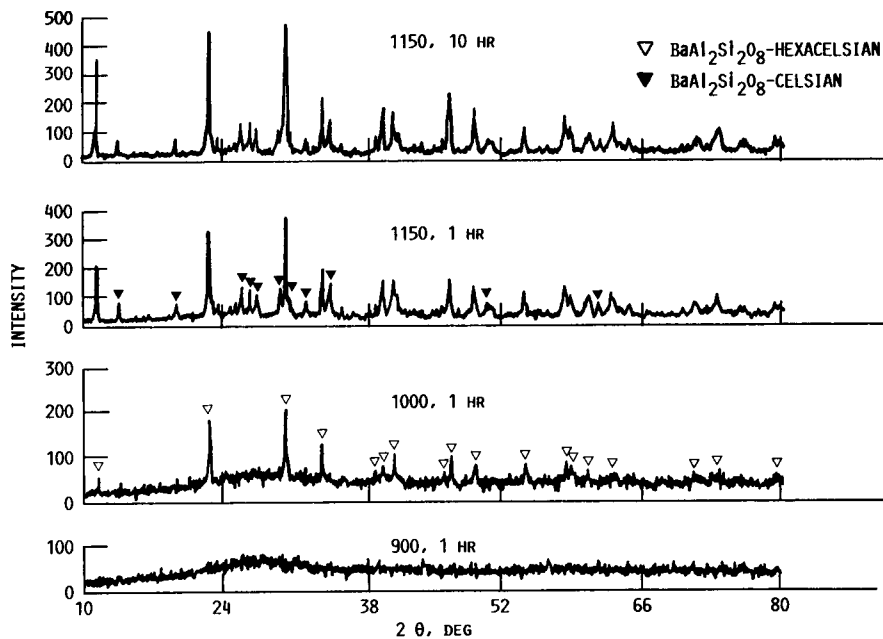


FIGURE 8. - POWDER X-RAY DIFFRACTION SPECTRA OF BARIUM ALUMINOSILICATE GLASS OF COMPOSITION B AFTER DIFFERENT THERMAL TREATMENTS AS SHOWN.

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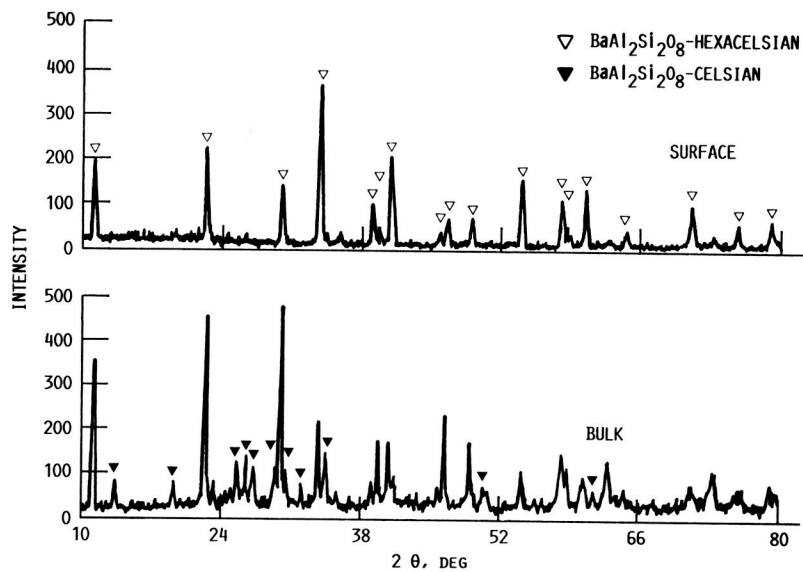


FIGURE 9. - X-RAY DIFFRACTION PATTERNS SHOWING THE DEVELOPMENT OF DIFFERENT CRYSTALLINE PHASES ON THE SURFACE AND IN THE BULK OF A BARIUM ALUMINO-SILICATE GLASS OF COMPOSITION B ON HEATING FOR 10 HR AT 1150 °C.

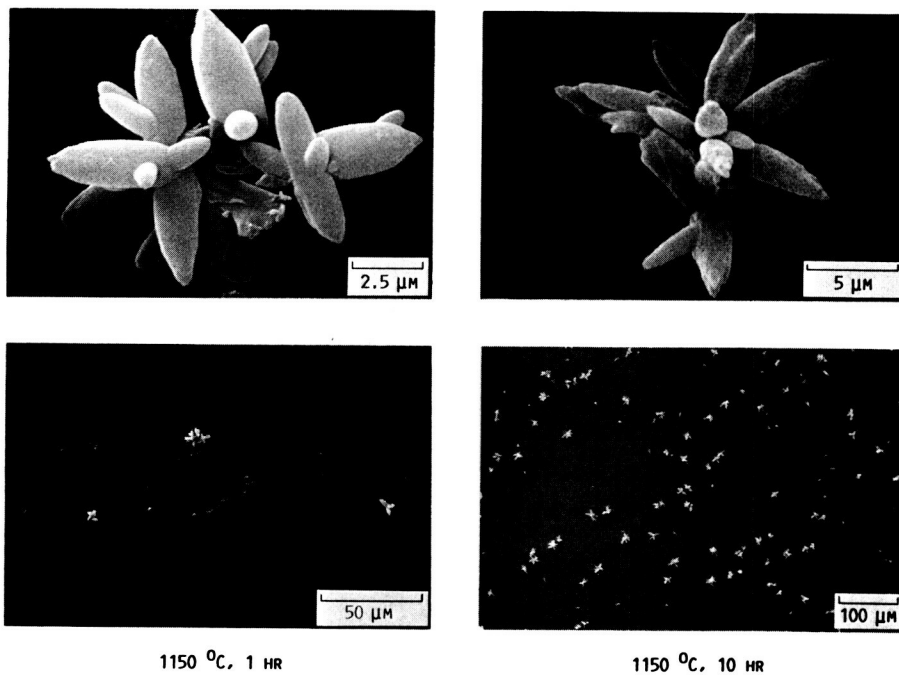
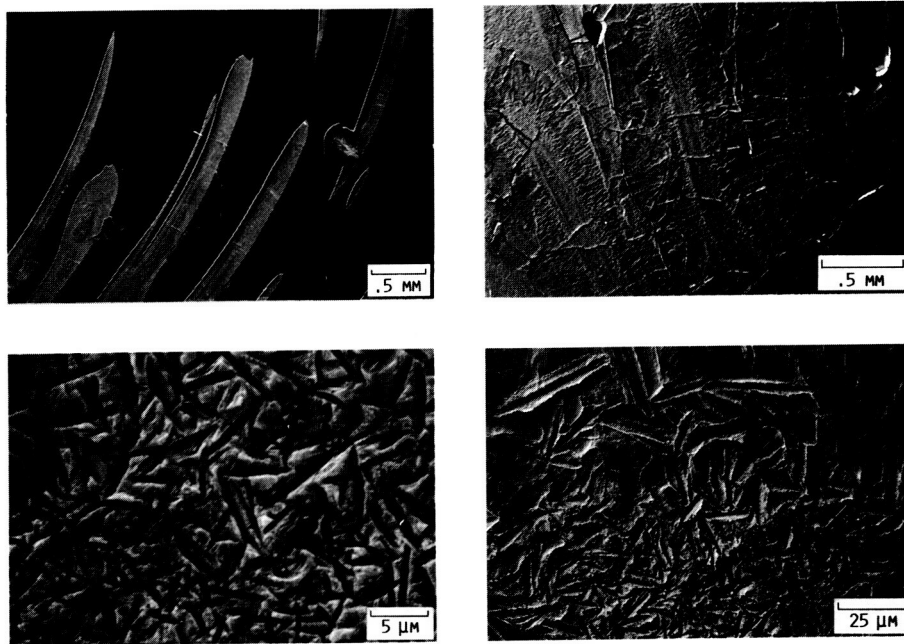


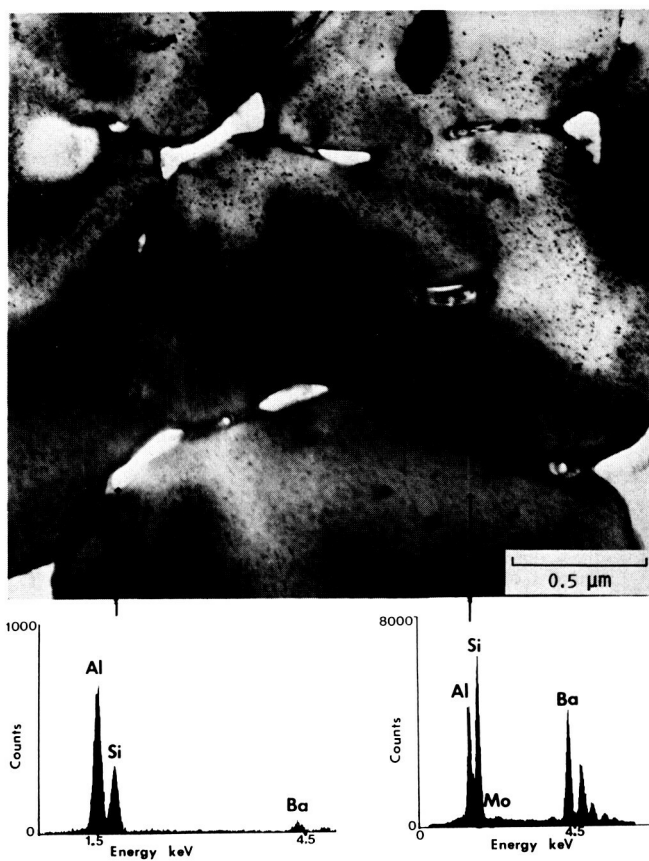
FIGURE 10. - SCANNING ELECTRON MICROGRAPHS OF BARIUM ALUMINOSILICATE GLASS OF COMPOSITION A AFTER HEATING AT 1150 °C FOR 1 HR AND 10 HR.



1000 °C, 1 HR

1150 °C, 1 HR

FIGURE 11. - SCANNING ELECTRON MICROGRAPHS OF BARIUM ALUMINOSILICATE GLASS OF COMPOSITION B HEATED FOR 1 HR AT 1000 AND 1150 °C.



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FIGURE 12. - TRANSMISSION ELECTRON MICROGRAPH AND ENERGY DISPERSIVE SPECTRA OF GLASS B HEATED FOR 1 HR AT 800 °C AND FOR 48 HR AT 1000 °C. THE SMALL CRYSTALS ALONG THE GRAIN BOUNDARIES OF LARGE HEXACELSIAN CRYSTALS ARE SEEN¹⁸ TO BE OF MULLITE.

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16. Abstract Barium aluminosilicate glasses are being investigated as matrix materials in high-temperature ceramic composites for structural applications. Kinetics of crystallization of two refractory glass compositions in the barium aluminosilicate system have been studied by differential thermal analysis (DTA), x-ray diffraction (XRD), and scanning electron microscopy (SEM). From variable heating rate DTA, the crystallization activation energies for glass compositions (wt %) 10BaO-38Al ₂ O ₃ -51SiO ₂ -1MoO ₃ (glass A) and 39BaO-25Al ₂ O ₃ -35SiO ₂ -1MoO ₃ (glass B) were determined to be 553 and 558 kJ/mol, respectively. On thermal treatment, the crystalline phases in glasses A and B were identified as mullite (3Al ₂ O ₃ -2SiO ₂) and hexacelsian (BaO.Al ₂ O ₃ .2SiO ₂), respectively. Hexacelsian is a high-temperature polymorph which is metastable below 1590 °C. It undergoes structural transformation into the orthorhombic form at ~300 °C accompanied by a large volume change which is undesirable for structural applications. A process needs to be developed where stable monoclinic celsian, rather than hexacelsian, precipitates out as the crystal phase in glass B.					
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