JOURNAL OF MATERIALS SCIENCE 30 (1995) 405–409

Study of the preparation process for $BaO–Al_2O_3–SiO_2$ powders by a two-step method

LIU ZHIEN, HU YING, YUAN JIANJUN
Department of Inorganic Materials, East China University of Science and Technology, Shanghai 200237, People's Republic of China

$BaO–SiO_2$ and $Al_2O_3–SiO_2$ dried gel powders were prepared by the sol–gel process using TEOS, aluminium nitrate and barium acetate as raw materials. By using these starting materials, β-$BaAl_2Si_2O_8$ (hexacelsian) powders with small particle size were obtained after calcining at 1000 °C. The effects of solvents and prehydrolysis of TEOS on the gelation were studied. The physical and chemical changes, and phase transformation of the gel powders for $BaO(Al_2O_3)–SiO_2$ and $BaO–Al_2O_3–SiO_2$ systems during heating were examined using differential thermal analysis, gas chromatography and X-ray diffraction. The particle sizes of the gel powders obtained were also observed by SEM and TEM.

1. Introduction

Because of its good performance, glasses and ceramics in the $BaO–Al_2O_3–SiO_2$ system have attracted much research interest. For example, $BaO–Al_2O_3–SiO_2$ ceramic has high hardness, resistance to high temperature (the maximum use temperature is as high as 1500 °C), and low thermal expansion coefficient (especially for a ceramic with celsian composition). It can be used as high-temperature structural materials.

The sol–gel process is an effective way to prepare $BaO–Al_2O_3–SiO_2$ ceramic with high quality. Tredway and Risbud [1] synthesized glass powders in the $BaO–Al_2O_3–SiO_2$ system by the sol–gel process using TEOS, aluminium-sec-butoxide and barium acetate as starting materials. However, it is difficult to obtain homogeneous $BaO–Al_2O_3–SiO_2$ gel when using barium acetate, aluminium nitrate and TEOS as starting materials. Therefore, in present work, $BaO–SiO_2$ and $Al_2O_3–SiO_2$ gel were formed by the sol–gel process. Then $BaO–Al_2O_3–SiO_2$ powders were obtained by mixing them thoroughly. In this way, high-performance ceramics can be prepared using $BaO–Al_2O_3–SiO_2$ powders, with small particle size and high reactivity, as starting materials.

Because $Al_2O_3–SiO_2$ gel is easily formed, the synthesis of $BaO–SiO_2$ gel was systematically studied in this work.

2. Experimental procedure

2.1. Preparation of $BaO–Al_2O_3–SiO_2$ powders

The starting materials were TEOS (SiO_2 28.0%), aluminium nitrate ($Al(NO_3)_3 \cdot 9H_2O \geqslant 99.0\%$) and barium acetate ($Ba(CH_3COO)_2 \geqslant 99.0\%$). Alcohol and distilled water were used as solvents, hydrochloric acid and ammonia as catalysts. Gel formation and powder preparation are shown in Fig. 1.

2.2 Characterization of powders

The physical and chemical changes of $BaO–SiO_2$ and $Al_2O_3–SiO_2$ dried gel powders during heating were studied using CRY-1 DTA equipment and a 100 gas chromatogram meter. The crystalline phases and grain size of the powders prepared were examined by a D/max-II X-ray diffractometer and a 250-MK3 SEM (or H-800 TEM), respectively. The flexural strength of $BaO–Al_2O_3–SiO_2$ ceramics and composites were determined using a 1195 (Instron) Universal Testing Machine. The samples were cut and ground into the form of $2.5 \times 5 \times 30\ mm^3$. The specimens were loaded at a uniform rate of $0.5\ mm\ min^{-1}$.

3. Results and discussion

3.1. Formation of $BaO–SiO_2$ gel

3.1.1. *Effect of solvents on the formation of $BaO–SiO_2$ gel*

The effects of the concentration of barium acetate aqueous solution and the amount of ethanol on gelation are summarized in Table I. It is seen that the amount of solvent is comparatively important for obtaining homogeneous and transparent $BaO–SiO_2$ gel. When the ratio of TEOS:EtOH:H_2O was 1:4:1, no homogeneous gel was obtained in the range 0.5–2.0 M barium acetate aqueous solution. Precipitation occurred in the solution. X-ray diffraction patterns show that the precipitations were silicic acid for lower barium concentration, and silicic acid and barium acetate for higher barium concentration, respectively (Fig. 2). Because TEOS solution has weak acidity and barium acetate aqueous solution has weak basicity, the following reaction occurred after barium acetate aqueous solution was added to TEOS ethanol solution with a higher TEOS content

$$Si(OC_2H_5)_4 + H_2O \xrightarrow{OH^-} Si(OH)_4\downarrow + C_2H_5OH \quad (1)$$

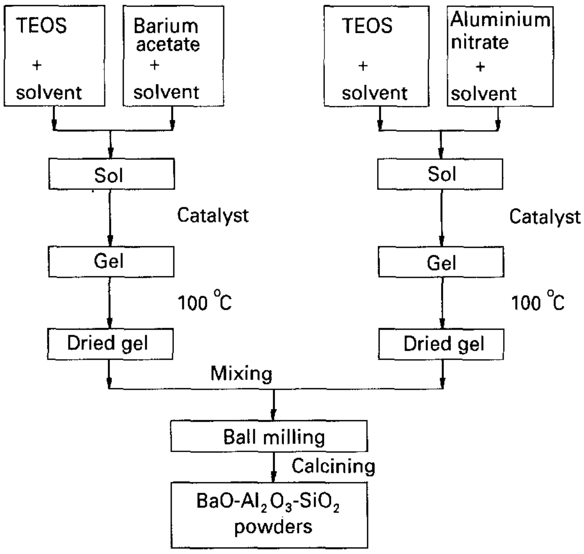

Figure 1 Preparation process of BaO–Al$_2$O$_3$–SiO$_2$ powders.

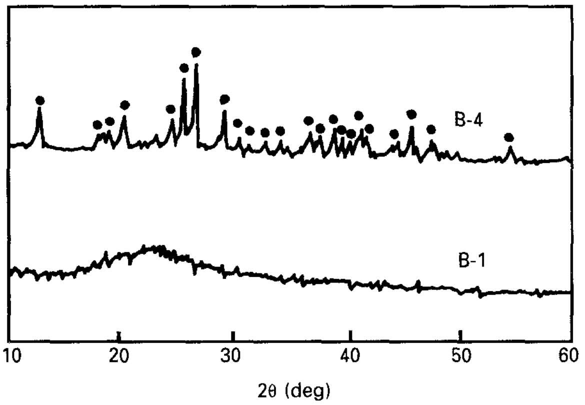

Figure 2 X-ray diffraction curves of precipitation from BaO–SiO$_2$ sol solution. (●) Ba(CH$_3$COO)$_2$.

Therefore, silicic acid was formed. On the other hand, barium acetate is not easily dissolved in the sol solution because of the low solubility of barium acetate in ethanol. Therefore, barium acetate precipitation began to occur with increasing concentration of barium acetate. For the TEOS solution with higher addition of ethanol, homogeneous BaO–SiO$_2$ gel was obtained when the concentration of barium acetate was in the range 1.0–1.5 M. When the concentration of barium acetate aqueous solution was lower than 1 M, its mixture with the TEOS ethanol solution fell in the immiscible range of H$_2$O–EtOH–TEOS system. When M_{Ba} was higher than 1.5 M, Ba(CH$_3$COO)$_2$ precipitation occurred in the solution.

3.1.2. Effect of TEOS prehydrolysis on gelation of BaO–SiO$_2$ sol solution

The prehydrolysis of TEOS is important for obtaining homogeneous BaO–SiO$_2$ gel. Some results are summarized in Table II. It is shown that, without catalyst, the prehydrolysis rate of TEOS was very slow, and the TEOS ethanol solution was immiscible with barium acetate aqueous solution. The addition of hydrochloric acid could expand the miscible range of the EtOH–H$_2$O–TEOS system [2]. On the other hand, the hydrolysis reaction of TEOS was accelerated by hydrogen ions, that is

$$n\text{Si(OR)}_4 + n\text{H}_2\text{O} \xrightarrow{\text{H}^+} n\text{Si(OR)}_3\text{(OH)} + n\text{ROH} \quad (2)$$

The longer the time of prehydrolysis, the more complete was the hydrolysis reaction. This promoted the following condensation reaction

$$2 \equiv\text{Si–OH} \longrightarrow \equiv\text{Si–O–Si}\equiv + \text{H}_2\text{O} \quad (3)$$

Therefore, the gelation time decreased with increasing time of prehydrolysis.

TABLE I The effect of solvents on the gelation of the BaO–SiO$_2$ system

No.	Concentration of barium acetate aqueous solution (mol l^{-1})	TEOS:EtOH:H$_2$O (mole ratio)	BaO:SiO$_2$ (mole ratio)	Gelation time at 60 °C (min)
B-1	0.5	1:4:1	1:1	Precipitation
B-2	1.0	1:4:1	1:1	Precipitation
B-3	1.5	1:4:1	1:1	Precipitation
B-4	2.0	1:4:1	1:1	Precipitation
B-5	0.5	1:16:1	1:1	Insoluble in each other
B-6	1.0	1:16:1	1:1	40
B-7	1.5	1:16:1	1:1	20
B-8	2.0	1:16:1	1:1	Precipitation

TABLE II The effect of TEOS prehydrolysis on the gelation of BaO–SiO$_2$ system

No.	Concentration of barium acetate aqueous solution (mol l^{-1})	Catalyst	Temperature of prehydrolysis (°C)	Time of prehydrolysis (h)	Gelation time (min)
B-6	1	HCl	60	1.5	40
B-6-1	1	HCl	60	0.5	80
B-6-2	1	None	60	1.5	Insoluble in each other

TABLE III Preparation of Al_2O_3–SiO_2 gel

No.	Starting materials	Solvent	Catalyst	Gelation time at 60 °C (h)
AS	$Al(NO_3)_3 \cdot 9H_2O$ + TEOS	Alcohol	Acid + base	2

3.1.3. *Formation of Al_2O_3–SiO_2 gel*

It is easier to prepare Al_2O_3–SiO_2 gel than BaO–SiO_2 gel, because aluminium easily forms a uniform sol solution with TEOS when ethanol is used as solvent. By the addition of a catalyst, the gelation time can be easily controlled. The related experimental results are given in Table III.

3.2. Observation of dried gel powders by electron microcscopy

The micrographs of different dried gel powders are shown in Fig. 3. The average grain size of BaO–SiO_2 powders decreased from about 2 μm to 0.5 μm as the gelation time decreased from 40 min to 10 min. In

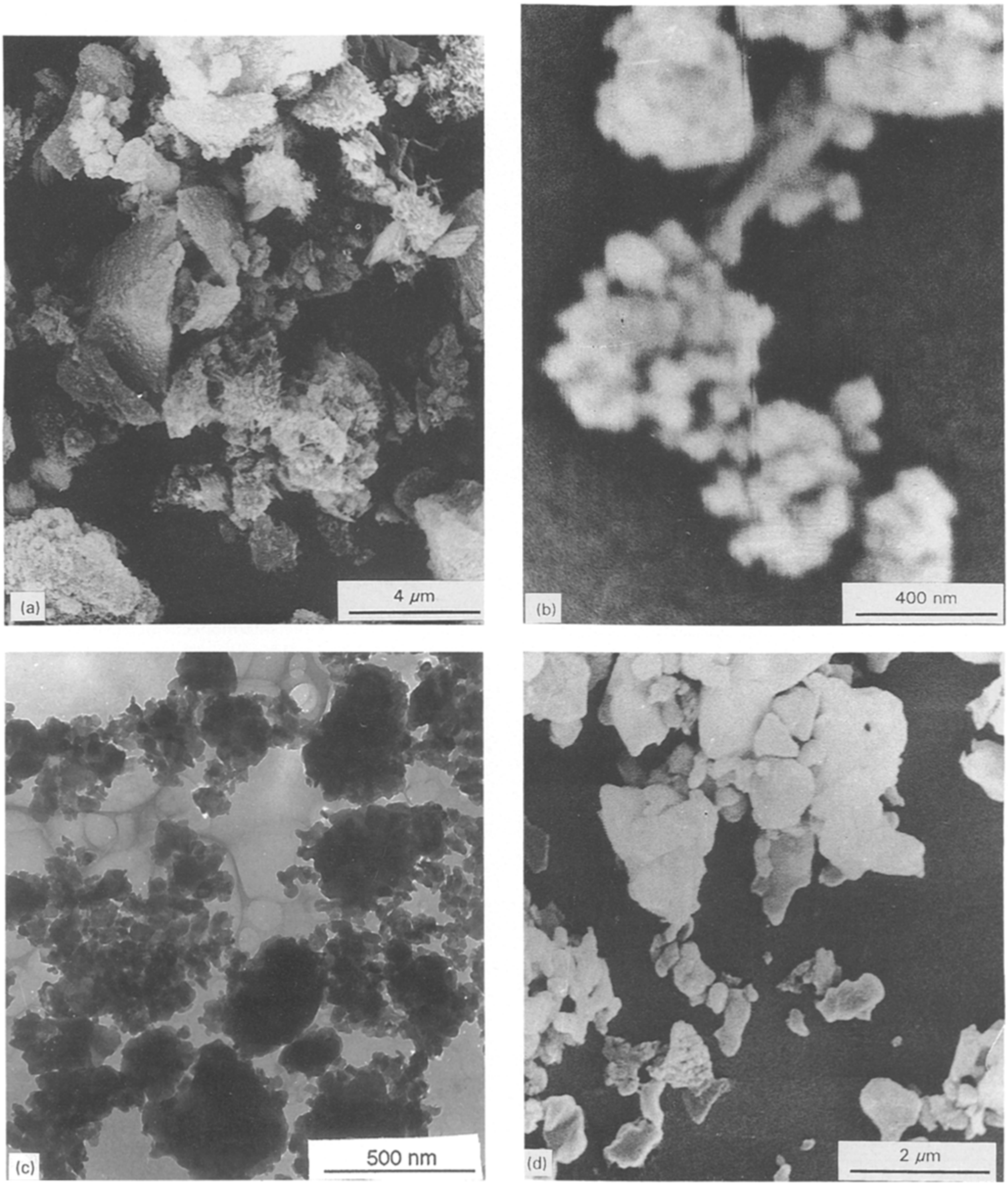

Figure 3 Electron micrographs of dried gel powders. (a, b) BaO–SiO_2 powders calcined at 300 °C, SEM. (c) Al_2O_3–SiO_2 powders calcined at 500 °C, TEM. (d) BaO–Al_2O_3–SiO_2 powders calcined at 1000 °C, SEM.

addition, the particles resulting in a sample of quick gelation were aggregates of some smaller grains. Small number of needle-like $Ba(CH_3COO)_2$ crystals existed in the slow gelation sample. The gel with a longer gelation time had a lower strength, but ions in this gel could easily migrate from one position to another. Therefore, owing to the low solubility, barium acetate might precipitate from the sol solution near the interface with the evaporation of solvents. The size of most particles for Al_2O_3–SiO_2 dried gel powders was in the range 0.1–0.2 μm. Only a few grains were 0.5–0.7 μm in size. BaO–Al_2O_3–SiO_2 powders, calcined at 1000 °C after mixing Al_2O_3–SiO_2 and BaO–SiO_2 dried gels, also have a small size, about 2 μm. From the above experimental results, it can be seen that BaO–SiO_2 and Al_2O_3–SiO_2 dried gel powders prepared in present work have a small size, a high specific surface area and, therefore, high reactivity. They are ideal starting materials for manufacturing BaO–Al_2O_3–SiO_2 ceramics with high quality.

3.3. Physical and chemical changes of dried gel powders during heating

Fig. 4 shows differential thermal analysis-gas chromatograph (DTA-GC) curves of BaO–SiO_2 dried gel. The broad endothermic peak sustained to about 150 °C on the DTA curve could be assigned to the evaporation of ethanol and water. The strong exothermic peak at 450 °C was due to the decomposition and oxidation of barium acetate, that is

$$Ba(CH_3COO)_2 + 4\,O_2 \longrightarrow BaCO_3 + 3\,CO_2 + 3\,H_2O \qquad (4)$$

A corresponding CO_2 peak appeared on the GC curve. Thus, the oxygen peak obviously decreased.

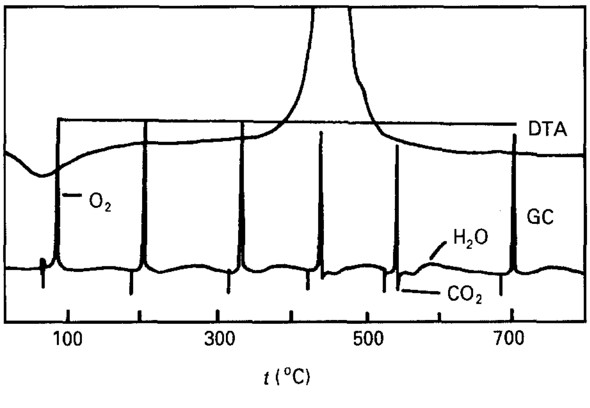

Figure 4 DTA and GC curves for dried gel powders of the BaO–SiO_2 system.

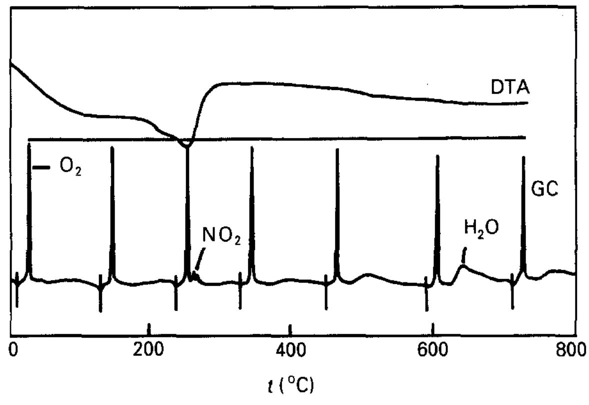

Figure 5 DTA and GC curves for Al_2O_3–SiO_2 dried gel powders.

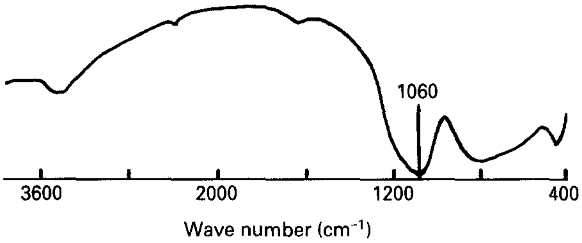

Figure 6 IR spectrum for Al_2O_3–SiO_2 powders calcined at 500 °C.

The DTA–GC curves for Al_2O_3–SiO_2 dried gel are shown in Fig. 5. It can be seen that aluminium nitrate decomposed at 275 °C and released NO_2 gas. Above 400 °C, residual organic groups were oxidized, and hydroxy ions were removed. The GC curve shows an increase in the water peak and a decrease of the oxygen peak.

The infrared (IR) spectrum of Al_2O_3–SiO_2 powders shows the shift from 1100 cm^{-1} to 1060 cm^{-1} and widening of the stretching vibration of the S–O–Si bond. This demonstrated that aluminium ions substituted for some of the silicon atoms in the network to form Si–O–Al bond. The vibration energy decreased. Therefore, the distribution of aluminium and silicon atoms was uniform in Al_2O_3–SiO_2 dried gel powders.

3.4. Sintering of BaO–Al_2O_3–SiO_2 powders

Phase constitution of BaO–SiO_2 and BaO–Al_2O_3–SiO_2 powders calcined at different temperatures are summarized in Table IV. Barium acetate was found in BaO–SiO_2 powder when the calcining temperature was low. Then barium acetate was converted to barium carbonate as the calcining temperature increased. Finally, barium silicate was formed at 800 °C. In contrast to the BaO–SiO_2 powders, barium acetate in

TABLE IV X-ray diffraction data of powders calcined at different temperatures

Powders	Calcining temperature (°C)				
	300	600	800	1000	1400
BaO–SiO_2	Barium acetate	Barium carbonate	Barium silicate	–	–
BaO–Al_2O_3–SiO_2	Barium carbonate	Barium carbonate	Barium carbonate	β-barium alumino silicate	β-barium alumino silicate

TABLE V Properties of BAS ceramic and SiC_w/BAS composite

	BAS	SIC_w/BAS
Content of SiC whisker (wt %)	0	20
Hot-pressing temperature (°C)	1200	1250
Hot-pressing time (min)	30	30
Volume density (g cm^{-3})	2.80	2.97
Flexural strength (MPa)	109	280
Thermal expansion coefficient (10^7 °C^{-1}, RT–500 °C)	–	46

$BaO–Al_2O_3–SiO_2$ powders decomposed into barium carbonate at a temperature lower than 300 °C; this was stable up to 800 °C. β-$BaAl_2Si_2O_8$ (hexacelsian) was formed at 1000 °C. Using $BaO–Al_2O_3–SiO_2$ powders prepared in this work as starting materials, $BaO–Al_2O_3–SiO_2$(BAS) ceramic and SiC_w/BAS composite were fabricated by hot-pressing. The SiC whisker used (supplied by The Shanghai Institute of Ceramics) were 0.5–1.0 μm diameter and 30–100 μm long. Related properties of BAS ceramic and composite are listed in Table V. Both BAS ceramic and SiC_w/BAS composite have low hot-pressing temperatures, which may be attributed to the high reactivity of $BaO–Al_2O_3–SiO_2$ powders. When the SiC whisker content was 20 wt %, the flexural strength of BAS ceramic was increased by about two times. Owing to the low thermal expansion coefficient, SiC_w/BAS composite can be used as structural material and as material resistant to thermal shock. Further research is in progress.

4. Conclusions

1. $BaO–SiO_2$ and $Al_2O_3–SiO_2$ dried gel powders with a grain size of 0.1–0.5 μm were prepared by the sol–gel process using TEOS, barium acetate and aluminium nitrate as starting materials.
2. The $Al_2O_3–SiO_2$ gel prepared were homogeneous single gel. Aluminium atoms were substituted for some of the silicon atoms forming an Si–O–Al bond. Micro-heterogeneity occurred in the $BaO–SiO_2$ dried gel.
3. The grain size of $BaO–SiO_2$ dried gel powders decreased with decreasing gelation time.
4. $BaO–Al_2O_3–SiO_2$ powders with an average grain size of 1–1.5 μm were obtained by calcining a mixture of $BaO–SiO_2$ and $Al_2O_3–SiO_2$ powders at 1000 °C. By using them as starting materials, BAS ceramic and SiC_w/BAS composite were prepared, which have low thermal expansion coefficients.

Acknowledgement

The authors thank Associate Professor Du Yongjuan, East China University of Science and Technology, for her advice and help.

References

1. W. K. TREDWAY and S. H. RISBUD, *J. Non-Cryst. Solids* **100** (1988) 278.
2. M. PRASAS and L. L. HENCH, in "Ultrastructure processing of ceramics, glasses and composites", edited by L. L. Hench and D. R. Ulrich (Wiley, New York, 1984) p. 100.

Received 28 September 1993
Revised 27 July 1994