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Glass Formation in the System Y_2O_3–Al_2O_3–SiO_2 Under Conditions of Laser Melting

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Abstract

Glass formation in the Y_2O_3–Al_2O_3–SiO_2 *system was investigated by means of laser melting using a* CO_2 *laser source (wavelength 10·6 μm) with a maximum output power of 1700 W. The glass-forming region was found to be more extensive than that observed by other investigators. No glassy phase formed in compositions with less than 20 wt%* SiO_2*. A non-equilibrium phase diagram corresponding to the conditions of laser-induced rapid melting and self-quenching was also determined. All the phases reported in the relevant binary diagrams with the exception of yttrium silicate* $2Y_2O_3 . 3SiO_2$ *were observed.*

Die Glasbildung im System Y_2O_3–Al_2O_3–SiO_2 *wurde mittels Laserschmelzens unter Verwendung eines* CO_2*-Lasers (Wellenlänge 10·6 μm) mit einer maximalen Augangsleistung von 1700 W untersucht. Die dabei beobachtete Glasbildungszone war größer als die bei anderen Untersuchungen beobachtete Zone. Es konnte keine Bildung von Glasphase in Verbindungen mit weniger als 20 Masse.%* SiO_2 *beobachtet werden. Das Nichtgleichgewichtsphasendiagramm, das den Bedingungen beim laserinduzierten, schnellen Schmelzen und Abkühlen entspricht, wurde ermittelt. Alle aus dem Zweiphasendiagramm bekannten Phasen konnten nachgewiesen werden, ausgenommen Yttriumsilikat* $2Y_2O_3 . 3SiO_2$.

Nous avons étudié la formation de verre dans le système Y_2O_3–Al_2O_3–SiO_2 *par fusion laser, en utilisant une source laser* CO_2 *(longueur d'onde: 10·6 μm) d'une puissance maximale de 1700 W. Le domaine de formation du verre semble plus important qu'il n'a été constaté dans les études précédentes. Pour des compositions contenant moins de 20% pond. de* SiO_2*, aucune phase vitreuse ne se forme. Nous avons aussi déterminé le diagramme de phases hors équilibre pour les conditions de fusion sous laser et de trempe spontanée. Toutes les phases notées sur les diagrammes binaires correspondants ont été observées, à l'exception du silicate d'yttrium* $2Y_2O_3 . 3SiO_2$.

1 Introduction

In this work, a laser melting technique was used to determine the range of glass formation in the Y_2O_3–Al_2O_3–SiO_2 system. The background to the work is primarily the occurrence of these oxides as secondary phases in silicon nitride based ceramics. The study also has relevance to the use of laser as a means of creating surface glazes.

The chemical and mechanical properties of sintered silicon nitride based ceramics are known to be strongly dependent on the second phases that are generally formed in their grain boundaries. The intergranular phases are usually glassy and therefore exert a negative influence on mechanical properties as well as providing paths for rapid diffusion and chemical attack.[1] The oxide system Y_2O_3–Al_2O_3–SiO_2 is of a special interest in this respect since Y_2O_3 and Al_2O_3 are commonly used as sintering additives in silicon nitride based ceramics. Together with the SiO_2 that is always present on the surface of silicon nitride powder these oxides form an intergranular glassy phase which is often retained on cooling from the high sintering temperature.[2] Thus, knowledge of the glass formation and subsequent glass crystallization in this system is of practical importance.

The glass-forming region in the system has been reported by a number of investigators.[2–4] These investigations were carried out by conventional melting and cooling procedures using electric furnaces with a variety of heating elements and crucibles. Such methods are tedious and time consuming and involve the risk of contamination

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of the glass, e.g. from the crucible material. An alternative method involves the rapid local melting of small samples by laser.[5] No crucibles are necessary and it is possible to determine the glass-forming region very quickly. Although large homogeneous samples with well-characterized thermal history cannot be obtained, the method provides a basis for the selection of the most promising compositions to be prepared by conventional melting in order to produce the larger samples for further property characterization.[5] The laser melting technique provides the possibility of forming glass from compositions of high melting temperature and strong devitrification tendency.[6]

In the present work the glass-forming region in the system Y_2O_3–Al_2O_3–SiO_2 in air was determined using a CO_2 laser. The formation of crystalline phases in the system under the conditions of laser melting and subsequent self quenching is also reported in the form of a ternary 'phase' diagram. It is efficient to use a CO_2 laser to produce glass because the ability of most materials for glass-making to absorb the infrared wavelength of 10·6 μm. It results in an effective coupling of the laser energy and the working material.

2 Experimental

Fifty compositions in the ternary oxide system (Fig. 1) were prepared as 2 g samples from high purity Y_2O_3, Al_2O_3 and SiO_2 crystalline powders. They were mixed and dry milled in a vibratory device, using an agate jar and balls, for 5 min each and then compacted to 0·5-grams pellets with a diameter of approximately 10 mm by cold isostatic pressing (pressure of 200 MPa).

The laser melting was achieved using a Rofin Sinar 1700 HF CO_2 laser with a maximum output power of 1700 W. The beam was strongly defocused to give a spot diameter of 6 mm. The distance between the laser nozzle and the surface of the sample (68 mm), the time of sample exposure to the beam (30 s) and the applied laser power (180 W) were kept constant in order to achieve similar melting conditions. Nitrogen at a pressure of 0·11 MPa was used as a shielding gas to protect the lens. Samples were prevented from moving during irradiation by use of a sample holder. After the laser was switched off the pellet was allowed to cool at its natural rate (approximately 200°C/s). Figure 2 shows schematically the typical appearance of a pellet after the treatment.

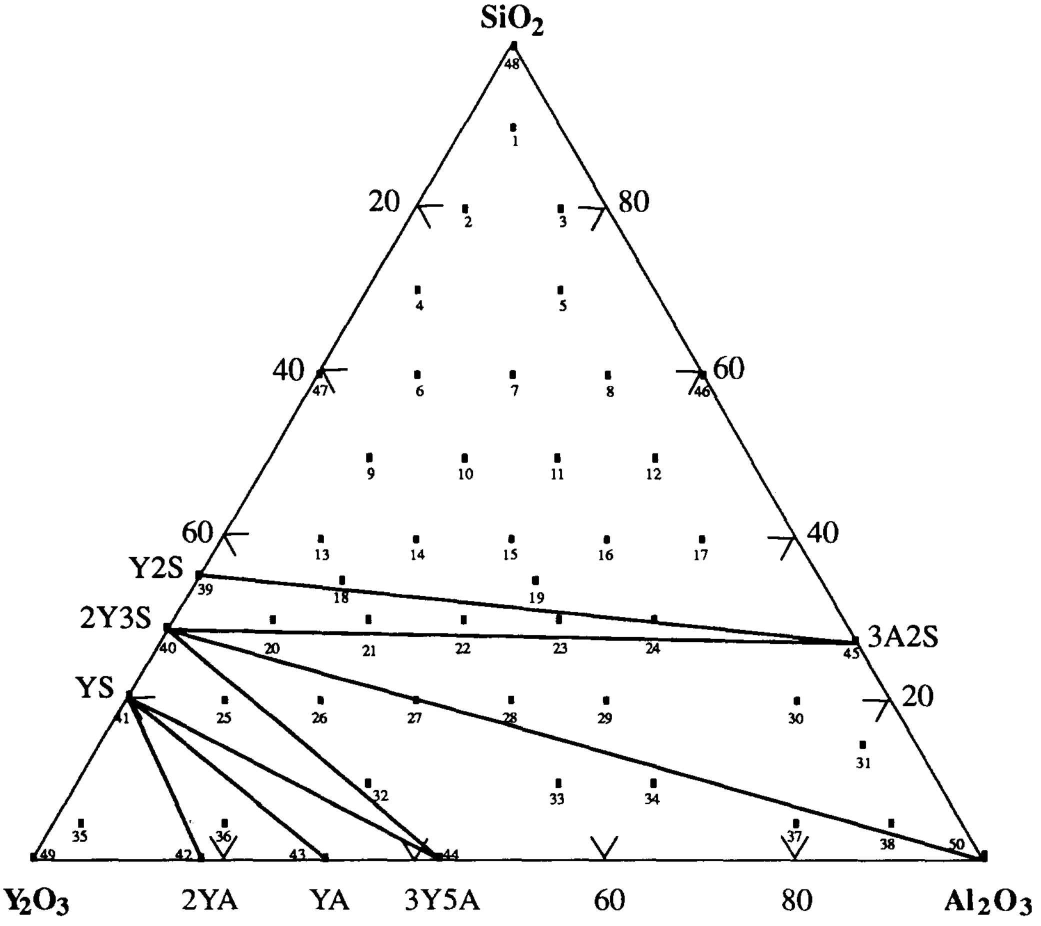

Fig. 1. Phase relationships in the Y_2O_3–Al_2O_3–SiO_2 system predicted from the relevant binary diagrams[7] and investigated compositions with concentrations in wt% (YS = $Y_2O_3 . SiO_2$; Y2S = $Y_2O_3 . 2SiO_2$; 2Y3S = $2Y_2O_3 . 3 SiO_2$; YA = $Y_2O_3 . Al_2O_3$; 2YA = $2Y_2O_3 . Al_2O_3$; 3Y5A = $3Y_2O_3 . 5Al_2O_3$; 3A2S = $3Al_2O_3 . SiO_2$).

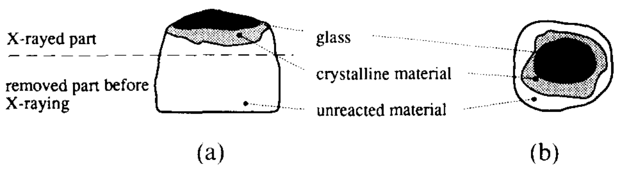

Fig. 2. Self-quenched pellet after irradiation by the laser beam: (a) side view, (b) top view.

The treated pellets were first examined at low magnification in a stereomicroscope in order to determine whether or not glass had formed. Any trace of clear transparent glass was taken as an evidence of glassy-phase formation. Further investigation of the presence of glassy phase and the formation of crystalline phases were carried out by X-ray powder diffractometry (Philips diffractometer with APD 1700 software). To improve the detectability of phases formed during the laser processing, the lower section of each sample with only unreacted material was removed, as indicated in Fig. 2, by careful grinding using SiC paper.

To obtain an indication of the temperature reached during the irradiation cycle, selected samples with representative compositions were monitored with a Landmark X pyrometer. For all compositions temperatures between 1800 and 1900°C were attained.

3 Results and Discussion

3.1 Glass-forming region

On the basis of the optical microscope observations of the samples it was possible to distinguish three different regions in the ternary system (Fig. 3): (i) the samples clearly formed a small bead of glass (I); (ii) a thin glassy layer or shell formed on the surface of the melted portion of the sample (II); (iii) no trace of glassy phase was observed (III).

X-Ray diffraction patterns from compositions in the glass-forming region I exhibited a high background due to the relatively large amount of the glassy phase present. Diffraction patterns from compositions in the glassy shell-forming region II exhibited a low background indicating that the amount of glassy material present was small. Neither the X-ray diffraction pattern or optical observation revealed any glass formation in region III samples; these all had a SiO_2 content of less than 20 wt%.

The centre of region I is located near a composition of 27 wt% of Al_2O_3, 38 wt% of Y_2O_3 and 35 wt% of SiO_2 and can therefore be identified with the glass-forming region of the earlier investigations of Makishima *et al.*[3] and Sedych *et al.*[4]

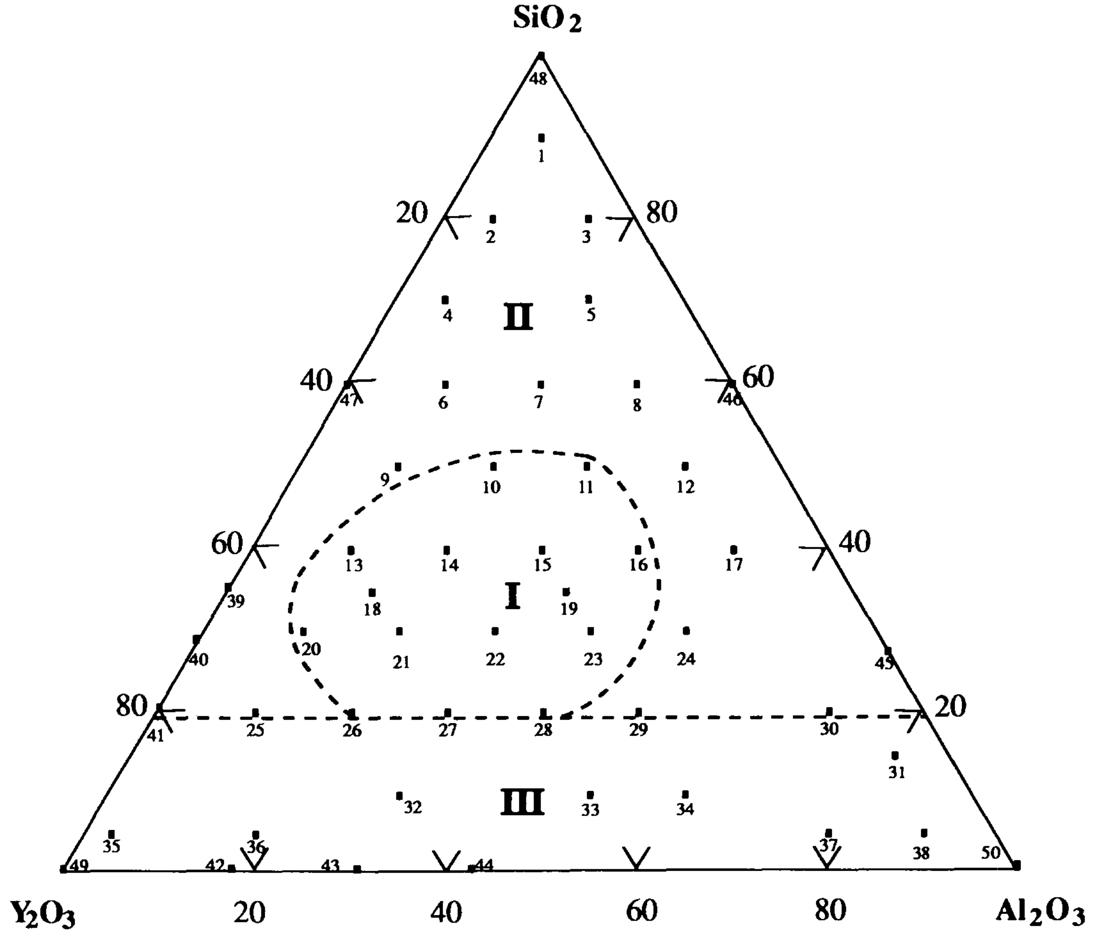

Fig. 3. Glass-forming regions in the Y_2O_3–Al_2O_3–SiO_2 system in air after CO_2-laser melting; glass-forming region I, glassy shell-forming region II and no glass-forming region III.

However, here the glass-forming region is considerably extended, compared to that of these earlier studies. It is reasonable to assume that this difference is due to the rapid cooling that occurs when using the laser method, thus reducing the time available for incubation and nucleation of crystallization. It is to be noted that O'Meara *et al.*[7] reported glass formation for compositions containing >25 wt% of SiO_2 when conventional melting was applied. It has been suggested by Yi & Strutt[6] that in glass the first and second coordinations of atoms are similar to those of the corresponding primary crystalline phase. Thus the Al or Y atoms in glasses with high Al- or Y-content would have 'mullite'- or 'yttrium silicate'-like arrangements in combination with the (SiO_4) tetrahedra of the glass to form a three-dimensional network.

3.2 Identification of crystalline phases

Although the primary purpose of this work was to determine the limits of glass formation in the system, the crystalline phases that formed are also of some interest. Although the extremely rapid cooling conditions of the experiment prevent the attainment of phase equilibrium it is convenient to report the observations in the form of a phase diagram (Fig. 4). This diagram is then specific to the conditions of the laser treatment. In constructing the diagram the presence of pure Al_2O_3, SiO_2 and Y_2O_3 in the diffraction patterns was ignored, since portions of the unmelted powder were always retained in the X-ray samples.

The observed crystalline phase combinations could be divided into five regions in the ternary diagram (Fig. 4). All the phases predicted in the diagram by Bondar & Galakov[8] were observed, with the exception of 2Y3S. In fact, the existence of the 2Y3S phase has been questioned by other investigators.[9] It should also be noted that the 2YA and YA phases forming in the Y_2O_3-rich part of the diagram were detected clearly only in compositions 42, 43 and 44 with no SiO_2 present. There was also a weak indication of these phases forming in compositions 35 and 36.

When melting pure SiO_2 (composition 48) the formation of glass without any crystalline phases present was observed as expected. A pale yellow surface modification of the Y_2O_3 and Al_2O_3 samples (49 and 50) was observed, possibly due to

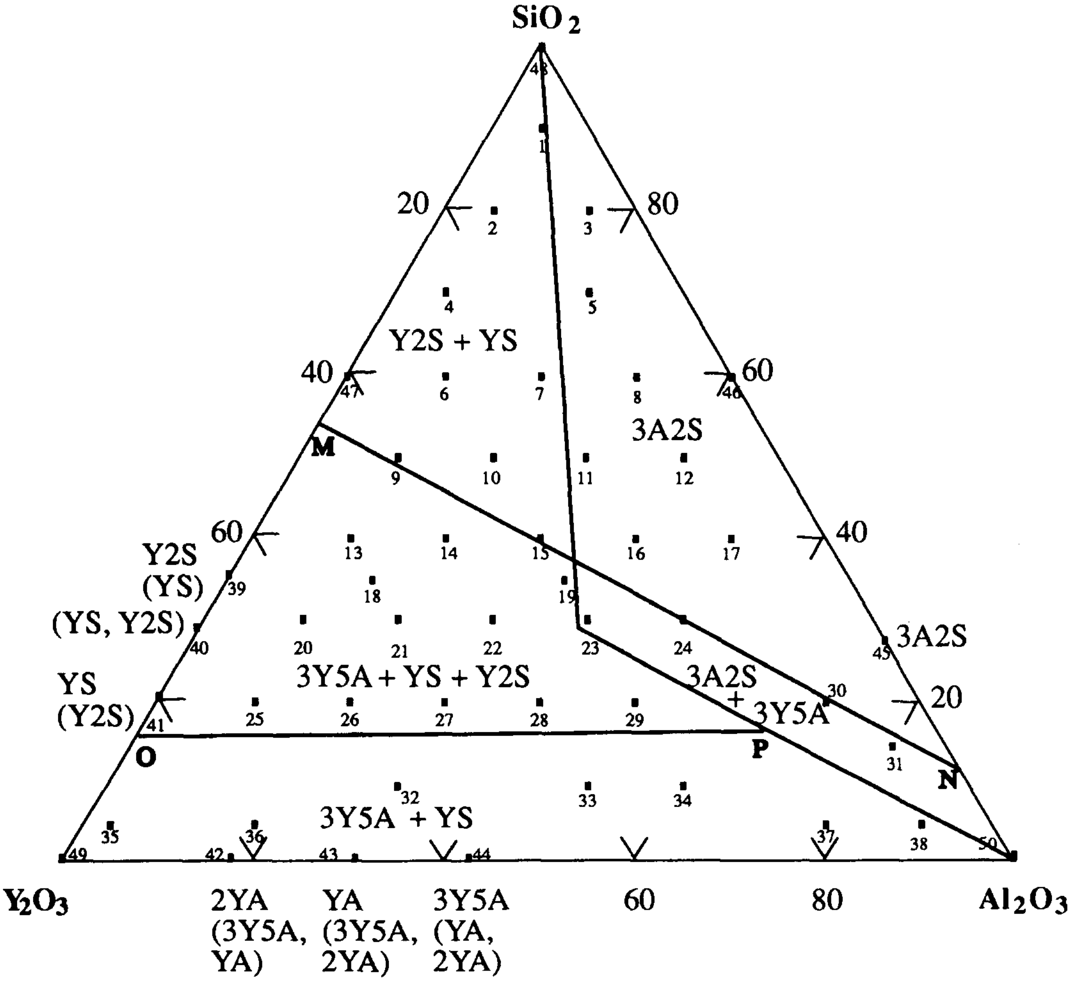

Fig. 4. Experimental phase diagram for the Y_2O_3–Al_2O_3–SiO_2 system obtained under conditions of a CO_2 laser-induced rapid melting and self-quenching process (YS = $Y_2O_3 . SiO_2$; Y2S = $Y_2O_3 . 2SiO_2$; YA = $Y_2O_3 . Al_2O_3$; 2YA = $2Y_2O_3 . Al_2O_3$; 3Y5A = $3Y_2O_3 . 5Al_2O_3$; 3A2S = $3Al_2O_3 . SiO_2$; parentheses indicate minor phases).

an interaction with the nitrogen or air. A similar yellow coloration also occurred on the surfaces of some samples on the low SiO_2 side (SiO_2 content less than 20%). The 2Y3S phase was not found even when melting composition 40. Samples 39, 40 and 41 consisted of Y2S and YS as indicated in Fig. 4. Only 3A2S (mullite) was detected in the sample with composition 45.

The observed upper limit for the formation of the YAG-phase (yttrium–aluminum–garnet, 3Y5A) was the line M–N in Fig. 4. This limit is higher than expected from the equilibrium diagram in Fig. 1 (line 2Y3S–Al_2O_3), probably due to a compositional shift in the glass region such that SiO_2 formed silica-rich glass on the top of the sample, causing a local depletion of SiO_2 in the region close to the unmelted material.

In the experimental diagram, mullite (3A2S) is observed in a more restricted composition range than in the equilibrium diagram, being confined to two regions bordered by the SiO_2–Al_2O_3 binary line. The larger of these two regions contains no other phase than mullite. These mullite containing regions correspond approximately to the region of primary crystallization of mullite in the solidification diagram.[8] Because of the fast cooling it is probable that mullite formation other than by primary crystallization cannot occur so that no mullite is observed to the left of the line SiO_2–P–Al_2O_3. Similarly, the difficulty of crystallization other than by primary crystallization of mullite in the regions to the right of this line explains the absence of Y2S and YS in them.

4 Conclusions

A method involving CO_2 laser-induced melting and self-quenching of small powder samples was used to determine the range of glass formation in the Y_2O_3–Al_2O_3–SiO_2 system in air. The method permits rapid melting and cooling as well as avoiding the need of crucibles.

Two types of glass formation were observed in the system; one range of compositions formed a bead of glass while a second range formed only a thin glassy layer on the melted material. The glass-forming region in the system was found to be more extensive than in earlier studies. No glass formed in compositions with less than 20 wt%. SiO_2.

The crystalline phases observed to form in the system could be reported in the form of a ternary phase diagram appropriate to the specific conditions of melting and quenching used. All the phases reported in the three relevant binary systems were detected, with the exception of yttrium silicate $2Y_2O_3 \,.\, 3SiO_2$.

References

1. Ekström, T., Transient liquid phase sintering of silicon nitride. In *Proceedings of the International Ceramic Conference Austceram 90*, Perth, Australia, ed. P. J. Darragh & R. J. Stead. Trans. Tech Publications, 1990, pp. 586–91.
2. Arita, I. H., Wilkinson, D. S. & Purdy, G. R., Crystallization of yttria–alumina–silica glasses. *J. Am. Ceram. Soc.*, **75**(12) (1992) 3315–20.
3. Makishima, A., Tamura, Y. & Sakaino, T., Elastic moduli and refractive indices of alumino-silicate glasses containing Y_2O_3, La_2O_3 and TiO_2. *J. Am. Ceram. Soc.*, **61**(5–6) (1978) 247–9.
4. Sedych, T. S., Pustilnik, A. I. & Mikheikin, V. I., Refractive indices in the system Y_2O_3–Al_2O_3–SiO_2 in the vitrification region. *Akad. Nauk SSSR, Neorg. Mater.*, **11**(6) (1975) 1153–4.
5. Quackenbush, C. L. & Kolbeck, A. G., Determination of glass formation in the system Al_2O_3–B_2O_3–P_2O_5 by laser melting. *Ceramic Bulletin*, **56**(9) (1977) 789–92.
6. Yi, J. J. L. & Strutt, P. R., Glass formation by laser melting. In *Proceedings of the 1st Int. Conf.-Advances in the Fusion of Glass*. NY, 1988, pp. 49.1–49.9.
7. Meara, C. O., Dunlop, G. L. & Pompe, R., Phase relationship in the system Y_2O_3–Al_2O_3–SiO_2. In *Proceedings of the World Congress on High Tech Ceramics (6th CIMTEC)*, Milan, Italy, 1986, ed. P. Vincenzini. Elsevier Science Publishers, Amsterdam, pp. 265–70.
8. Bondar, I. A. & Galakov, F. Ya., Phase equilibria in the system Y_2O_3–Al_2O_3–SiO_2. *Izv. Akad. Nauk SSSR Ser. Khim.*, **7** (1964) 1325–6.
9. Drummond III, C. H. & Lee, W. E., Crystallization and characterization of Y_2O_3–SiO_2 glasses. *Ceram. Eng. Sci. Proc.*, **9**(9–10) (1988) 1343–54.