3. Conclusions

The following conclusions may be drawn from the data presented in this paper.

Nucleated crystallisation in glasses of lithia-alumina-silica and cordierite composition is due to the initially spontaneous precipitation of compounds with structures which are isomorphous with the main crystalline phase observed at the higher temperature.

In contrast to the way in which metallic additions promote nucleated crystallisation these compounds dissolve in glasses and upon heat treatment at lower temperatures they are initially formed and behave as nucleating agents for the main phase.

Microseparation in lithium- and cordierite-containing glasses occurs, as in photosensitive glasses but is not dominant in nucleated crystallisation of these glasses.

References

1. V. A. BLINOV, in, "The Glassy State" (Science, Moscow-Leningrad, 1965) p. 88-90.
2. V. BLINOV and R. ROY, *Glass Ind.* **43** (1962) 494.

Letter

Hedvall Effect and Synthesis of Zircon

The synthesis of zircon, from the constituent oxides ZrO_2 and SiO_2, has been the subject of many investigations [1-8]. The most comprehensive study probably was that of Curtis and Sowman [7] who showed that the lowest temperature at which zircon can be synthesised from ZrO_2 and SiO_2 is approximately 1315° C and the rate of synthesis increases rapidly as the temperature is increased from 1425 to 1535° C.

Hedvall [9] has shown that a material undergoing a polymorphic transformation or decomposition is in a very reactive state and consequently the rate of reaction is greatest at the transformation or decomposition temperature. Zirconia undergoes a reconstructive, disruptive transformation from monoclinic to tetragonal symmetry at 1170° C, at which temperature the synthesis of zircon from ZrO_2 and SiO_2 may be expected to take place at an enhanced rate. The purpose of this investigation is to verify the Hedvall effect in the synthesis of zircon from ZrO_2 and SiO_2.

Monoclinic zirconia, obtained from the Bhabha Atomic Research Center, Bombay (having the impurities: 200 ppm Hf, 150 ppm Fe, 275 ppm Mg, 150 ppm Ti) and quartz powder, SiO_2 99.9% from Pennsylvania Glass Sand Corporation (with impurities : 230 ppm Fe_2O_3, 90 ppm TiO_2 and 900 ppm Al_2O_3) were employed in the present investigation. An equimolecular mixture of ZrO_2 and SiO_2, thoroughly mixed in a glass mortar, was used in the experiments. Using a Temp-Pres Research furnace mounted on a General Electric XRD-6 X-ray diffractometer, the mixture was heated at 1155, 1170 1200, 1300 and 1400° C for varying periods of time. Filtered CuK_α radiation was used and the range $20° < 2\theta < 45°$ was scanned. At the end of each temperature run, the furnace was cooled and the room temperature X-ray pattern recorded. A fresh sample was used for each temperature run.

By plotting the intensity of the $(11\bar{1})$ line (at 2θ: 28.3°) of monoclinic zirconia and of the (101) line (at 2θ : 29.7°) of the tetragonal phase versus temperature, the monoclinic to tetragonal transformation was seen to start at 1130° C and to be completed at about 1200° C.

The role of temperature and time on the rate of formation of zircon from ZrO_2 and SiO_2 is brought out clearly in fig. 1, where the intensity of the (200) line of zircon (which occurs at 2θ : 27°) is plotted as a function of temperature with time as a parameter. The amount of zircon formed goes through a maximum at 1200° C. This marked peak in the 1170 to 1200° C region is attributed to the high reactivity of ZrO_2 at the monoclinic-tetragonal phase transformation in this range. As the temperature is increased beyond 1300° C, the amount of zircon formed increases due to the increased thermal energy. Further, cristobalite formation from quartz via a transitional phase with a disordered structure [11], becomes significant at 1300°C and beyond. This transformation contributes to the enhanced formation of zircon at temperatures beyond 1300° C. Preliminary studies indicate a decrease of quartz and increase of cristobalite at 1300° C. Detailed studies of this are under way.

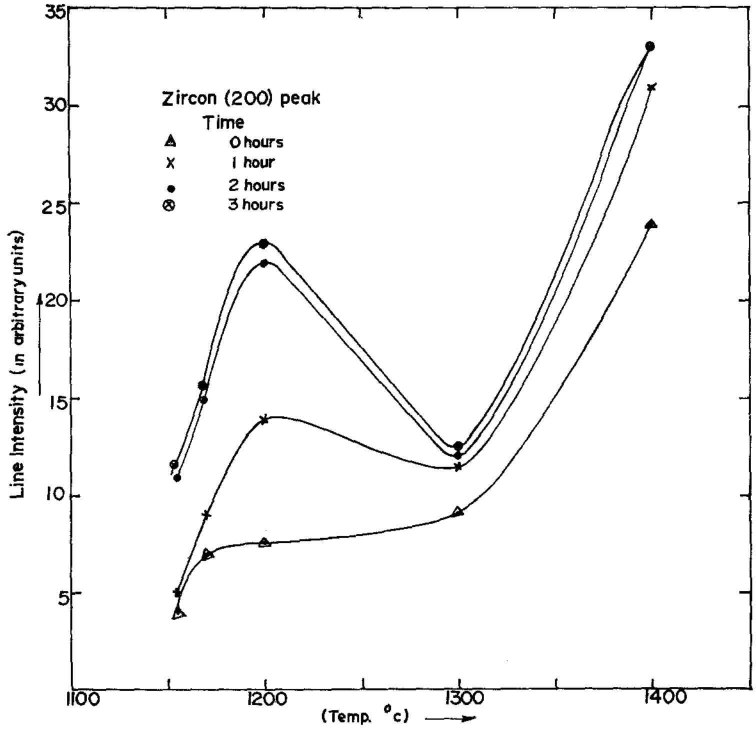

Figure 1 X-ray diffraction intensity of (200) line of zircon vs. temperature of synthesis, with time at temperature as a parameter.

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References

1. R. F. GELLER and P. J. YAVORSKY, *J. Res. Nat. Bur. Stand.* **35** (1945) 109.
2. R. F. GELLER and S. M. LANG, "Phase diagrams for ceramists" (Amer. Cer. Society, Columbus).
3. C. MATIGNON, *Compt. Rend.* **177** (1923) 1290.
4. H. GEORGE and R. LAMBERT, *Compt. Rend.* **204** (1937) 688.
5. A. HILLARD and V. H. STOTT, *Trans. Brit. Ceram. Soc.* **48** (1949) 143.
6. N. ZHIRNOVA, *Z. Anorg. Chem.* **218** (1934) 193.
7. C. E. CURTIS and H. E. SOWMAN, *J. Amer. Ceram. Soc.* **36** (1953) 190.
8. W. C. BUTTERMAN and W. R. FOSTER, *Amer. Min.* **52** (1967) 880.
9. J. A. HEDVALL, "Reaktionsfaehigkeit fester stoffe" (Reactivity of solids) (Verlag Johann Ambrosius Barth, Leipzig, 1938).
10. E. RYSKEWITCH, "Oxide Ceramics" (Academic Press, New York, 1960).
11. A. L. ROBERTS, in "Kinetics of high temperature processes", edited by W. Kingery (Massachusetts Inst of Tech; Cambridge, Mass, 1959) pp. 222-227.

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