

Liquid immiscibility in $K_2O-FeO-Al_2O_3-SiO_2$

VISSER and Koster van Groos¹ present a new phase equilibrium diagram for the plane leucite-fayalite- SiO_2 in the quaternary system $K_2O-FeO-Al_2O_3-SiO_2$, in which the field of immiscibility differs significantly from that which I presented earlier², and from that presented by Greig on the binary $FeO-SiO_2$ (ref. 3) (Fig. 1). Here I suggest the reason for the discrepancy, as no discussion or explanation is given by Visser and Koster van Groos.

The few details presented on the laboratory procedures used in the new work¹ suffice to indicate that their results should differ somewhat from mine. First, the oxygen fugacity during their work was slightly higher, as they note, because they used molybdenum rather than iron containers. The resulting presence of more Fe^{3+} in the melts would almost certainly expand the field of immiscibility⁴. I am assuming that they were able to overcome the difficult problems of obtaining adequate transfer of oxygen through their evacuated system to achieve PO_2 buffering. Second, the use of a vacuum during the runs in their work might cause loss of potassium which would also increase the degree of oxidation of the charges. Third, the molybdenum containers must have put some molybdenum into

the charges, either as Mo^{4+} or Mo^{6+} , both of which might be expected to increase the field of immiscibility⁵. I do not believe, however, that these three effects, even though additive, are adequate to explain the major differences found in the extent of the field of immiscibility.

Neither the work of Visser and Koster van Groos, nor my work gives the compositions studied nor the temperatures of the individual runs, but the numbers involved—~500 runs on 26 compositions in my work and >150 runs on an unspecified number of compositions in theirs—would both seem adequate to delineate the phase boundaries. (Although my diagram was presented as "preliminary" at the time, it has since been corroborated by additional data⁶.)

The differences between the two studies can be explained perfectly, however, by the assumption that some of immiscibility found by Visser and Koster van Groos took place during quenching, as the melt passed down through a field of metastable subliquidus immiscibility. The existence of such a field under the liquidus surface for silica in the system as I depicted it is self-evident from the geometry of the two immiscibility fields in a T-X section from the $FeO-SiO_2$ sideline through points C and D on Fig. 1. Furthermore, experimental evidence has been found for the existence of this metastable field, as well as for a metastable extension out under the very flat fayalite liquidus⁷. This evidence consisted of the presence of minute (~1 μm) globules having a high index, presumably high-FeO melt, in those glasses formed on relatively slow quenching, whereas the same charge quenched more rapidly yielded an optically uniform glass. Unfortunately, neither paper provides details on the quenching procedures. In my work, I quenched by dropping the iron foil envelope (~1 × 5 × 5 mm) containing the charge on to mercury while still in pure nitrogen. If the results suggested that phase changes had taken place on quench (for example, the minute globules, or dendritic crystals), faster quench was obtained by attaching platinum weights to the charge in the furnace to cause it to sink in the mercury on dropping⁸. All such minute globules were eliminated by this procedure.

The metastable sub-liquidus immiscibility indicated on Fig. 1 was originally drawn solely on the basis of the thermodynamic necessity of metastable extensions of the experimentally determined stable equilibria. It has been

verified experimentally by Irvine¹⁰, who determined the stable and metastable phase relations for composition Q (Fig. 1) at 1,350 °C. The stable assemblage consisted of tridymite crystals and a liquid. Irvine was able to realise metastable immiscibility in this composition, with exsolved globules as much as 7 μm diameter, by superheating to 1,550 °C for 1-2 h, then supercooling for 10-15 min before quenching. The metastable solvus was 'roughly bracketed at 1,350 °C', which agrees well with the extension sketched in Fig. 1. Additional corroboration of the phase relations as sketched in Fig. 1 comes from some runs by Watson¹¹, establishing the 1,180 °C isotherm on the upper surface on the stable immiscibility field. He found this isotherm to intersect the stable two-liquid field at point P on the section (Fig. 1).

Metastable sub-liquidus immiscibility is commonly observed in the field of ceramics, and an extensive literature exists⁹. Visser and Koster van Groos have used a very sensitive test for such immiscibility (electron scanning microscopy on etched surfaces), and they may even have detected such metastable immiscibility in samples that would seem optically homogeneous. Such metastability would explain many of the features they describe that are otherwise extremely puzzling. (Thus the field of immiscibility as drawn by Visser and Koster van Groos indicates a precipitous drop of 517 °C in the liquidus for silica in the system $FeO-SiO_2$ by the addition of only 1.35% FeO , and the metastable subliquidus extension of the immiscibility field would have to be even steeper). In view of the above evidence, I cannot accept their diagram as representing stable equilibria. I would suggest that the 'submicroscopic' immiscibility reported by them probably is metastable immiscibility from too slow quenching, and that only their coarser globules (as much as to 3 mm) represent stable immiscibility at furnace temperature.

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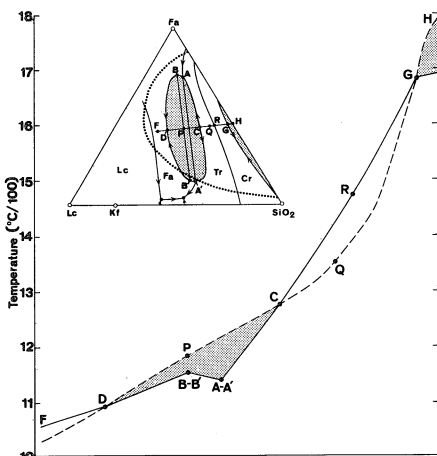


Fig. 1 Phase relations in the system $K_2O-FeO-Al_2O_3-SiO_2$ (inset), showing two fields of stable immiscibility (shaded), projected on the plane leucite (Lc)-fayalite (Fa)- SiO_2 , plotted in wt. % from the early work of Roedder². The outline of the larger field of immiscibility newly reported by Visser and Koster van Groos¹ is also shown (dotted). Tr, tridymite; Cr, cristobalite; Kf, K-feldspar. The T-X section along the line F-H is based on early work of Roedder², plus the work of Watson¹¹ (point P) and Irvine¹⁰ (point Q). Two immiscible liquids exist in stable equilibrium along D-P-C and G-H.

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