ON SOME REGULARITIES IN THE STRUCTURE OF MELTS IN THE SYSTEMS $\mathrm{Me}_2\mathrm{O}_3$–$\mathrm{SiO}_2$

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Abstract

Full Text

CHEMISTRY

B. I. MARKHASEV, I. D. SEDLETSKII

ON SOME REGULARITIES IN THE STRUCTURE OF MELTS IN THE SYSTEMS Me_2O_3–SiO_2

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It was shown earlier that the basic principles of crystal chemistry can be successfully applied in considering the structure of silicate melts (^{1}). In particular, the presence of two immiscible phases was related to the mismatch between the dimensions of the Me cations and the position assigned to the silicon cation by the oxygen framework. It was noted that, as the content of SiO_2 in the melt increases, the oxygen coordination of the metal cations increases. Below, these principles are applied in considering certain features of the structure of melts in the systems Me_2O_3–SiO_2.

Fig. 1. Liquidus lines of the systems Me_2O_3–SiO_2

1. Sc_2O_3–SiO_2
2. Al_2O_3–SiO_2
3. Cr_2O_3–SiO_2
4. La_2O_3–SiO_2
5. Nd_2O_3–SiO_2

In Fig. 1 the liquidus lines of a number of systems are plotted from the data of ($^{2-4}$). The corresponding numerical values are given in Table 1. The ionic radii of the cations were calculated taking into account the type of coordination and the magnitude of the Born repulsion coefficient according to the data of (^{5}). The last column of the table gives the values of the maximum oxygen coordination, determined from the diagram in (^{1}). In all the systems considered, with the exception–

Fig. 2. Content of SiO_2 in the melt maximally enriched in Me_2O_3, as a function of cation radius

Figure 2: Fig. 2. Content of SiO_2 in the melt maximally enriched in Me_2O_3, as a function of cation radius

In systems of the type Al_2O_3–SiO_2, two-phase regions of coexistence of two liquid melts are observed, one of which is close in composition to SiO_2. The composition of the second melt, enriched in Me_2O_3, as shown by the data in Table 1 and Fig. 2, depends on the size of the metal cation. As the radius decreases, the size restrictions that hinder the entry of the cation into the silicate framework increase, and the region of immiscibility of the silicate melt expands. A particularly sharp broadening of the immiscibility interval occurs on going from scandium ($R_{\mathrm{Sc}} = 0.78$ Å) to chromium ($R_{\mathrm{Cr}} = 0.64$ Å). The same broad immiscibility interval is observed in the TiO_2–SiO_2 system ($R_{\mathrm{Ti}} = 0.66$ Å) (Fig. 2). The Nd_2O_3–SiO_2 system deviates from the general regularity (Fig. 2). The immiscibility interval in this system is somewhat wider than might have been expected on the basis of the value of the ionic radius. At present it does not appear possible to give a rational explanation for this deviation.

Fig. 2. Content of SiO_2 in the melt maximally enriched in Me_2O_3, as a function of cation radius

The absence of immiscibility in melts of the Al_2O_3–SiO_2 system is explained by the fact that the aluminum cation can occur in fourfold oxygen coordination, forming tetrahedral groups isomorphous with silica tetrahedra. The possibilities for isomorphous replacement of silicon by aluminum, observed also in crystalline phases, are broadened in the molten state owing to a certain statistical smearing of the atomic positions, which is inherent in a liquid. In this connection, the restrictions on the placement of cations in the silicate framework in the Al_2O_3 –SiO_2 system are removed.

A comparison of the widths of the immiscibility intervals in melts of silicates of divalent and trivalent metals (Fig. 2) shows that, for the same value of R_k, the immiscibility interval in the Me_2O_3–SiO_2 systems proves to be narrower. This may be explained by the stronger polarizing action exerted by trivalent cations on oxygen ions, which somewhat increases the value of the maximum possible oxygen coordination.

Table 1

System	R_k, Å	SiO_2 content in the melt maximally enriched in Me_2O_3, mol.%	R_k/R_a	Maximum possible oxygen coordination
La_2O_3–SiO_2	1.07	77	0.811	8.9
Nd_2O_3–SiO_2	1.02	72	0.773	8.2
Sm_2O_3–SiO_2	1.00	76	0.758	8.1
Y_2O_3–SiO_2	0.94	75	0.712	8.0
Yb_2O_3–SiO_2	0.87	74	0.659	7.4
Sc_2O_3–SiO_2	0.78	71	0.591	7.0
Cr_2O_3–SiO_2	0.64	12	0.485	6.7
Al_2O_3–SiO_2	0.50	Without restrictions	0.379	6.0

It is interesting to note an analogous relationship between cation sizes and the possibilities of their existence in silicate groups in crystalline phases. In systems formed by metals with appreciable values of R_k (La_2O_3–SiO_2, Nd_2O_3–SiO_2), there are three crystalline phases ($Me_2O_3 \cdot SiO_2$; $2Me_2O_3 \cdot 3SiO_2$; $Me_2O_3 \cdot 2SiO_2$); in the Sc_2O_3–SiO_2 system there are two crystalline phases ($Sc_2O_3 \cdot SiO_2$ and $Sc_2O_3 \cdot 2SiO_2$). In the Cr_2O_3–SiO_2 system,

and also in TiO_2–SiO_2, crystalline phases representing the product of the interaction of the metal oxide with SiO_2 are absent. In the Al_2O_3–SiO_2 system there is one crystalline phase ($3Al_2O_3 \cdot 2SiO_2$).

Thus, it has been shown that the appearance of two immiscible liquid phases in Me_2O_3–SiO_2 systems is caused by a disruption of the coordination ratios existing in silicate melts near liquidus temperatures.

Institute of Foundry Production
Academy of Sciences of the Ukrainian SSR

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CITED LITERATURE

[1] B. I. Markhasev, I. D. Sedletskii, DAN, **148**, No. 4, 916 (1963).
[2] E. M. Levin, H. F. McMurdie, F. P. Hall, *Phase Diagrams for Ceramists* (1956).
[3] N. A. Toropov, I. A. Bondar, *Silikattechnik*, **13**, 4, 137 (1962).
[4] N. A. Toropov, T. P. Kiseleva, Proc. Leningrad Technological Institute named after Lensovet, **52**, 76 (1961).
[5] S. S. Batsanov, *Journal of Structural Chemistry*, **3**, No. 5, 616 (1962).

Note: Figure translations are in progress. See original paper for figures.