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INFLUENCE OF DEGREE OF CATION OXIDATION ON SEPARATION OF A SILICATE MELT

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16. Abstract

A calculation of the energy parameters of ions is made to systematize cations with variable valence in inorder of increasing binding energy with oxygen. It is shown that polyvalent cations in a state of lower valence have reduced ability to cause separation of a silicate melt.

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V. I. Min'ko

Stable and metastable liquefactions, observed beyond the limits of the liquefaction cupula on diagrams of state [1] are functions of temperature. Electron microscope methods were used in [2, 3] and it was shown that with an increase in the temperature of the silicate melt its microheterogeneity decreases and the melt becomes more homogenized. Nevertheless, for real cupulas, the characteristics of microheterogeneity are such that it is difficult to study the phenomenon of differentiation of silicate melts. Some researchers have assumed that microliquefaction is an intermediate and necessary stage (in the form of the precrystallization period [4, 5] or an independent phase transition [6, 7]), which specifies or facilitates finely-dispersed volumetric crystallization. The homogeneous-heterogeneous mechanism for the action of catalysts of the oxide type is also based on their ability to cause separation of the silicate melt [8, 9]. However, in no case was consideration given to the degree of oxidization of polyvalent cations leaving the silicate melt, whereas a variable valence is characteristic for the majority of them, particularly glassceramic catalysts of the oxide type. / 1249*

* Numbers in the margin indicate pagination of original foreign text.

The nature of the liquefaction phase decomposition is regarded from different points of view based on the principles of crystallochemistry, which reflect the energy non-equivalence of ions in a silicate melt and the structural incompatibility of the different cation-oxygen groups which are produced. However, there are presently no criteria for evaluating the structural factor of the cation-oxygen groups produced. The use of energy parameters of the ions to characterize the tendency to cause separation of the silicate melt has been confirmed experimentally and is therefore valid. The following are used as such energy characteristics: The ion potential Z_{Me}/r_M [10], the force of the field Z_{Me}/r_{M-O} [11], the valence force Z_{Me}/cn [12], where M- is the cation, r_M its radius, Z- valence, RM- O - interatomic distance between the cation and oxygen, cn- coordinate number of the cation in glass, e- electrostatic charge. Calculations were performed in [13] using the method of least squares to determine the width of the liquefaction region, in which the variable is Z/r^2.

In this article, a calculation of all these parameters makes it possible to systematize the cations with variable valence in order of their increasing binding energy with oxygen (Table 1). In calculations of these parameters, the ion radii r are used according to [14], cn - according to [15]. The missing data on cn for Sn^{2+}, V^{3+}, Nb^{4+}, Ti^{2+}, Ti^{3+}, Cr^{3+}, Mn^{2+}, Mn^{4+}, Mn^{7+} и Co^{3+} were calculated from the ratio r_a/r_k. The inter-ion distances were calculated as the sum of the ion radius of a given cation and oxygen, for which $r_{O^{2-}} = 1{,}36$ Å were used according to [14]. The electrostatic charge was not taken into account to simplify the calculations. / 1250

According to modern theoretical concepts and data, cations have a more pronounced ability to cause separation of a silicate melt, the closer are the values of the energy characteristics of a given cation and silicon. Taking this fact into account, it may be seen from Table 1 that all of the cations examined

TABLE 1*

ion	Z/r	ion	Z/r^2	ion	Z/R^2_{M-O}	ion	Z/cn
Cu_6^{1+}	1,02	Cu_6^{1+}	1,04	Cu_6^{1+}	0,18	Cu_6^{1+}	0,17
Sn_6^{2+}	1,06	Sn_6^{2+}	1,92	Sn_6^{2+}	0,35	Ti_6^{3+}	0,33
Mn_6^{2+}	2,20	Mn_6^{2+}	2,41	Mn_6^{2+}	0,39	Mn_6^{2+}	0,33
Fe_6^{2+}	2,50	Ce_6^{3+}	2,89	Fe_6^{2+}	0,43	Fe_6^{2+}	0,33
Cu_6^{2+}	2,50	Fe_6^{2+}	3,13	Cu_6^{2+}	0,43	Co_6^{2+}	0,33
Ti_6^{2+}	2,56	Cu_6^{2+}	3,13	Ti_6^{2+}	0,44	Cu_6^{2+}	0,33
Co_6^{2+}	2,56	Ti_6^{2+}	3,28	Co_6^{2+}	0,53	Sn_6^{2+}	0,33
Ce_6^{3+}	2,94	Co_6^{2+}	3,28	Ce_6^{3+}	0,53	Ti_6^{3+}	0,50
Sb_4^{3+}	3,33	Sb_4^{3+}	3,70	Sb_4^{3+}	0,59	V_6^{3+}	0,50
Mn_6^{3+}	4,29	Ce_6^{4+}	5,19	Mn_6^{3+}	0,71	Cr_6^{3+}	0,50
Ti_6^{3+}	4,35	Mn_6^{3+}	6,12	Ti_6^{3+}	0,72	Mn_6^{3+}	0,50
As_6^{3+}	4,35	Ti_6^{3+}	6,25	As_6^{3+}	0,72	Fe_6^{3+}	0,50
V_6^{3+}	4,48	As_6^{3+}	6,25	V_6^{3+}	0,73	Co_6^{3+}	0,50
Fe_6^{3+}	4,48	V_6^{3+}	6,67	Fe_6^{3+}	0,73	As_6^{3+}	0,50
Ce_6^{4+}	4,55	Fe_6^{3+}	6,67	Cr_6^{3+}	0,75	Ce_6^{3+}	0,50
Cr_6^{3+}	4,69	Cr_6^{3+}	7,31	Co_6^{3+}	0,75	Ti_6^{4+}	0,67
Co_6^{3+}	4,69	Co_6^{3+}	7,31	Ce_6^{4+}	0,80	Nb_6^{4+}	0,67
W_4^{4+}	5,88	W_4^{4+}	8,69	W_4^{4+}	0,96	Sn_6^{4+}	0,67
Nb_6^{4+}	5,97	Nb_6^{4+}	8,89	Nb_6^{4+}	0,97	Ce_6^{4+}	0,67
Sn_6^{4+}	5,97	Sn_6^{4+}	8,89	Sn_6^{4+}	0,97	Sb_4^{3+}	0,75
Ti_6^{4+}	6,25	Ti_6^{4+}	9,76	Ti_6^{4+}	1,00	Nb_6^{5+}	0,83
V_4^{4+}	6,56	V_4^{4+}	10,81	V_4^{4+}	1,03	Si_4^{4+}	1,00
Nb_6^{5+}	7,58	Nb_6^{5+}	11,36	Mn_4^{4+}	1,13	V_4^{4+}	1,00
Mn_4^{4+}	7,69	Sb_4^{5+}	13,16	Nb_6^{5+}	1,23	Mn_4^{4+}	1,00
Sb_4^{5+}	8,07	W_4^{6+}	14,26	Sb_4^{5+}	1,28	W_4^{4+}	1,00
W_4^{6+}	9,23	Mn_4^{4+}	14,81	Si_4^{4+}	1,31	Ce_4^{4+}	1,00
Si_4^{4+}	10,26	As_4^{5+}	22,78	W_4^{6+}	1,48	As_4^{5+}	1,25
As_4^{5+}	10,64	Si_4^{4+}	26,33	As_4^{5+}	1,49	Sb_4^{5+}	1,25
V_4^{5+}	12,50	V_4^{5+}	31,25	V_4^{5+}	1,61	Cr_4^{6+}	1,50
Mn_4^{7+}	15,22	Mn_4^{7+}	33,33	Cr_4^{6+}	2,05	W_4^{6+}	1,50
Cr_4^{6+}	17,14	Cr_4^{6+}	50,00	Mn_4^{7+}	2,11	Mn_4^{7+}	1,75

* Translator's note: Commas in numbers represent decimal points.

in a lower valence state have a less pronounced tendency toward separation, since they are located farthest from silicon. With an increase in the valence of the cation, its ability to cause separation of the silicate melt increases.

This property of polyvalent cations is apparent if the systemization is performed according to the value of the binding energy M - O (Table 2), calculated from the Coulomb and other relationships, taking into account the crystallochemical parameters of the cations:

$$E'_{M-O} = Z_M Z_{O^{2-}} e^2 / R_{M-O} \; [10, 12, 16]; \quad E''_{M-O} = K Z_M Z_{O^{2-}} e^2 / R_{M-O} \quad [17];$$

$$E''' = K Z_{M-O} Z_{O^{2-}} e^2 / \text{к. ч.} \cdot R^2_{M-O} \quad [18]$$

TABLE 2*

ion	E'_{M-O}	ion	E''_{M-O}	ion	E'''_{M-O}	ion	E
Cu_6^{1+}	0,86	Cu_6^{1+}	1,11	Cu_6^{1+}	0,079	Cu_6^{1+}	27
Sn_3^{22+}	1,68	Sn_6^{2+}	2,14	Mn_6^{2+}	0,168	Cu_6^{2+}	29
Mn_6^{+}	1,76	Mn_6^{2+}	2,29	Ti_6^{2+}	0,186	Mn_6^{2+}	36
Fe_6^{2+}	1,85	Ti_6^{2+}	2,31	Co_6^{2+}	0,192	Co_6^{2+}	36
Cu_6^{2+}	1,85	Fe_6^{2+}	2,43	Cu_6^{2+}	0,207	Fe_6^{2+}	37
Ti_6^{2+}	1,87	Co_6^{2+}	2,45	Ce_6^{3+}	0,217	As_6^{3+}	30
Co_6^{2+}	1,87	Cu_6^{2+}	2,68	Sn_6^{2+}	0,226	V_6^{3+}	46
Ce_6^{3+}	2,52	Ce_6^{3+}	3,09	As_6^{3+}	0,335	Fe_6^{3+}	48
Sb_6^{2+}	2,66	Sb_4^{3+}	3,52	Ti_6^{3+}	0,339	Sn_3^{4+}	50
Mn_6^{3+}	2,91	As_6^{3+}	4,12	V_6^{3+}	0,344	Mn_4^{4+}	52
Ti_6^{3+}	2,93	Ti_6^{3+}	4,14	Fe_6^{3+}	0,352	Cr_6^{4+}	53
As_6^{3+}	2,93	V_6^{3+}	4,24	Mn_6^{3+}	0,363	Sn_6^{4+}	55
V_6^{3+}	2,96	Fe_6^{3+}	4,28	Ce_6^{4+}	0,367	Sb_4^{3+}	58
Fe_6^{3+}	2,96	Mn_6^{3+}	4,41	Cr_6^{3+}	0,372	Ce_6^{3+}	65
Cr_6^{3+}	3,00	Cr_6^{3+}	4,46	Co_6^{3+}	0,379	Cr_4^{6+}	69
Co_6^{3+}	3,00	Co_6^{3+}	4,54	Sb_6^{3+}	0,390	Mn_6^{4+}	70
Ce_6^{4+}	3,57	Ce_6^{4+}	4,93	Nb_6^{4+}	0,450	Ti_6^{4+}	75
W_4^{4+}	3,92	W_4^{4+}	5,31	Sn_6^{4+}	0,494	P_4^{5+}	76
Nb_6^{4+}	3,94	Nb_6^{4+}	5,55	Ti_6^{4+}	5,95	Ce_6^{4+}	77
Sn_6^{4+}	3,94	Ti_6^{4+}	5,95	Nb_6^{5+}	0,586	Nb_6^{4+}	81
Ti_6^{4+}	4,00	Sn_6^{4+}	6,02	Mn_4^{4+}	0,616	As_4^{5+}	82
V_6^{4+}	4,06	V_6^{4+}	6,31	V_4^{4+}	0,651	Sb_4^{5+}	82
Mn_4^{4+}	4,26	Si_4^{4+}	6,91	W_4^{4+}	0,800	V_4^{+4}	87
Si_4^{4+}	4,57	Mn_4^{4+}	6,95	Mn_4^{4+}	0,932	Si_4^{4+}	102
Nb_6^{5+}	4,95	Nb_6^{5+}	7,11	Si_4^{4+}	0,989	P_4^{3+}	104
Sb_4^{5+}	5,05	Sb_4^{5+}	8,12	Sb_4^{5+}	1,025	V_4^{5+}	114
As_4^{5+}	5,46	W_4^{6+}	8,64	W_4^{6+}	1,075	W_4^{4+}	115
V_4^{5+}	5,68	As_4^{5+}	8,85	As_4^{5+}	1,209	Mo_4^{6+}	129
W_4^{6+}	5,97	V_4^{5+}	9,21	V_4^{5+}	1,307	W_4^{6+}	145
Cr_4^{6+}	7,02	Cr_4^{6+}	12,28	Cr_4^{6+}	1,796		
Mn_4^{7+}	7,69	Mn_4^{7+}	14,69	Mn_4^{7+}	2,025		

* Translator's note: Commas in numbers represent decimal points.

In the calculations of E_{M-O}, where K is the coefficient characterizing the degree of covalence of the M - O bond, the differences in the electronegativities of the cation and oxygen were determined, with subsequent determination of the percent of the bond covalence [18].

The lesser ability of polyvalent cations in a state of lower valence to cause separation of the silicate melt is completely retained, if they are systematized in order of increasing binding energy of the cations with oxygen, used according to [15], according to which this value may be calculated on the basis of the formation enthalpy of oxides of the elements (Table 2).

The differing ability of polyvalent cations to cause separation of a silicate melt, depending on the degree of their oxidation, definitely requires experimental corroboration. In an experimental verification of the properties of cations of variable valence, the investigation and the formulation of diagrams of state for silicate systems must be carried out individually for the oxides of higher and lower valence. It will then be possible to explain several contradictions existing in the literature. One example is the diagram of state for $SnO - SiO_2$ [19], in which according to data of Gregg, the liquefaction cupula does not have a liquidus line, and stannic oxide may be used in the production of enamels as a buffer.

CONCLUSIONS

Cations are systematized, which have a variable valence in order of their increasing calculated energy characteristics, based on the crystallochemical and thermodynamic properties of these cations.

On the basis of theoretical concepts, it is shown that polyvalent cations in a state of lower valence must have a reduced ability to cause separation of a silicate melt. This ability increases when the cations change to a state of higher valence.

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