Computational Study on Structure of Non-crystalline Oxides $2\text{MeO} \cdot \text{SiO}_2$ (Me = Mg, Ca, Sr, Ba, Fe)

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Atomic models of the series of amorphous and liquid oxides $2\text{MeO} \cdot \text{SiO}_2$ (Me = Mg, Ca, Sr, Ba, Fe) containing approximately 500 ions in the basic cube with periodic boundary conditions were built with the help of continuous static relaxation (CRS) and molecular dynamics (MD) methods. The structural and thermodynamic properties of oxides at $T=0$ and 2000 K depending on the Me^{2+} ion radius were analysed. We discovered the structural transformation of the oxide at $\text{Mg} \rightarrow \text{Ca}$ transition in the series, which is caused by the Me^{2+} ion radius change. The polymerization constants of the polymer theory of slags were calculated. The MeO oxide activity is not equal to the ion fraction of the "free ions O^{2-} ".

KEY WORDS: oxides; structure; simulation; liquids; amorphous state.

1. Introduction

In the presented research we tried to find out if the computer simulation of atomic models could adequately reflect the behaviour of structural and other characters of real liquid or amorphous (vitreous) oxide $2\text{MeO} \cdot \text{SiO}_2$ during Me^{2+} ion radius change and to ascertain the field of its applicability. If these characters were simply determined by this radius (at other conditions being constant), we could forecast the properties of any oxide of the considered composition. On the other hand, the experimental data analysis is difficult because in many cases the required properties of oxides are either unknown or measured with sufficiently large errors. As far as we know the computer investigation of above mentioned series of oxides has not yet been conducted.

2. Choice of the Interparticle Potentials and Simulation Methods

The simulation of the oxide models was conducted in the approximation of pure ionic binding.¹⁻³⁾ The pair potentials were chosen in the following form:

$$u_{ij}(r) = Z_i Z_j e^2 / r + B_{ij} \exp(-r/\rho_{ij}) \dots \dots \dots (1)$$

where r is the distance between ions, Z_i are the ion charges (in the units of the elementary charge e), B_{ij} and ρ_{ij} are the ionic cores repulsion parameters. In accordance with Refs. 1)-4), the values ρ_{ij} were taken to be 29 pm for all ion pairs. Further, $Z_1=2$ for Me ions ($i=1$), $Z_2=4$ for Si ($i=2$) and $Z_3=-2$ for O ($i=3$). Now the values B_{ij} are only to be chosen. These values are of little significance for the ions of the same charge sign (*i.e.* for the pairs 11, 12, 22 and 33), because these particles

are situated at large distances. In accordance with the structure data for a series of liquid silicates we took the following values for B_{ij} : $B_{11}=B_{12}=0$, $B_{22}=2055.38 \text{ eV}$,⁴⁾ $B_{23}=1848.0 \text{ eV}$ ²⁾ and $B_{33}=1500.0 \text{ eV}$.⁴⁾ These values lead to distances between the near neighbours in pairs 22, 23 and 33, corresponding to the diffraction data for the silicates. Finally, the parameter B_{13} can be determined using normal (at pressure $p=0$) volume of simple crystalline oxide MeO. The crystal lattices of all the previously mentioned MeO oxides are of NaCl type and their parameters are known for all these oxides. The ionic lattice energy equals to:

$$E = Z_i Z_j e^2 N_A A_M / a + E_{\text{rep}} \dots \dots \dots (2)$$

where a is the lattice parameter, N_A is Avogadro number and A_M is Madelung constant. The first term in the right side of the equation represents Coulomb interaction and E_{rep} is the ion cores repulsion energy. The condition $dE/da=0$ determines the equilibrial value of the a_0 parameter at zero pressure. Since there is only one free parameter B_{13} , it can be determined using a_0 . The values B_{13} for different Me^{2+} ions, thus calculated, are represented in Table 1. This table includes also the following data: the calculated values of the components of full energy, the value of this energy at zero temperature (zero oscillations being ignored) and actual value of energy calculated using reference data⁵⁾ (zero of energy corresponds to the system of ions separated by infinite distances). The error of the full energy estimation is rather low (2.2-7.5%). So the description of oxides in ionic variant is sufficiently adequate.

The authors of Ref. 7) selected the interaction potentials for MeO oxides using their dielectric properties and lattice parameters. The potentials were of (1) type

Table 1. B_{13} coefficients and energy of MeO crystals at $T=0$.

Oxide	Lattice parameter a , (nm) ⁵⁾	B_{13} (eV)	Components of the energy of crystal (kJ/mol)			
			E_{Coulomb}	E_{rep}	E_{full}	E_{exp}
MgO	0.4213	1 441.4	-4 610.6	618.9	-3 991.7	-3 711.4
FeO	0.4299	1 626.0*	-4 518.3	596.6	-3 921.7	-3 835.7
MnO	0.4425	1 936.0	-4 389.7	565.6	-3 824.0	-3 718.7
CaO	0.4812	3 283.0	-4 036.6	482.5	-3 554.0	-3 378.0
SrO	0.5083	4 744.1	-3 821.4	433.8	-3 387.6	-3 192.4
BaO	0.5542	8 885.1	-3 504.9	366.0	-3 138.9	-3 049.6

Note: Atomization energies were taken from Ref. 5), where the O atom's affinity to two electrons was taken according to Sherman⁶⁾ (-7.29 eV). Null oscillations energy was ignored.

* For the simulation we actually took $B_{13}=1\,900$ eV.

but included also the component cr^{-6} , which describes the dispersion interaction between the O^{2-} ions. The interaction of the cores Me-Me was ignored. The authors⁷⁾ obtained the values of $\rho(\text{Me-O})$, which changed from 0.3012 nm (Mg-O) to 0.4084 (Ba-O); thus the parameters $B(\text{Me-O})$ are less than those in Table 1. However the difference between values of repulsive forces of ion cores for the pairs Me-O calculated for the parameters from Table 1 and for the data of Ref. 7) at actual interparticle distances does not exceed 4%. Hence the structure of a disordered oxide turns out to be almost the same for both arrays of B_{ij} and ρ_{ij} parameters.

Earlier the models of FeO at $T=0$ and 1 700 K⁴⁾ and of CaO at 2 000 K⁸⁾ had been built. Here we have created the models of disordered MeO oxides with the values $B(\text{Me-O})=1\,441.4$ eV (MeO), 2 550.0 and 8 885.1 (BaO) at zero temperature (CRS method) and at 2 000 K (MD method). The models contain 216 particles in the basic cube with periodic boundary conditions. The initial arrangement of the particles was random. Coulomb interaction was included with the help of Evald-Hansen method.³⁾ The error of the energy determination is about 0.2%. The basic cube dimension was fixed either with respect to the actual oxide density or so that the pressure of the system was as close to the zero as possible. In the case of pure SiO_2 and oxides, rich in silica, the properties change with hysteresis^{1,3)} and the pressure depends on the history of the system. Hence the density of the SiO_2 models was equal to the actual one (2.2 g/cm³).

The models of complex oxides $2\text{MeO}\cdot\text{SiO}_2$ consisted of 497 ions and were built analogously to the simple oxides. The method of the system building is described in articles.^{3,8)}

The characters of the models are given in Tables 2 and 3. Besides the thermodynamic data the Table 2 contains topological characters, described in previous articles:⁸⁻¹⁰⁾

$$\tilde{\rho}_1 = \sum_{i,j} X_i X_j r_1(ij)/d_o \quad \dots\dots\dots (3)$$

$$\tilde{g}_1 = \left[\sum_{i,j} X_i X_j g_1^{-1}(ij) \right]^{-1} \quad \dots\dots\dots (4)$$

Table 2. Characters of the models of pure disordered MeO oxides. The number of ions is 216 in every model.

B_{13}	Cube edge length (nm)	T (K)	p (GPa)	E_{full} (kJ/mol)	$\tilde{\rho}_1$	s
1 441.4	1.4077	0	-0.15	-3 900.3	1.05	0.95
	1.4245	2 000	-0.12	-3 808.1	1.04	1.07
1 900.0	1.3980	0	-0.29	-3 760.2	1.10	0.96
	1.4265	2 000	-1.56	-3 658.0	1.11	1.03
2 550.0	1.4878	0	0.07	-3 590.1	1.08	1.02
	1.5106	2 000	0.00	-3 487.9	1.08	1.16
3 283.0	1.5300	0	0.54	-3 458.3	1.09	1.13
	1.5450	2 000	-0.40	-3 360.6	1.09	1.00
4 744.1	1.5912	0	0.00	-3 302.4	1.13	1.16
	1.6297	2 000	0.00	-3 189.6	1.12	1.14
8 885.1	1.7500	0	0.12	-3 032.6	1.10	1.08
	1.7797	2 000	0.62	-2 933.9	1.08	0.91

Table 3. Characters of the models of disordered oxides $2\text{MeO}\cdot\text{SiO}_2$. Number of ions in the models is 497. V is the volume of 1 g-ion of an oxide.

B_{13} (eV)	T (K)	Cube edge length (nm)	p (GPa)	E_{full} (kJ/g-ion)	V (cm ³ /g-ion)	E_f^* (kJ/mol)
1 441.4	0	1.8385	0.13	-2 871.6	7.53	61.9
	2 000	1.9515	-0.46	-2 806.7	9.00	38.4
1 900.0	0	1.8807	0.08	-2 823.1	8.06	81.7
	2 000	1.9841	0.0	-2 766.3	9.36	32.5
2 550.0	0	1.9630	-0.07	-2 779.6	9.17	69.8
	2 000	1.9907	0.76	-2 728.8	9.56	6.8
3 283.0	0	1.9490	0.26	-2 753.9	8.97	41.9
	2 000	1.9690	1.14	-2 702.9	9.25	-17.8
4 744.1	0	2.0979	0.0	-2 710.7	11.19	16.6
	2 000	2.1208	0.0	-2 656.4	11.56	-12.4
8 885.1	0	2.2670	0.13	-2 637.3	14.12	30.2
	2 000	2.2670	-0.16	-2 589.5	14.12	-37.5

* E_f : formation energy.

Note: 1 g-ion contains Avogadro number of ions. Formation energy of a complex oxide (out of simple ones) is calculated for 1 mol of a complex oxide $(\text{MeO})_{0.667}(\text{SiO}_2)_{0.333}$, i.e. for 7/3 g-ions.

$$\tilde{y} = \sum_{i,j} X_i X_j y_{ij} \quad \dots\dots\dots (5)$$

and $y_{ij} = d_o/r_{\min}(ij) - d_o/r_1(ij)$. Here X_i is the atomic fraction of the i -th component, $d_o = (V/N)^{1/3}$, N is the number of particles in volume V , $r_1(ij)$ and $r_{\min}(ij)$ are the coordinates of the first peak and of the point where the pair correlative function (PCF) $g_{ij}(r)$ for the pairs ij approxes to zero, $g_1(ij)$ are the heights of the first peaks of PCF's. For dense disordered systems $\tilde{\rho}_1 = 1.08^{9,10)}$ and the theoretical value of $\tilde{g}_1$ can be calculated using the following formula^{4,8)}:

$$g_{1r} = 1 + 0.5725\tilde{y}^{-0.81525} + 0.000366\tilde{y}^{-3} \quad \dots\dots\dots (6)$$

For friable disordered systems $\tilde{\rho}_1 < 1.08$ and $s = g_1/g_{1r} > 1.4^{9,10)}$ It can be seen in Table 2 that the structure of simple MeO oxides is like the dense one except MgO but even for the latter the deviation of $\tilde{\rho}_1$ from 1.08 is very small.

3. Structure of Disordered Oxides $2\text{MeO}\cdot\text{SiO}_2$

Table 4 represents the structure characters of the oxide

Table 4. Structure characters of the models of oxides $2\text{MeO} \cdot \text{SiO}_2$. ($N=497$)

B_{13} (eV)	1441.4		1900.0		2550.0		3283.0		4744.1		8885.1	
T (K)	0	2000	0	2000	0	2000	0	2000	0	2000	0	2000
r_1 (nm) for pairs												
11	0.296	0.309	0.322	0.321	0.313	0.337	0.342	0.365	0.368	0.359	0.380	0.380
22	0.326	0.318	0.328	0.321	0.324	0.326	0.329	0.326	0.323	0.329	0.329	0.326
33	0.254	0.261	0.253	0.258	0.254	0.257	0.256	0.265	0.261	0.263	0.262	0.262
12	0.329	0.326	0.326	0.334	0.330	0.335	0.339	0.339	0.377	0.363	0.352	0.377
13	0.197	0.190	0.208	0.203	0.221	0.214	0.232	0.231	0.244	0.243	0.271	0.268
23	0.165	0.163	0.163	0.164	0.164	0.163	0.163	0.163	0.161	0.162	0.161	0.161
g_1 for pairs												
11	2.55	2.01	2.48	2.01	2.47	1.93	3.00	2.31	2.32	1.90	2.29	1.62
22	5.97	3.24	5.02	3.76	4.77	3.91	5.94	4.70	7.40	4.69	9.37	4.00
33	2.32	2.18	2.47	2.16	3.04	2.39	3.04	2.24	4.61	3.26	5.52	3.76
12	3.20	2.63	3.45	2.80	3.28	2.98	3.49	2.91	3.43	2.81	3.24	2.73
13	5.94	4.48	5.73	4.16	6.13	3.71	5.30	3.33	5.95	3.74	5.70	3.36
23	12.8	13.1	13.7	11.9	15.1	12.8	16.0	12.7	29.0	17.5	30.7	22.4
$\tilde{r}_1$	1.00	0.94	1.00	0.95	0.97	0.95	1.01	1.00	0.98	0.95	0.933	0.94
$\tilde{y}$	0.1534	0.2670	0.1360	0.2654	0.1458	0.2878	0.1642	0.2541	0.1340	0.2643	0.1819	0.2563
$\tilde{g}_1$	3.71	3.20	3.82	3.14	4.28	3.10	4.28	3.19	5.18	3.66	5.41	3.61
s	0.99	1.19	0.94	1.16	1.11	1.19	1.20	1.15	1.26	1.35	1.61	1.31

Fig. 1. Dependence of the coordinates of first peaks of partial PCF's and d_o parameter on B_{13} . To the right of the curves the pairs of ions are noted.

models. **Figure 1** shows the dependence of the first peak coordinates $r_1(ij)$ and d_o parameter at ~ 2000 K on the value $\ln B_{13}$ (for the pairs 22 and 23 these coordinates depend weakly on B_{13} and are not shown on the figure). The values of coordinates mostly depend on B_{13} parameter monotonously with the highest scatter of ~ 4 pm and the interval of sharp r_1 change is seen only for 11 pairs at $B_{13}=2550\text{--}3283$ eV.

The data obtained for the models can be compared with the experimental ones. However we could not find

any precise analysis of our oxide structures with partial PCF's deciphering and the authors usually have to limit themselves with the approximate decomposing and identification of different peaks of the mean-weighted (total) PCF's during the structure investigation, the thing that can not be always done with accuracy. For example, the first peaks for the pairs 13 and 33 for oxides CaO-SiO_2 overlap strongly. As a result of approximate deciphering of the silicate $(\text{CaO})_{0.45}(\text{SiO}_2)_{0.55}$ structure at 1973 K Waseda¹¹⁾ obtained the values $r_1(13)=0.240$ nm and $r_1(33)=0.266$ nm. These values agree with our calculation reasonably (see Table 4), although the $r_1(13)$ coordinate of the model is less than the experimental one by ~ 10 pm. It is hard to explain this misfit with the difference of concentrations. For the glass $\text{CaO} \cdot \text{SiO}_2$ the authors of Ref. 12) conducted the approximate deciphering and obtained the following values: $r_1(13)=0.234$ nm for the nearest 4 O^{2-} neighbours of the Ca^{2+} ion and $r_1(13)=0.254$ nm for the next two O^{2-} neighbours. In the case of $2\text{FeO} \cdot \text{SiO}_2$ the author of Ref. 11) gives the value $r_1(13)=0.203$ nm at 1523 K (and 0.205 nm in pure FeO at 1693 K). The diagram on Fig. 1 gives the value $r_1(13)=0.196$ nm for $B_{13}=1626$ eV (see Table 1) at 2000 K. As can be seen from Table 4, the temperature decrease from 2000 K to zero leads to the $r_1(13)$ increase of approximately 6–7 pm in the interval $B_{13}=1441\text{--}2550$ eV. Hence during the cooling from 2000 to 1523 K the calculated distance $r_1(13)$ is bound to increase by $\sim 1.5\text{--}2$ pm and to reach ~ 0.198 nm. This value is less than that mentioned in Ref. 11) (0.203 nm) by 5 pm, but the difference lies within the range of the oxide structure deciphering error. In order to obtain the value $r_1(13)=0.203$ nm it is necessary to increase the B_{13} coefficient up to ~ 1900 eV. In the article⁴⁾ the models of oxides FeO-SiO_2 were built with this very value B_{13} . Respective data are given in Table 4.

Much greater misfit with the experiments was revealed

Fig. 2. Dependence of Me-O distances in the models of disordered oxides (marked as $r_1(\text{dis})$) on Me-O distances in crystalline oxides MeO (marked as $r_1(\text{cr})$). 1: model with $B_{13}=1441.4$ eV; 2: data^[13]; 3: ferric silicate at 1 673 K (Y. Waseda,^[11] 1980); 4: model with $B_{13}=1900$ eV at $T=2000$ K; 5: model with $B_{13}=2550$ eV; 6: model with $B_{13}=3283$ eV; 7: calcium silicate at 1 873 K (Y. Waseda,^[11] 1980); 8: model with $B_{13}=8885.1$ eV.

Table 5. Average coordination numbers $\bar{z}(13)$ in disordered oxides $2\text{MeO} \cdot \text{SiO}_2$. (in MeO crystals $z=6$)

Element Me	Mg	Fe	Ca
Model, 2200 K	3.7	4.0	5.3
Experiment	4.7 (1 973 K ^[11]) 5 (1 973 K ^[13])	4.2 (1 673 K ^[10])	6.6 (1 873 K ^[11]) 6 (1 873 K ^[13])
Model, 0 K	4.2		
Experiment	4.5 (300 K ^[11]) 4.1 (300 K ^[14])		7.2 (300 K ^[11]) 4+2 (300 K ^[12]) 6 (300 K ^[13])

for the oxides MgO-SiO_2 . In other articles^[11,13] the value $r_1(13)=0.216$ nm is given for the composition $\text{MgO} \cdot \text{SiO}_2$ at 1 973 K and the value 0.214 at 300 K. On the other hand, the authors of Ref. 14) obtained the value $r_1(13)=0.208$ nm for the glass of the same composition at 300 K. Computer calculation at zero temperature leads to the value $r_1(13)=0.196$ nm which is noticeably lower than the experimental one.

Let us consider the phenomenon of the $r_1(13)$ lowering in the models in detail. **Figure 2** shows the dependence of $r_1(13)$ in the disordered oxide models, $r_1(\text{dis})$, on $r_1(13)$ in crystal lattice of NaCl type of the corresponding simple oxide, $r_1(\text{cr})$. The tendency of the $r_1(\text{dis})$ lowering against $r_1(\text{cr})$ is clearly seen. Moreover, this effect intensifies with the $r_1(\text{cr})$ lowering. However the experimental $r_1(13)$ behave differently. The lowering is slight for the Ca-O pairs, is very considerable for the Fe-O pairs and the data of the articles^[11,13] contradict the noted tendency for the Mg-O pairs while the data of Ref. 14) behave in accordance with it. Some part of the divergence of the model and the experimental values of $r_1(13)$ can be caused by errors of the diffraction experiment and the procedure of its deciphering. Another reason is the possible physical difference of structures of different samples of a liquid oxide or glass with identical chemical composition. Finally, it is possible that MgO falls out

Fig. 3. Partial PCF's of the model with $b_{13}=1441.4$ eV at 2000 K. To the right of the curves the ion pairs are noted.

of the general regularity thanks to a yet obscure reason.

In the case of $B_{13} < 3200$ eV the $r_1(13)$ lowering at the transition from simple crystalline MeO oxide to disordered $2\text{MeO} \cdot \text{SiO}_2$ oxide is accompanied by the average coordination number $\bar{z}(13)$ diminishing. This diminishing is seen both in models and in real oxides (see **Table 5**). The model data show that while $r_1(13)$ lowers, the octahedric coordination of O^{2-} ions around Me^{2+} ones turns gradually into the tetrahedric one. Melting of ion crystals of MeX type (alkali halogenides) is also accompanied by the Me-X distance lowering and by simultaneous coordination number $\bar{z}(\text{Me-X})$ diminishing (see the survey in Ref. 11)). The $r_1(13)$ distance increase at the transition from MgO crystal to the silicate $\text{MgO} \cdot \text{SiO}_2$, observed in Refs. 11) and 13), does not accord with the $\bar{z}(13)$ lowering, observed in those same articles.

Thus, the question of the actual $r_1(13)$ distances in magnesium silicates remains vague and requires further investigation.

Figures 3 and 4 show the partial PCF's of $2\text{MeO} \cdot \text{SiO}_2$ oxides at 2000 K for the values $B_{13}=1441.4$ and 8 885.1 eV. We will not some peculiarities of these data, namely:

- (1) In the case of 11 pairs (*i.e.* Me-Me) one can see the splitting of the first peak, the coordinate of which increases together with B_{13} . This peak is very wide.
- (2) The first peak of the 12 PCF also reveals tendency to split. Its height diminishes with the B_{13} increase beyond ~ 3000 eV (see **Table 4**) while a little

additional maximum appears on the right side of it. The second maximum is low and its shape is complex.

(3) 22 PCF reveals higher ripples to the right of the first peak because of the small number of silicon ions in the model (71 ions).

(4) The $g_{13}(r)$ functions behave analogously at $B_{13}=1441.4$ and 8885.1 eV, but the first peak moves to the right and its height diminishes with the B_{13} increase.

(5) The qualitative difference is seen for the 33 pairs. At $B_{13}=1441.4$ eV the first PCF peak is not high and the accessory maximum is seen to the right of it. It indicates the presence of at least two characteristic O–O distances. At $B_{13}=8885.1$ the first PCF peak is much higher and more narrow, and the accessory maximum does not exist. This means that the transformation of

Fig. 4. Partial PCF's of the model with $B_{13}=8885.1$ eV at 2000 K. To the right of the curves the ion pairs are noted.

the oxygen subsystem structure takes place during the B_{13} increase.

The coordination numbers distributions provide additional information. At first we will consider the average $\bar{z}(ij)$ values (see Table 6). At $B_{13} \leq 1900$ eV $\bar{z}(13)$ values are close to 4 while at $B_{13} \geq 2550$ they increase sharply (up to 5–6). Hence in the short interval of B_{13} from 1900 to 2550 eV roughly tetrahedric configuration of O^{2-} ions around Me^{2+} turns into octahedric. Diffraction methods give the same result. In magnesium silicate $\bar{z}(13)=4.5-4.7$; in iron silicate ~ 4.2 and in calcium silicate $6.8-7.2^{(1)}$ (see Table 5).

Analogous situation was observed experimentally for liquid and amorphous silicates $Me_2O \cdot SiO_2$ ($Me = Li, Na, K$). In lithium silicate $\bar{z}(13)=3.8-4.1$ while in natrium silicate it is $5.8-6.1^{(1)}$. Here the Me^{2+} ion dimension increase also causes transition from tetrahedric configuration of the first coordination sphere to octahedric one.

The structure transformation within the first coordination sphere of $Me-O$ pairs leads to considerable changes of the oxide structure as a whole. As a sign of these changes we observe the sharp decrease of $\bar{z}(33)$ (almost in two times!) with the B_{13} growth in the short interval between 1900 and 2550 eV (see Table 6), which is obviously conditioned by the above mentioned $g_{33}(r)$ function shape changes. Even more striking changes are observed on $z(33)$ distributions (see Table 7).

Table 6. Average coordination numbers for different ion pairs, calculated for the interval of the corresponding partial PCF of $2MeO \cdot SiO_2$ system from zero to the first minimum.

B_{13} (eV)	T (K)	Ion pairs					
		11	22	33	12	13	31
1441.4	0	7.3	2.2	6.3	3.1	4.2	2.1
	2000	5.8	2.1	8.5	3.4	3.7	1.8
1900.0	0	8.1	2.2	6.2	3.8	4.4	2.2
	2000	6.0	2.2	6.9	3.0	4.0	2.0
2550.0	0	5.9	2.2	3.4	3.6	4.4	2.2
	2000	8.2	2.4	3.8	3.6	5.1	2.5
3283.0	2000	9.7	2.4	3.0	3.7	6.6	3.3
4744.1	2000	8.5	1.4	3.3	3.3	5.4	2.7
8885.1	0	8.8	1.7	3.2	3.7	5.3	2.6
	2000	9.4	1.4	3.2	3.7	6.0	3.0

Table 7. Coordination numbers $z(33)$ distributions in $2MeO \cdot SiO_2$ oxides.

B_{13} (eV)	T (K)	Number of O atoms with z O neighbours													
		$z=0$	1	2	3	4	5	6	7	8	9	10	11	12	13
1441.4	0	—	—	1	5	23	50	84	69	35	14	3	—	—	—
	2000	—	—	—	—	—	5	18	42	82	66	47	18	5	1
1900.0	0	—	—	—	12	26	53	66	73	31	18	5	—	—	—
	2000	—	—	1	6	12	30	58	84	48	31	14	—	—	—
2550.0	0	4	10	16	123	21	22	45	11	2	—	—	—	—	—
	2000	19	15	13	92	51	34	42	15	3	—	—	—	—	—
3283.0	2000	37	10	—	100	50	10	52	20	3	2	—	—	—	—
4744.1	2000	31	10	2	151	33	6	44	7	—	—	—	—	—	—
8885.1	0	47	3	—	154	16	3	53	8	—	—	—	—	—	—
	2000	42	1	—	164	21	15	32	8	1	—	—	—	—	—

At $B_{13}=1441.4$ and 1900 eV the $\bar{z}(33)$ distribution resembles the gaussian one. Hence the O^{2-} ions arrangement resembles simple liquids with low density. At $B_{13} \geq 2550$ eV the shape of the distribution changes sharply. One can distinguish groups of ions with low $z(33)$ (0, 1 and 2) and two specific peaks appear: one of them at $z=3$ is very high and the other at $z=6$ is 2–5 times lower. This fact indicates appearance of such structural elements as tetrahedra, centred triangles and hexagons in the oxide.

Similar arrangement of ions is typical for crystalline fayalite $2FeO \cdot SiO_2$, where two-layer packing of the oxygen particles exists, the coordination numbers being 6 for 13 pairs, 3 for 31 pairs, 4 for 23 pairs and 1 for 32 pairs.¹⁵⁾ Hence the structure of disordered silicates of calcium and barium is very like the fayalite structure, where the coordination of particles is octahedric around Me^{2+} ions and is tetrahedric around Si^{4+} . However, some part of O^{2-} ions in disordered oxides avoids the layered subsystem and behaves like “free ions” of the polymer theory of slags. At $B_{13}=1441.4$ the layered elements in the oxygen subsystem structure are already negligible.

Thus, the Me^{2+} ion dimension and $r_1(13)$ distance decrease leads not only to transition to the tetrahedric coordination of particles around the Me^{2+} ions but also to the sharp transformation of the entire structure of the silicate. Fayalite-like structure of the oxygen subsystem “dissociates”, turning into the structure of the simple liquid type.

Scrutiny of the Table 6 shows that average coordination numbers for 11 and 12 pairs generally grow slowly with the B_{13} increase and do not feel influence of

the O^{2-} subsystem structure changes. At the same time values $\bar{z}(22)$ decrease slowly.

4. Topological Characters of Disordered Oxides $2MeO \cdot SiO_2$

The structure data allow to calculate the $\bar{\rho}_1$ and s values of oxides using the (2)–(6) formulae. These values are given in Table 4. The $\bar{\rho}_1$ value oscillates in the interval 0.94–1.01 while B_{13} changes. This value is sufficiently less than the standard one for dense systems (~ 1.08); this indicates the friability of oxide structures, *i.e.* the considerable fraction of the particles with low coordination numbers exists in oxide.

Now we are to find out why the parameter s grows obviously (from ~ 1.00 to 1.31–1.62) with the B_{13} increase, while the $\bar{\rho}_1$ value changes weakly. We have proposed a hypothesis earlier that s parameter is sensitive to the structure elements of continuous network type (as in B_2O_3 , SiO_2 *etc.*). This hypothesis is confirmed here for $2MeO \cdot SiO_2$ oxides as well. In fact, as it was noted above, the B_{13} increase leads to the oxygen subsystem structure transformation into layered fayalite-like structure. The intervals of sharp growth of s and $\bar{z}(33)$ decrease coincide roughly (2 000–2 500 eV, see Tables 4 and 6). Temperature lowering intensifies the formation of above-described specific structure. Thus, the ratio s is indeed a sensitive parameter which detects appearance of network-like elements in the structure.

5. Verification of the Applicability of the Polymer Theory of Slags

It is supposed in the polymer theory (PT) of slags that

Table 8. Polymer model applicability verification. Numbers of ions of Me, Si and O are 142, 71 and 284.

B_{13} (eV)	1 441.4		1 990.0		2 550.0		3 283.0		4 744.1		8 885.1	
T (K)	0	2 000	2 000	0	2 000	2 000	2 000	2 000	0	2 000	0	2 000
Number of O atoms with												
$z(32)=0$	55	56	51	48	52	53	46	50	43			
1	173	173	184	188	179	178	192	184	198			
2	56	55	48	48	53	53	46	50	43			
3	—	—	1	—	—	—	—	—	—			
Number of Si atoms with												
$z(23)=2$	—	—	—	—	1	—	—	—	—			
3	6	7	6	8	7	6	1	2	1			
4	58	58	59	55	53	59	69	67	69			
5	7	6	6	8	10	6	1	2	1			
At radius												
r_o (nm)	0.180	0.189	0.188	0.182	0.188	0.189	0.190	0.184	0.190			
K_p	0.103	0.103	0.072	0.065	0.086	0.089	0.057	0.074	0.047			
K_{11}	1.36	1.12	0.68	0.66	2.15	0.94	0.25	0.59	0.48			
$X_*(O^{2-})$	0.76	0.76	0.68	0.67	0.74	0.74	0.65	0.68	0.61			
α	0.39	0.39	0.34	0.34	0.37	0.37	0.32	0.35	0.30			
Bound groups												
	$1^9 2^2$	$1^{10} 2^2$	$1^{15} 2^3$	$1^{17} 2^4$	$1^{11} 2^5$	$1^{13} 2^3$	$1^{19} 2^2$	$1^{16} 2^3$	$1^{19} 2^4$			
	$3^2 5^1$	$3^{14} 1^1$	$3^2 6^1$	$6^1 11^1$	$3^{14} 7^1$	$4^9 1^1$	$3^2 5^1$	$3^2 4^2$	$4^2 6^1$			
	$7^1 18^1$	$7^{19} 1^1$	$9^1 12^1$	29^1		39^1	37^1	35^1	$12^1 18^1$			
	22^1	10^1										
		24^1										

Si particles are bound with four O particles exactly. Further, if an O particle is bound with two Si atoms, then it is a "bridge" one; if it has one bond with Si, then it is an "end ion O^{2-} ". Otherwise, if it has no Si neighbours, then it is a "free ion O^{2-} " in the terms of PT.

Radii r_o at which $\bar{z}(23)=4.00$ were determined for the models. These radii are given in Table 8. If we know r_o , we can calculate the number of O atoms having two neighbours Si (n_o), one neighbour Si (n_1) or no neighbours Si (n_2). These values are also given in Table 8 (in Me_2SiO_4 oxide $\bar{z}(32)=\bar{z}(23)/4=1.00$ and hence $n_o=n_2$). The silicon anions polymerization process looks as follows:

It can be rewritten in such a way (H. Toop and C. Samis):

"Equilibrium constant" of this reaction (polymerization constant) equals $K_p=n_o n_2/n_1^2$. The values of K_p for $2MeO \cdot SiO_2$ oxides are given in Table 8. At constant temperature 2000 K they decrease gradually from 0.103 at $B_{13}=1441.4$ eV to 0.047 at $B_{13}=885.1$. This decrease is caused by comparatively weak n_o and n_2 decrease (from 56 to 43) and by corresponding n_1 growth (from 173 to 198). Hence the transition of the model of Mg_2SiO_4 to Ba_2SiO_4 causes a slight (in 1.3 times) decrease of the number of "free ions O^{2-} " of the polymer theory.

In the terms of PT two Si atoms disposed on distance $\leq r_o$ from a common O atom form a "polyanion". So it is possible to determine a polyanion as a bound group of Si particles and binding O particles and to find polyanions with different numbers of Si atoms in the model. These values are also given in Table 8. The entry $1^{10}2^{23}3^3 \dots$ means that the model contains 10 Si particles out of groups (*i.e.* anions SiO_4^{4-} in the terms of PT), 2 dimers $Si_2O_7^{6-}$, 3 trimers and so on. The number of monomers SiO_4^{4-} increases (at 2000 K—from 10 to 19) with B_{13} growth, *i.e.* depolymerization takes place, which correlates with K_p decrease.

Polymerization degree α can be calculated with the help of the following formula:

$$\alpha = n_o/2n(Si) \dots\dots\dots(9)$$

where $n(Si)=71$ is the number of Si particles. At 2000 K α changes with B_{13} growth comparatively slowly—from 0.387 to 0.303 (see Table 8). Finally, we can calculate the ion fraction of "free ions O^{2-} ":

$$X_*(O^{2-}) = n_2/(n_2 + n_{pa}) \dots\dots\dots(10)$$

(n_{pa} is the number of all polyanions), and the equilibrium constant k_{11} of the (7) reaction as well. The values $X_*(O^{2-})$ decrease very little with B_{13} growth (from 0.76 to 0.61); k_{11} values also decrease a bit, though with considerable oscillations caused by a very low number of dimers in the models (from 2 to 5).

The analysis of α and K_p correlation for $(MeO)_x-(SiO_2)_{1-x}$ oxides leads to the formula⁸⁾:

$$K_p = \alpha[x - 2(1-x)(1-\alpha)]/[8(1-x)(1-\alpha)^2] \dots\dots(11)$$

which follows automatically from the condition $\bar{z}(23)=4$ and agrees with calculations of G. Toop and C. Samis,

I. B. Bobylev and V. N. Anfilogov (see the survey in Ref. 16)). At $x=2/3$ we have $K_p=\alpha^2/[4(1-\alpha)^2]$. The verification using the data of the Table 8 confirms this correlation. Nevertheless, the PT can hardly be considered fully adequate because not every atom Si has exactly 4 closest oxygen neighbours. The coordination number distributions shown in Table 8 indicate that there are Si atoms in the models which have $z(23)=2, 3$ and 5. However, the majority of them actually have 4 oxygen neighbours exactly (from 82 to 97%).

In the approximation of ideal ion solutions (M. I. Tyomkin) or at certain other assumptions the thermodynamic activity $a(MeO)$ of MeO oxide equals to the ion fraction of "free ions" $O^{2-} X_*(O^{2-})$.¹⁷⁾ In this case one can calculate the effective values of $X_*(O^{2-})$, K_p , k_{11} etc. using the experimental data of the MeO activity in the $MeO-SiO_2$ oxides. For instance, at $T=1873$ K we have $k_{11}=1.00$ for the $FeO-SiO_2$ system and $k_{11}=0.0016$ for $CaO-SiO_2$,¹⁷⁾ *i.e.* k_{11} changes in ~ 600 times. This does not correlate with the structure data (Table 8), because $k_{11} \sim 1.0$ for all the models. Estimations of Ref. 17) give at 1873 K in the $2CaO \cdot SiO_2$ oxide the ion fraction of "free ions O^{2-} " 0.01–0.02, *i.e.* the model must have approximately 3–6 such ions. Actually this value equals to 40–60 in the models.

This discrepancy can be explained by two reasons. Either the structure of our (purely ionic) models does not correspond to the actual one in spite of the good coincidence of the partial PCF peaks coordinates and coordination numbers, or the assumption $a(MeO)=X_*(O^{2-})$ does not come true. Both these reasons can act simultaneously. The second one is more probable because the mentioned assumption seems to be weakly grounded for the systems with sufficient fraction of ionic bond. The fairly great dispersion of the nearest distances Si–O in the glasses ($\pm 18\%$ in $MgSiO_3$ ¹⁴⁾ and $\pm 15\%$ in $CaSiO_3$ ¹²⁾), which can be estimated using the width of the first PCF peak for 23 pairs, would have been rather difficult to explain on the basis of the polymer theory. This fact is also of no little importance.

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