

On the plasticity of Si–O framework of alkali zinc silicates

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The configuration of the Si–O framework in alkali zinc silicates has been investigated on the basis of recently determined structures. The results have shown that there is a linear correlation between the ionic radii of alkali ions and the molar abundance of $\text{ZnO}+\text{SiO}_2$ per one alkali ion in the structure. This indicates that in the case of zinc silicates, the configuration of the Si–O frameworks is largely influenced by the ionic radii of alkali ions in the structure. On the contrary, in the case of alumino-silicates, the configuration of the Si–O framework is independent of ionic radii of alkali ions. In the former, the Si–O framework is considered to be plastic, while in the latter, it could be called rigid. The latter extreme cases are those of zeolites. In this case, the configuration of frameworks is not entirely influenced by the ionic radii of alkali atoms present. These results are discussed in connection with the historical investigations of silicate structures.

Keywords: silicate, zinc silicate, alumino-silicate, framework, ionic radii, framework configuration

1 Introduction

During the course of the structural investigations of zinc silicates, structures containing new Si–O topologies have been found. (Klaska, Eck & Pohl, 1978; Marumo & Syono, 1968; Hesse, Liebau & Böhm, 1977; Plakhov & Belov, 1977, 1979; Simonov, Belokoneva & Belov, 1976; Simonov, Belokoneva & Belov, 1980; Kohara & Kawahara, 1990; Kawahara, Kohara, Konishi, Horiuchi & Kawamura, 1991).

According to the results of these investigations, the coordination number of Zn atoms is four and, like aluminum atoms, they can be considered to play the same role as Si atoms in framework silicates. These were discussed by Zoltai (1966).

On the other hand, alkali zinc silicates have attracted the interests of investigators on ceramic materials, and the syntheses of

these phases, such as those by solid–solid reactions, flux method and hydrothermal methods have been carried out by several workers (Belokoneva, Egorov-Tismenko, Simonov & Belov, 1966; Plakhov & Belov, 1977; Setoguchi, 1979; Yamaguchi & Akatsuka, 1979; West, 1980).

By careful examination on the investigation above, we found that alkali containing zinc silicates are more easily synthesized than are non alkali zinc silicates. The reason may be that the broadness of coordination number of alkali atoms present in the structures enhances plasticity. In this case, the state of coordination of alkali atoms in the structures should be considered.

Under these circumstances, we examined the relationship between the influence of the ionic radii of alkali atoms and the molar abundance of Si-O_4 and Zn-O_4 per one alkali atom in the structures.

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2 Consideration of Alkali zinc tectosilicates

Firstly, the discussion is confined to tectosilicates, and five specimens of tecto-alkali zinc silicates were compared on the basis of $M_2(\text{ZnSi}_p\text{O}_q)$ vs M: alkaline metals, $q=2(p+1)$. The result are shown in Table 1.

Table 1. Alkali zinco tectosilicates, The comparison between ionic radii of alkali ions vs $(\text{ZnO}+\text{SiO}_2) / \text{M}_2\text{O}$. C.N.: Coordination number; $r^{C.N.*}$: Alkali ion radius for C.N., * Effective ionic radii from Shannon and Prewitt(1969, 1970) and Shannon (1976).

Compo.	C.N.	$r^{C.N.}$	T/M
$\text{Li}_2\text{ZnSiO}_4$	4	0.59	2
$\text{Na}_2\text{ZnSiO}_4$	4	0.99	2
$\text{Na}_2\text{ZnSi}_2\text{O}_6$	5	1.00	3
$\text{Na}_2\text{ZnSi}_3\text{O}_8$	7	1.12	4
$\text{K}_2\text{ZnSi}_4\text{O}_{10}$	8	1.51	5
$\text{Rb}_2\text{ZnSi}_5\text{O}_{12}$	12	1.72	6
$\text{Cs}_2\text{ZnSi}_5\text{O}_{12}$	12	1.88	6

Compo.: Chemical compositions

C.N.: Coordination numbers

$r^{C.N.}$: Ionic radii of cations

T/M: $(\text{ZnO}+\text{SiO}_2)/\text{M}_2\text{O}$

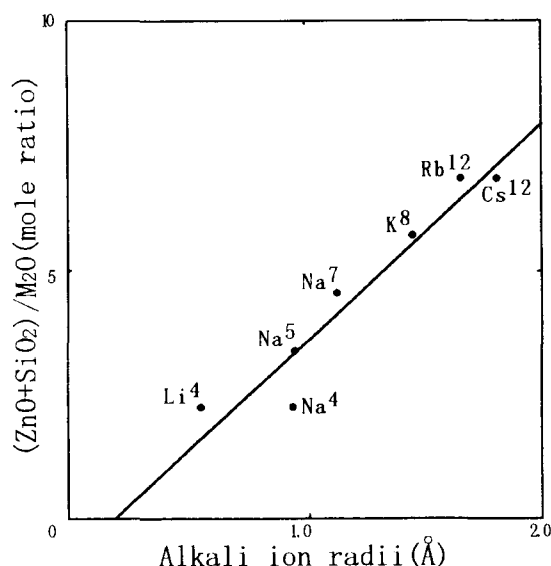


Fig.1. The graphic representation of the data in Table 1.

As far as the structures of zinc silicates

are concerned, whether Zn-O should be treated in the same role as, for example, Al-O and Si-O tetrahedra, Zoltai (1960) discussed that Zn atoms should be treated like Al atoms. Thus, the configuration of the T-O framework can be considered similarly for Si, Al and Zn tetrahedra.

As shown in Fig.1, there is a strong correlation between the ionic radii of alkali ions vs $(\text{ZnO}+\text{SiO}_2) / \text{M}_2\text{O}$. This signifies that the T-O framework of Zn silicates is quite flexible and can change its configuration according to the ionic radii of alkali ions.

3 Consideration of sodium zinc silicates

Secondly, we consider the case of sodium zinc silicates. In Table 2, five sodium zinc silicates already investigated are tabulated. Furthermore, in Table 3, four sodium zinc silicates except for $\text{Na}_2\text{Zn}_2\text{Si}_2\text{O}_7$ are tabulated together with their chemical formula, $(\text{ZnSi}_p\text{O}_q)/\text{Na}_2\text{O}$, volumes per oxygen atom, densities and $D_{zn} \times D_{Si}$. These quantities are compared statistically on the basis of the compactness of the atoms in the structures.

Table 2. Comparison of sodium zinc silicates.

Compo.	C.N.	$r^{C.N.}$	T/M
$\text{Na}_2\text{ZnSi}_3\text{O}_8$	7	1.12	4
$\text{Na}_2\text{Zn}_3\text{Si}_2\text{O}_8$	6	1.02	5
$\text{Na}_2\text{Zn}_2\text{Si}_2\text{O}_7$	4	0.99	4
$\text{Na}_2\text{ZnSi}_2\text{O}_6$	5	1.00	3
$\text{Na}_2\text{ZnSiO}_4$	4	0.99	2

Compo.: Chemical compositions

C.N.: Coordination numbers

$r^{C.N.}$: Ionic radii of cations

T/M: $(\text{ZnO}+\text{SiO}_2)/\text{M}_2\text{O}$

The reason that $\text{Na}_2\text{Zn}_2\text{Si}_2\text{O}_7$ is removed from the statistical calculation mentioned in Table 2 is that this structure is not a framework structure. The fact that the

density, 1.77, is much smaller than the others tells us that this structure belongs to a different structure type.

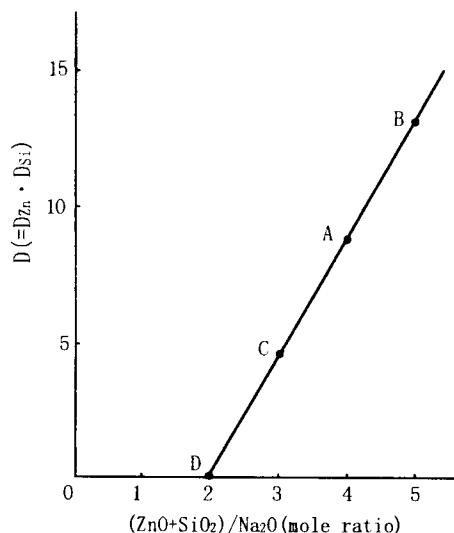


Fig.2. The data from Table 3 are represented graphically.

Table 3. Comparison between $(\text{ZnO}+\text{SiO}_2)/\text{Na}_2\text{O}$ vs average distortion indices of whole tetrahedra in the structures of sodium zinc silicates.

P	R	V_{Ox}	d_x	D_{Zn}	D_{Si}	D
A	4	22.4	2.95	2.31	3.70	8.5
B	5	33.7	3.64	4.12	3.07	13
C	3	23.6	3.1	0.976	4.17	4.1
D	2	25.1	3.4	0.210	0.177	0.037

A: $\text{Na}_2\text{ZnSi}_3\text{O}_8$

B: $\text{Na}_2\text{Zn}_3\text{Si}_2\text{O}_8$

C: $\text{Na}_2\text{ZnSi}_2\text{O}_6$

D: $\text{Na}_2\text{ZnSiO}_4$

P: Name of Phases

R: T/M Ratio, $(\text{ZnO}+\text{SiO}_2)/\text{Na}_2\text{O}$

V_{Ox} : Volume (unit cell)/Number of oxygen atom

d_x : Density (g/cm^3)

D_{Zn} : Distortion indices of Zn-O tetrahedra

D_{Si} : Distortion indices of Si-O tetrahedra

D: $D=D_{Zn} \times D_{Si}$

In order to discuss the internal distortion of the structures, the relation between the T/M ratio vs distortion indices for tetrahedra of ZnO and SiO₂ is examined. In Table 3, the comparison between $(\text{ZnO}+\text{SiO}_2)/\text{Na}_2\text{O}$ vs average distortion indices of whole tetrahedra in the struc-

tures of sodium zinc silicates is shown.

The D value signifies the quantity of the total distortion in the structure. The data are shown graphically in Fig.3. There is a linear correlation between D values and the quantities of $R:(\text{ZnO}+\text{SiO}_2)/\text{Na}_2\text{O}$. According to Fig.3, as $(\text{ZnO}+\text{SiO}_2)/\text{Na}_2\text{O}$ increases, the total distortion of ZnO+SiO₂ also increases. This is based on the fact that the voids around Na atoms increase to fit the appropriate configurations of ZnO and SiO₂ tetrahedra. The reason that the molar abundance of Na in Zn-silicate is high is that besides the plasticities of coordination polyhedra of Na atoms, the plasticities of both ZnO+SiO₂ tetrahedra play an important rôle in the structures.

4 Consideration of aluminum silicates

Next, we consider aluminum silicates in the same way. Firstly, the discussion is confined to tectosilicates. Fifteen specimens of alkali aluminosilicates were compared on the basis of the ionic radii and $(\text{Al}_2\text{O}_3 + 2\text{SiO}_2)/\text{M}_2\text{O}$. The values are tabulated in Table 4.

Fig. 3 shows that there is no correlation between alkali ionic radii and $(\text{Al}_2\text{O}_3 + 2\text{SiO}_2)/\text{M}_2\text{O}$. This is also evident from the fact that, for example, there are large cavities in the structure of zeolites and no correlations apparently exist between the radii of ions present and the aperture of the cavities. In this case, the cavities have been formed at the time of the crystal growth of zeolite without any influence of the cations in the cavities.

Table 4. The compositions, the values of coordination numbers, $r^{C.N.}$ (Å) and $(Al_2O_3+SiO_2)/M_2O$ of fifteen alkali aluminosilicates.

Compo.	C.N.	$r^{C.N.}$	T/M
LiAlSiO ₄	4	0.59	3
NaAlSiO ₄	8	1.18	3
KAlSiO ₄	9	1.55	3
RbAlSiO ₄	11	1.69	3
CsAlSiO ₄	13	1.90	3
LiAlSi ₂ O ₆	4	0.59	5
NaAlSi ₂ O ₆	6	1.02	5
KAlSi ₂ O ₆	12	1.64	5
RbAlSi ₂ O ₆	12	1.72	5
CsAlSi ₂ O ₆	12	1.88	5
LiAlSi ₃ O ₈	4	0.59	7
NaAlSi ₃ O ₈	8	1.18	7
KAlSi ₃ O ₈	9	1.55	7
RbAlSi ₃ O ₈	9	1.63	7
CsAlSi ₃ O ₈	-	-	(unknown)

C.N.: Coordination numbers

$r^{C.N.}$: Radii of alkali ion corresponding to C.N. above.

* Effective ionic radii from Shannon and Prewitt (1969, 1970) and Shannon (1976).

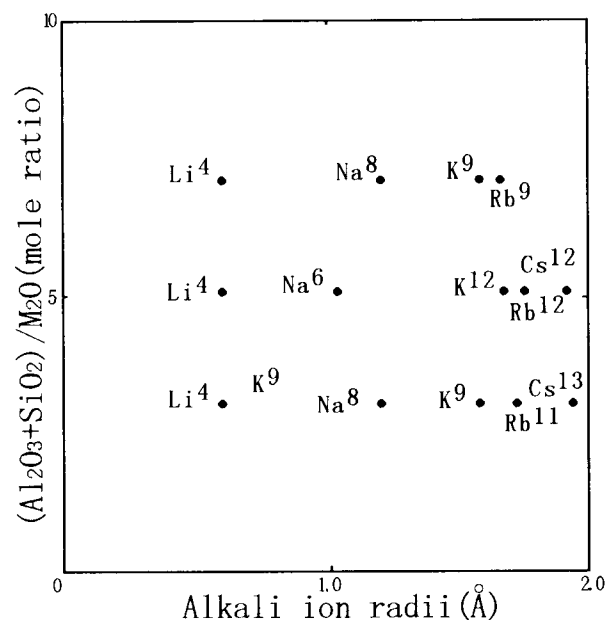


Fig. 3. The graphic representation of the data from Table 4.

5 Discussions

In our opinion, there seems to have been two main ideas on the crystallization of silicates. That is, the question "by what order or sequence are the T - O frameworks formed at the time of crystallization of the silicate structure?". The first idea is that the form or degree of polymerization of Si-O tetrahedra are already determined in the melts or solutions, and the metal cations are filled among these predetermined Si-O frameworks at the time of crystallization. The second idea is that each isolated T-O tetrahedra is filled among the metal cations, and the polymerization is established at the time of crystallization under the influence of coexisting metal cations.

The former idea corresponds to the English school of W.L. Bragg and the latter to those of the Russian school of N.V. Belov. In the idea proposed by the English school, the silicate framework is rigid and is not affected by the coexistence of cations. On the contrary, the Russian school suggests that the form of the Si-O framework is strongly influenced by the ionic radii of coexisting metal cations.

At present, these two discussion have been phased out. But recently, in the course of the studies of alkali zinc silicates, the authors re-discussed the idea of the importance of the discussion of these two relations on the basis of new quantitative data obtained by several investigations.

These relations can be applied to the prediction of the compositions of new phases, and make the preparation of the starting materials easier than those based on the random ratios of each atom in the reagents. In fact, the authors could succeed in the syntheses of new phases according to the ideas mentioned above.

6 Conclusion

1. The frameworks of alkali zinc silicates are soft and flexible and change their shapes and sizes according to the ionic radii of the alkali atoms present. There are no cavities in the crystal structure.

2. The frameworks of tectosilicates, including aluminum silicates, are essentially hard or rigid. The types of frameworks are determined in spite of the ionic radii of ions inserted in the cavities. Their shapes and sizes are influenced only by quite large ions.

3. In the case of alkali zinc silicates, the syntheses of new phases will be able to anticipate by consideration of the molecular ratios of starting materials from the curve indicated in Fig.2.

7 References

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