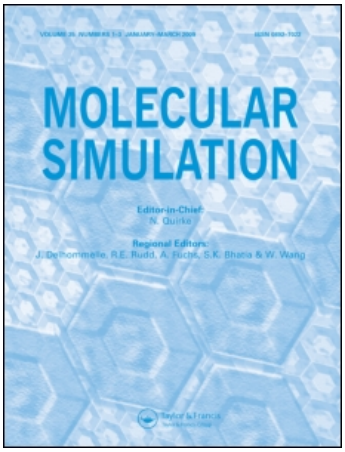

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Molecular Dynamics of Solid Solution and Coexisting Liquid

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MOLECULAR DYNAMICS OF SOLID SOLUTION AND COEXISTING LIQUID

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Two-phase molecular dynamics (MD) simulations of coexisting solid and liquid were performed for binary systems MgO-CaO and NaCl-KCl. Solid solution crystal and its melt having the same composition were placed in a basic cell, and the compositional change of solid and liquid during MD calculation was observed. The starting compositions were Mg-rich ($Mg_{0.875}$, $Ca_{0.125}$)O, Ca-rich ($Mg_{0.125}$, $Ca_{0.875}$)O, Na-rich ($Na_{0.875}$, $K_{0.125}$)Cl, and K-rich ($Na_{0.125}$, $K_{0.875}$)Cl. The concentration of "minor element" in the liquid was detected for some calculations where solid-liquid interface was maintained for a long period of time, more than 400 ps ($= 200 \times 10^3$ steps). These minor elements were swept out into liquid during the growth of the crystal lattice, because of the mismatch of cationic size. It was easier to cause the differentiation in MgO-CaO system than in NaCl-KCl system.

Keywords: Two-phase molecular dynamics; solid-liquid interface; partitioning of elements; NaCl-KCl; MgO-CaO

1. INTRODUCTION

The differentiation of elements between solid and coexisting liquid is an important phenomenon in the fields of material and earth sciences. There are several experimental studies concerning the partitioning of elements between solid and liquid. However, in the field of computer chemistry, there have been not enough studies treating this phenomenon. The purpose of this

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study is to observe and consider the mechanism of the differentiation of elements in atomic scale through molecular dynamics (MD) simulation.

There have been some two-phase MD calculations of coexisting solid and liquid: NaCl crystal and melt [1, 2], MgO crystal and melt [2], $MgSiO_3$-perovskite crystal and melt [3], and stishovite and its melt [4]. However, these calculations were restricted only to end member crystals and their melts, and did not treat the differentiation of elements between solid and liquid. In order to cause some differentiation of elements in an MD cell, two-phase MD calculation of solid solution crystal and its melt is desirable.

The MD simulations of solid solution were performed by Akamatsu *et al.* [5]. They utilized (Mg, Ca)O and (Na, K)Cl of *NPT* ensembles ($N = 512$), and succeeded in showing the followings: (1) The molar volume and enthalpy of the crystals can vary smoothly along with composition. (2) The excess volume and enthalpy of mixing in these systems are positive, which is consistent with the experimental results [6]. In this study we have made the two-phase MD simulations of coexisting solid and liquid having the compositions of (Mg, Ca)O and (Na, K)Cl.

The MgO-CaO binary system forms MgO-rich solid solution and CaO-rich solution, and there exists a miscibility gap between them [*e.g.*, 7, 8]. The eutectic point is near the composition of $Ca/(Mg + Ca) = 0.59$ [7]. This means that the partitioning of Mg and Ca between coexisting solid and liquid, in equilibrium, should be as follows:

(1) In Mg-rich composition [$Ca/(Mg + Ca) < 0.59$], Ca tends to concentrate in liquid.
(2) In Ca-rich composition [$Ca/(Mg + Ca) > 0.59$], Mg tends to concentrate in liquid.

The NaCl-KCl binary system forms complete solid solution [*e.g.*, 9]. The solidus curve and liquidus curve in the phase diagram have a common temperature minimum near the composition of $K/(Na + K) = 0.5$ [9]. The partitioning of Na and K between coexisting solid and liquid, in equilibrium, should be as follows:

(1) In Na-rich composition [$K/(Na + K) < 0.5$], K tends to concentrate in liquid.
(2) In K-rich composition [$K/(Na + K) > 0.5$], Na tends to concentrate in liquid.

In this study, we have started the MD calculations of coexisting solid and liquid that have the same composition, and observed the compositional

change of the coexisting solid and liquid, during the calculation. The starting compositions are (1) Mg-rich ($Mg_{0.875}$, $Ca_{0.125}$)O, (2) Ca-rich ($Mg_{0.125}$, $Ca_{0.875}$)O, (3) Na-rich ($Na_{0.875}$, $K_{0.125}$)Cl, and (4) K-rich ($Na_{0.125}$, $K_{0.875}$)Cl.

2. CALCULATION

Two body interatomic potentials for MgO-CaO and NaCl-KCl based on the equation of state for end member crystals (MgO, CaO, NaCl, and KCl) [10, 11] were used during the calculation. The potential function consists of Coulomb, short-range repulsion, and dispersion terms:

$$U_{ij}(r_{ij}) = \frac{z_i z_j e^2}{r_{ij}} + f_0(b_i + b_j) \exp\left(\frac{a_i + a_j - r_{ij}}{b_i + b_j}\right) - \frac{c_i c_j}{r^6}, \quad (1)$$

where r_{ij} is the distance between ions i and j, e the elementary electric charge, z_i the effective valence of ion i and $f_0 = 6.948 \times 10^{-6}$ dyn for unit adaptation. The parameters z_i, a_i, b_i, and c_i are shown in Table I, and potential curves for cation-anion pairs in Figure 1. The MD program MXDORTO [12] was used and the step time was 2 fs. Periodic boundary conditions were applied to x-, y- and z- directions. The temperature and pressure (= 0.1 MPa for all the calculations) were controlled by means of scaling of ion velocities and basic cell parameters.

2.1. Preparation of Solid Solutions and their Melts

The solid solution crystals (Mg_{1-x}, Ca_x)O and (Na_{1-x}, K_x)Cl with $x = 0.125$ and 0.875 were prepared by substituting 1/8 cations of end member crystals ($x = 0, 1$) with the cations of the opposite end member. Two kinds of cations in the solid solution were randomly distributed. The number of particles in

TABLE I Parameters of interatomic potential model in the equation (1) for MgO-CaO [10] and NaCl-KCl [11] systems

Ion	z_i	a_i/Å	b_i/Å	c_i/[(kcal mol^{-1})$^{1/2}$ Å^3]
Cl	−1.00	2.0555	0.1895	30.0
K	1.00	1.7600	0.1100	15.0
Na	1.00	1.5010	0.1185	10.0
O	−1.56	1.8137	0.172	22.0
Ca	1.56	1.5590	0.090	9.0
Mg	1.56	1.2391	0.075	3.0

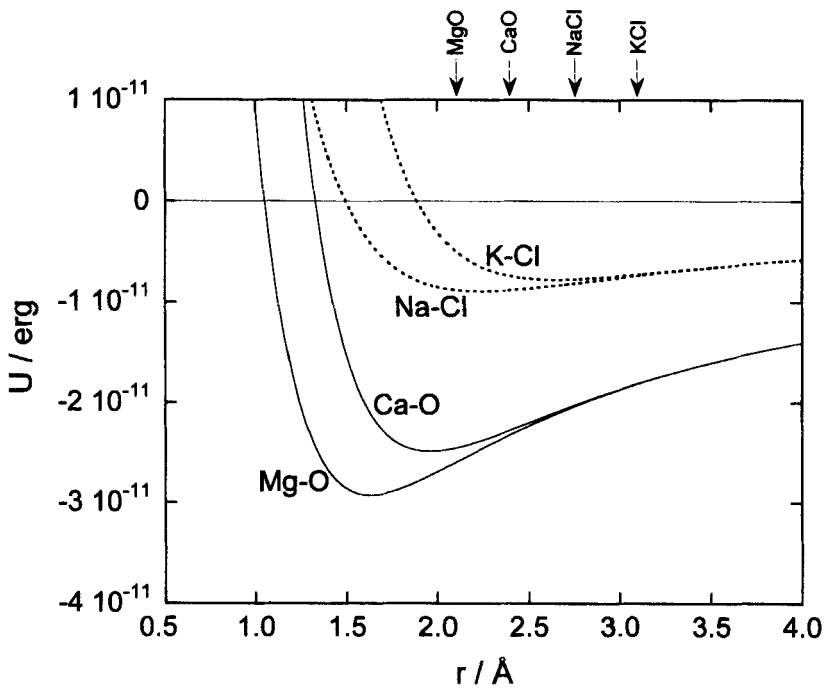

FIGURE 1 Potential curves for Mg-O, Ca-O, Na-Cl, and K-Cl bonds. The approximate values of the nearest cation-anion bond lengths in the end member crystals are shown by arrows: MgO ~ 2.1 Å, CaO ~ 2.4 Å, NaCl ~ 2.8 Å, and KCl ~ 3.1 Å. The slope of the potential curves for (Mg, Ca)O around $r = 2.1 \sim 2.4$ Å is larger than that for (Na, K)Cl around $r = 2.8 \sim 3.1$ Å, which indicates that the magnitude of cation-anion interaction in (Mg, Ca)O is larger than that in (Na, K)Cl.

the basic cell was 1728 [(Mg, Ca)O and (Na, K)Cl] or 4096 [(Mg, Ca)O]. The melts were produced from the structures of solid solutions by the calculations at 3500 K [(Mg, Ca)O] or 1500 K [(Na, K)Cl], which were much higher than the liquidus temperature of the corresponding composition. The melt structures were equilibrated for more than 40 ps ($= 20 \times 10^3$ steps).

2.2. Construction of the Solid-liquid Interface

Two phases (solid solution and its melt) equilibrated under the same temperature were placed in a basic cell. The temperature conditions were 2300 K for $(Mg_{0.875}, Ca_{0.125})O$, 2500 K for $(Mg_{0.125}, Ca_{0.875})O$, and 900 K for (Na, K)Cl. The total number N of particle in the cell was 3456

($= 2 \times 1728$) or 8192 ($= 2 \times 4096$). The configuration of cations for $(Mg_{0.875}, Ca_{0.125})O$ ($N = 3456$), as an example, is shown in Figure 2. After the annealing of $2 \sim 6$ ps calculation, the space between solid and liquid disappeared.

2.3. Calculation of Crystallization and Melting

Two-phase MD calculations were performed at several temperatures from the structures prepared in 2.2. We can observe the crystallization or melting according to the temperature. The compositional change of the coexisting liquid and solid was also observed.

3. RESULTS

3.1. Crystallization and Melting

The summary of two-phase MD calculations is shown in Table II. In the calculations at high temperatures, the liquid part of the cell was observed to

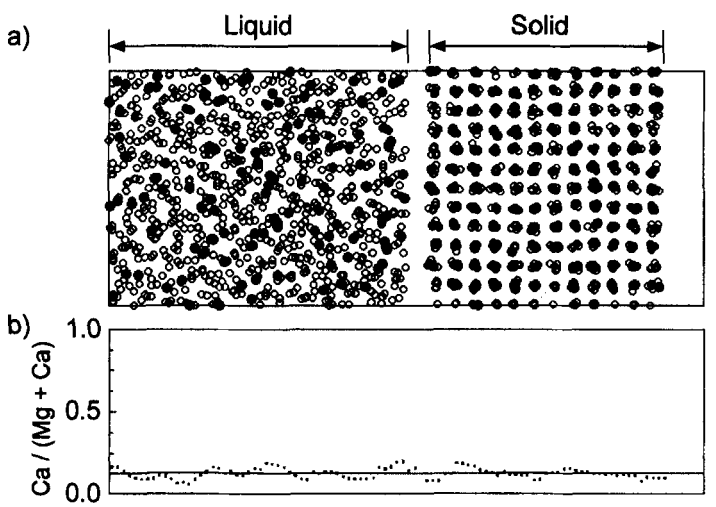

FIGURE 2 Initial distribution of cations in the system $(Mg_{0.875}, Ca_{0.125})O$ ($N = 3456$). The solid and liquid equilibrated at $P = 0.1$ MPa, $T = 2300$ K are placed in a basic cell. (**a**) Configuration of Ca (large solid circles) and Mg (small open circles). Right and left parts of the figure contain 864 cations each. (**b**) Concentration of Ca along with the direction perpendicular to the solid-liquid interface. The ratio of Ca / (Mg + Ca) is almost 0.125. The data points for the concentration of cations in Figures 2 and $4 \sim 9$ are as the results of the average of the nearest five data.

TABLE II Summary of two-phase molecular dynamics calculations

Composition	N^{*1}	*T*/*K*	*Results*	*Differentiation*
$(Mg_{0.875}, Ca_{0.125})O$	3456	2450	Melted after 100 ps[*2]	–[*3]
	3456	2400	Crystallized after 450 ps[*4]	Ca → Liquid[*5]
	8192	2400	Crystallized after 440 ps	Ca → Liquid
	3456	2300	Crystallized after 70 ps	–
$(Mg_{0.125}, Ca_{0.875})O$	3456	2750	Melted after 70 ps	–
	3456	2720	S + L (More than 1500 ps)[*6]	Mg → Liquid
	8192	2720	S + L (More than 1000 ps)	Mg → Liquid
	3456	2700	Crystallized after 140 ps	Mg → Liquid?
	3456	2500	Crystallized after 20 ps	–
$(Na_{0.875}, K_{0.125})Cl$	3456	1000	Melted after 40 ps	–
	3456	960	Melted after 680 ps	–
	3456	950	Crystallized after 920 ps	K → Liquid
	3456	940	Crystallized after 480 ps	–
	3456	930	Crystallized after 170 ps	–
	3456	900	Crystallized after 110 ps	–
$(Na_{0.125}, K_{0.875})Cl$	3456	1050	Melted after 60 ps	–
	3456	1020	Melted after 150 ps	–
	3456	1010	S + L (More than 1200 ps)	Na → Liquid
	3456	1005	Crystallized after 350 ps	–
	3456	1000	Crystallized after 320 ps	–
	3456	950	Crystallized after 80 ps	–
	3456	900	Crystallized after 50 ps	–

[*1] Total number of particles in the basic cell.
[*2] The system has completely melted after the calculation of 100 ps ($= 50 \times 10^3$ steps).
[*3] No differentiation of cations between solid and liquid was observed.
[*4] The system has completely crystallized after the calculation of 450 ps ($= 225 \times 10^3$ steps).
[*5] Ca ions have concentrated in the liquid.
[*6] The solid-liquid interface has been maintained for more than 1500 ps ($= 750 \times 10^3$ steps).

spread, resulting in total melting. At low temperatures, on the other hand, the solid part was observed to spread, resulting in total crystallization. Under intermediate temperatures, the solid-liquid interface was maintained for a long period of time, more than 400 ps ($= 200 \times 10^3$ steps). An example of density change during calculation is shown in Figure 3. In this case for $(Mg_{0.875}, Ca_{0.125})O$ ($N = 3456$, $T = 2400$ K), complete crystallization occurred after the calculation of about 460 ps ($= 230 \times 10^3$ steps). Two snapshots for this calculation are shown in Figures 4 ($t = 440$ ps) and 5 ($t = 450$ ps).

3.2. Concentration of "Minor Elements" in Liquid

In most of the calculations where solid-liquid interface could be maintained for more than 400 ps, differentiation of elements between solid and liquid was observed as follows:

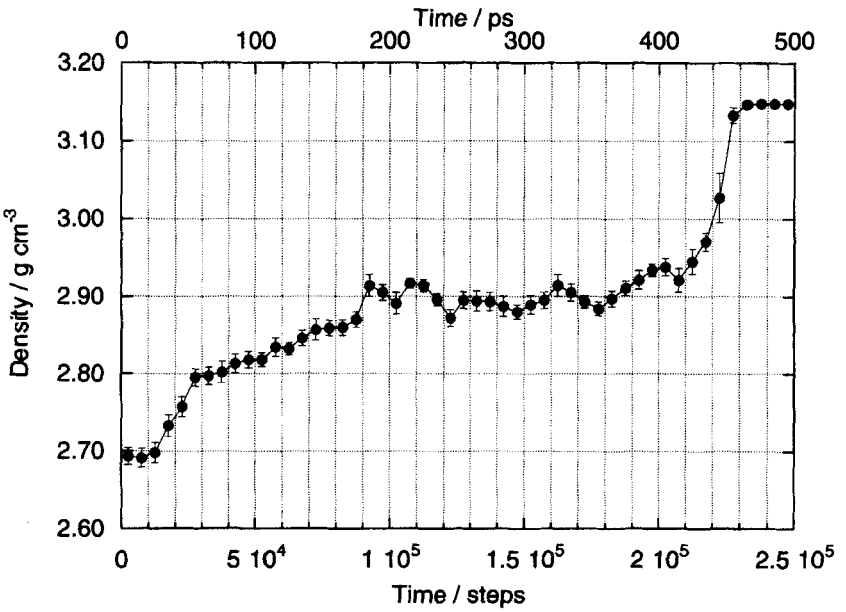

FIGURE 3 Time dependence of density for the calculation of $(Mg_{0.875}, Ca_{0.125})O$ ($N = 3456$, $P = 0.1$ MPa, $T = 2400$ K). The increase and decrease of density during the calculation is reflected by crystallization and melting, respectively. After the calculation of about 460 ps ($= 230 \times 10^3$ steps), the system crystallized completely.

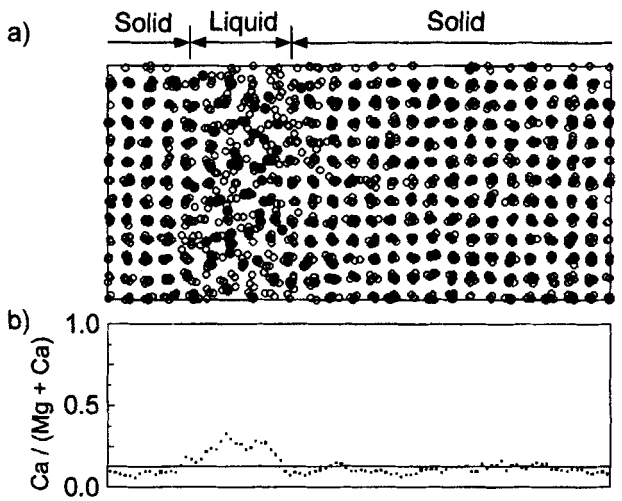

FIGURE 4 The distribution of cations in the system $(Mg_{0.875}, Ca_{0.125})O$ ($N = 3456$) after the calculation of 440 ps ($= 220 \times 10^3$ steps) at $P = 0.1$ MPa, $T = 2400$ K. (**a**) Configuration of Ca (large solid circles) and Mg (small open circles). (**b**) Concentration of Ca in the cell. The ratio of Ca/(Mg + Ca) in liquid is almost 0.25, which is twice the initial value, Ca/(Mg + Ca) = 0.125.

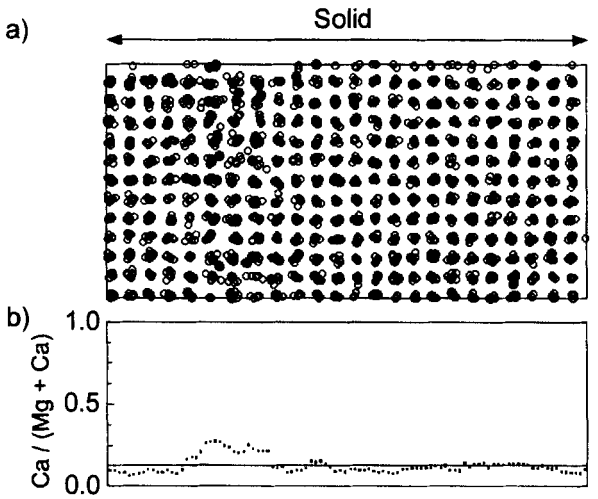

FIGURE 5 The distribution of cations in the system $(Mg_{0.875}, Ca_{0.125})O$ ($N = 3456$) after the calculation of 450 ps ($= 225 \times 10^3$ steps) at $P = 0.1$ MPa, $T = 2400$ K. (**a**) Configuration of Ca (large solid circles) and Mg (small open circles). (**b**) Concentration of Ca in the cell. The system has almost completely crystallized. There is a portion enriched with Ca, as a relic of residual liquid shown in Figure 4.

(1) Mg-rich Composition ($Mg_{0.875}$, $Ca_{0.125}$)O

Ca ions have concentrated in liquid in the calculations at 2400 K, as is shown in Figures 4 ($N = 3456$) and 6 ($N = 8192$). The ratio of Ca/(Mg + Ca) in these liquids is about 0.25, which is twice the initial value, Ca/(Mg + Ca) = 0.125.

(2) Ca-rich Composition ($Mg_{0.125}$, $Ca_{0.875}$)O

Mg ions have concentrated in liquid in the calculations at 2720 K. An example of the distribution of cations is shown in Figure 7 ($N = 8192$). The ratio of Mg/(Mg + Ca) in the liquid is about 0.25, which is twice the initial value, Mg/(Mg + Ca) = 0.125.

(3) Na-rich Composition ($Na_{0.875}$, $K_{0.125}$)Cl

K ions have concentrated in liquid at 950 K, as is shown in Figure 8. The ratio of K/(Na + K) in the liquid is about 0.2, which is higher than the initial value, K/(Na + K) = 0.125.

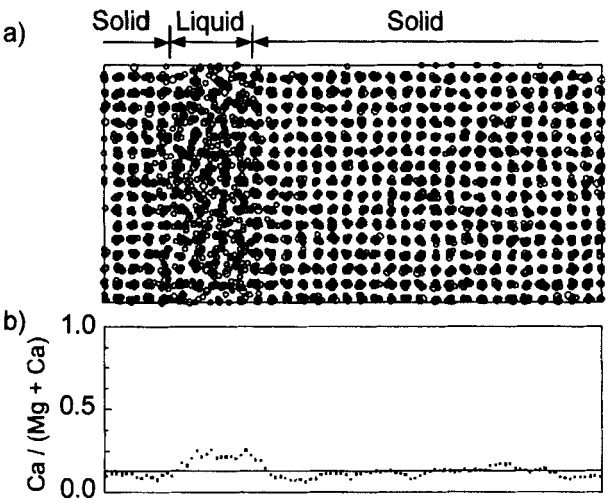

FIGURE 6 The distribution of cations in the system $(Mg_{0.875}, Ca_{0.125})O$ ($N = 8192$) after the calculation of 430 ps ($= 215 \times 10^3$ steps) at $P = 0.1$ MPa, $T = 2400$ K. (**a**) Configuration of Ca (large solid circles) and Mg (small open circles). (**b**) Concentration of Ca in the cell. As a result of a larger number of particles, the scattering of the profile is smaller than the case $N = 3456$ (Fig. 4).

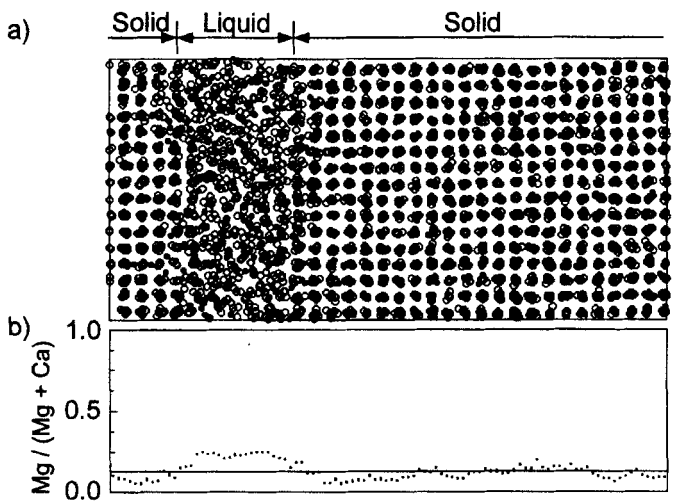

FIGURE 7 The distribution of cations in the system $(Mg_{0.125}, Ca_{0.875})O$ ($N = 8192$) after the calculation of 1000 ps ($= 500 \times 10^3$ steps) at $P = 0.1$ MPa, $T = 2720$ K. (**a**) Configuration of Mg (small solid circles) and Ca (large open circles). (**b**) Concentration of Mg in the cell. The ratio of Mg/(Mg + Ca) in liquid is almost 0.25, which is twice the initial value, Mg/(Mg + Ca) = 0.125.

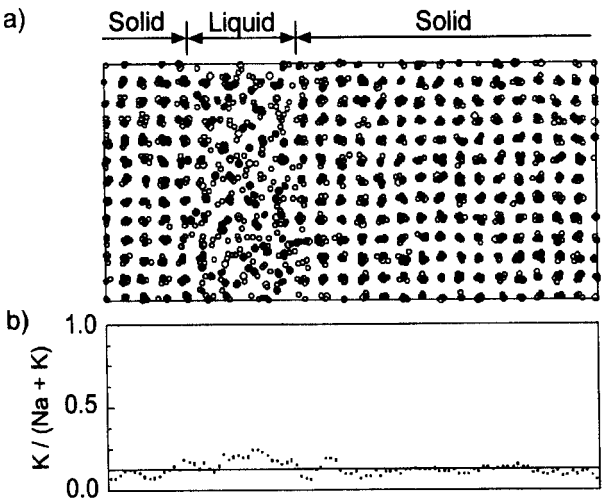

FIGURE 8 The distribution of cations in the system $(Na_{0.875}, K_{0.125})Cl$ ($N = 3456$) after the calculation of 900 ps ($= 450 \times 10^3$ steps) at $P = 0.1$ MPa, $T = 950$ K. (**a**) Configuration of K (large solid circles) and Na (small open circles). (**b**) Concentration of K in the cell. The ratio of K/(Na + K) in liquid is almost 0.2, which is higher than the initial value, K/(Na + K) = 0.125.

(4) K-rich Composition $(Na_{0.125}, K_{0.875})Cl$

Small concentration of Na ions in liquid was observed at 1010 K, as is shown in Figure 9. The ratio of Na/(Na + K) in the liquid is a little higher than the initial value, Na/(Na + K) = 0.125.

Namely, the concentration of the "minor element" in the liquid was observed in each composition, if the solid-liquid interface was maintained for a long period of time. This concentration is consistent with the expectation based on the shape of phase diagrams [*e.g.*, 7, 9] (see Chapter 1).

In the calculations of (1) and (3), compositional heterogeneity induced by the differentiation was preserved even when total crystallization occurred. There is a portion enriched with the minor element, as a relic of residual liquid (see Fig. 5).

4. DISCUSSION

In this study, we have succeeded in causing differentiation of elements between solid and liquid in an MD basic cell, in spite of restricted number of the particles N (= 3456 and 8192). The "minor elements" were swept out into liquid during the growth of crystal lattice, because of the mismatch of

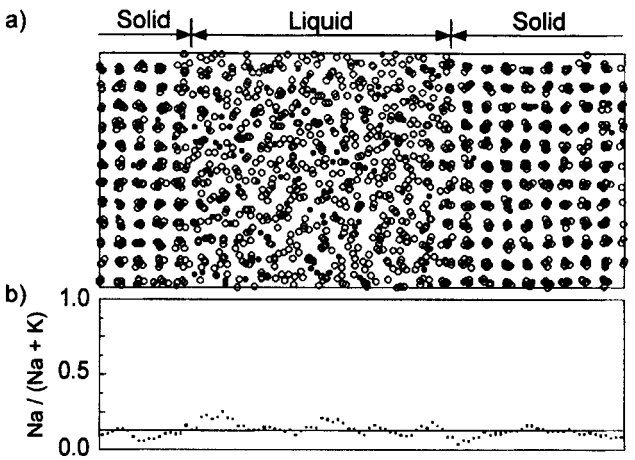

FIGURE 9 The distribution of cations in the system $(Na_{0.125}, K_{0.875})Cl$ ($N = 3456$) after the calculation of 1200 ps ($= 600 \times 10^3$ steps) at $P = 0.1$ MPa, $T = 1010$ K. (**a**) Configuration of Na (small solid circles) and K (large open circles). (**b**) Concentration of Na in the cell. The average of the ratio Na/(Na + K) in liquid is a little higher than the initial value, Na/(Na + K) = 0.125.

cationic size, which was reflected in the shape of the potential curve for cation-anion bond (Fig. 1). The increase and decrease of density during the calculation (Fig. 3) imply positional fluctuation of solid-liquid interface. This fluctuation caused the effective differentiation of cations between solid and liquid.

When we compare the profiles of Ca/(Mg + Ca) in Figures 4 ($N = 3456$) and 6 ($N = 8192$), it is clear that the larger number of particles in the cell reduces the scattering of data points. However, the nature of these profiles is the same: concentration of "minor elements" into liquid. This may suggests that the particle number $N = 3456$ is enough for the calculation intended to see the differentiation of elements between NaCl-type crystal and its melt.

It was easier to cause the cationic differentiation in MgO-CaO system than in NaCl-KCl system. In the calculations of MgO-CaO system, the ratio of Ca/(Mg + Ca) or Mg/(Mg + Ca) in liquid could reach to 0.25, which is twice the original value 0.125. However, in the calculations of NaCl-KCl system, neither the ratio of K/(Na + K) nor Na/(Na + K) in liquid could come up to that value. Further, in the calculation of $(Na_{0.875}, K_{0.125})Cl$ at 940 K, no differentiation could be observed although the solid-liquid interface was maintained for a long period of time, 480 ps (Tab. II). This difference between MgO-CaO and NaCl-KCl systems is consistent with the shape of phase diagrams: The distance between solidus and liquidus curves

of MgO-CaO system is larger than that of NaCl-KCl system [*e.g.*, 7, 9]. It is therefore expected that the magnitude of the differentiation in MgO-CaO system should be larger than that in NaCl-KCl system. In microscopic view, the slope of the potential curves for (Mg, Ca)O is larger than that for (Na, K)Cl, which indicates larger cation-anion interaction (Fig. 1). The strain energy induced from the variation of cation-anion bond length in (Mg, Ca)O solid solution should be larger than that in (Na, K)Cl. This may cause the greater differentiation in MgO-CaO system.

The distance x of ionic diffusion in a crystal is approximated by $x = (D \cdot t)^{1/2}$, where D is the diffusion coefficient, and t the duration time. The magnitude of diffusion coefficient of Mg in MgO and Na in NaCl around melting temperature are in the order of $10^{-7} \sim 10^{-8}\,\mathrm{cm^2\,s^{-1}}$ [13] and $10^{-8}\,\mathrm{cm^2\,s^{-1}}$ [14], respectively. If we use the value $D = 10^{-7}\,\mathrm{cm^2\,s^{-1}}$, the distance of ionic diffusion during the calculation of 1000 ps is evaluated to be $(10^{-7} \times 10^{-9})^{1/2} = 10^{-8}\,\mathrm{cm} = 1\,\text{Å}$, which is much smaller than the dimension length of MD cell ($\sim 30\,\text{Å}$ for the system $N = 1728$). It is clear that we can not expect the equilibration of the distribution of elements in the crystal during the calculation of 1000 ps. However, we could show the direction of the change of cationic partitioning between solid and liquid in an MD cell, through our simulation. If we use the crystal with very high concentration of point defects, faster diffusion of cations and the equilibration of distribution may be realized.

Acknowledgments

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