Pergamon

Available online at www.sciencedirect.com
SCIENCE DIRECT®

Cement and Concrete Research 33 (2003) 1771–1775

CEMENT AND CONCRETE RESEARCH

Cationic substitution in tricalcium aluminate

Koichiro Fukuda[a],*, Shinji Inoue[a], Hideto Yoshida[b]

[a]*Department of Materials Science and Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan*
[b]*Department of Earth and Planetary Science, Graduate School of Science, University of Tokyo, Tokyo 113-0033, Japan*

Received 23 January 2003; accepted 5 May 2003

Abstract

Cubic and orthorhombic crystals of tricalcium aluminate doped with Na_2O, Fe_2O_3 and SiO_2 were prepared and examined using an electron probe microanalyzer. The cationic ratios based on six oxygen atoms were derived from the oxide compositions. These data, together with those in previous studies for clinker aluminates containing Mg^{2+} and K^+, provided excellent correlations between Al + Fe and Si (Al + Fe = 2.001 − 1.03Si) and Ca + Mg and Na + K + Si [Ca + Mg = 3.006 − 0.51(Na + K + Si)]. The chemical variation that is constrained by these equations is well accounted for by the general formula $(Na,K)_{2x}(Ca,Mg)_{3-x-y}[(Al,Fe)_{1-y}Si_y]_2O_6$, where x is the amount of Ca substituted by Na and K ($0 \leq x < 0.158$), and y is the amount of Al substituted by Si ($0 \leq y < 0.136$). The crystal system changed from cubic to orthorhombic with increasing x value. The substitution of Si and Fe for Al extended the solid solution range of the orthorhombic phase to lower values of x, while its effect on the solid solution range of the cubic phase was reversed.

Keywords: $Ca_3Al_2O_6$; Microstructure; EPMA, electron probe microanalysis; Cationic substitution

1. Introduction

Tricalcium aluminate ($Ca_3Al_2O_6$) in normal Portland cement clinkers is generally modified in chemical composition by cationic substitutions. Among the major substituent ions such as Na^+, Si^{4+}, Fe^{3+}, K^+ and Mg^{2+}, their replacement effects for the first three ions have been most extensively studied [1–7]. Structural refinements have been done for a series of $Na_{2x}Ca_{3-x}Al_2O_6$ crystals with $0 \leq x \leq 0.25$ [6]. A prominent feature of the structures is the rings of the six AlO_4 tetrahedral surrounding holes [8]. The replacement of Ca^{2+} by Na^+ is accompanied by the occupation of the second Na^+ in the centers of the rings. With increasing x value, the crystal system changed from cubic ($0 \leq x \leq 0.10$) to orthorhombic ($0.16 \leq x \leq 0.20$) and then to monoclinic ($0.20 \leq x \leq 0.25$) [6].

In our preceding paper [9], a general formula was developed for the crystals doped with Na and Si as follows:

$$Na_{2x}Ca_{3-x-y}(Al_{1-y}Si_y)_2O_6 \tag{1}$$

where x is the amount of Ca substituted by Na, and y is the amount of Al substituted by Si. The atomic ratios on the basis of the six oxygen atoms are $2x$ for Na, $3 - x - y$ for Ca, $2 - 2y$ for Al and $2y$ for Si, which lead to the following equations:

$$Al = 2 - Si. \tag{2}$$

$$Ca = 3 - 0.5(Na + Si) \tag{3}$$

These two equations have nicely accounted for the chemical variation in the actual solid solutions.

Terrier and Hornain [10] have described a replacement scheme in which Al^{3+} in tricalcium aluminate is substituted for both Si^{4+} and Fe^{3+}. The replacement of Al^{3+} by Si^{4+} most probably leads to the removal of Ca^{2+} to maintain the charge balance; vacancies are formed in the Ca sites. Thus, the substitution reaction leads to the general formula

$$Ca_{3-z}[(Al, Fe)_{1-z}Si_z]_2O_6 \tag{4}$$

where z is the amount of Al substituted by Si. The atomic ratios based on the six oxygen atoms give the following equation:

$$Al + Fe = 2 - Si. \tag{5}$$

This equation is equivalent to Eq. (2) provided that the crystals are iron-free.

---

* Corresponding author. Tel.: +81-52-735-5289; fax: +81-52-735-5289.

E-mail address: fukuda@mse.nitech.ac.jp (K. Fukuda).

0008-8846/$ – see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0008-8846(03)00172-8

Table 1
Preparation of raw mixtures for calcium aluminate solid solutions

Reagent	Bulk composition (mass%)			
	A	B	C	D
SiO_2	3.34	3.44	3.49	3.34
Fe_2O_3	5.72	5.89	5.98	5.72
Al_2O_3	16.29	16.77	17.02	16.29
$NaHCO_3$	1.81	3.73	4.73	7.25
$CaCO_3$	72.83	70.18	68.79	67.40
Total	100	100	100	100

Substance	Bulk composition (mass%)[a]			
SiO_2	5.00	10.00	12.50	10.00
Fe_2O_3	8.56	8.00	7.74	7.19
Al_2O_3	24.38	22.83	22.05	22.31
Na_2O	1.00	2.00	2.50	4.00
CaO	61.06	57.17	55.21	56.50
Total	100	100	100	100

[a] Recalculated for nonvolatile components.

The present study deals with the substitution of Na^+, K^+, Mg^{2+}, Fe^{3+} and Si^{4+} in tricalcium aluminate. The general formula (Eq. (1)) has been modified so that it may be applicable to the wide range of chemical variations in the solid solutions.

2. Experimental

2.1. Materials

Crystals of tricalcium aluminate doped with Na_2O, Fe_2O_3 and SiO_2 were prepared from the mixtures of the chemical reagents A, B, C and D (Table 1). Each raw mixture was, after calcination at 1473 K for 20 min, ground in the agate container of a planetary micromill (Model P6, Fritsch, Idar-Oberstein, Germany) for 25 min and pressed into pellets (12-mm diameter and 3-mm thick). They were heated at 1673 K for 30 min, cooled to 1523 K at 2 K/min then quenched in air. During the slow cooling, the crystals developed in the presence of a liquid phase. These samples, prepared from the mixtures A, B, C and D, are designated by S-A, S-B, S-C and S-D, respectively, in the order of increasing Na_2O content.

2.2. Characterization

Polished thin sections were prepared for all the samples and the microtextures were observed with both transmitted and reflected light. Examination in transmitted light allowed the detection of any small inclusions within the crystals of the tricalcium aluminate solid solutions. This has enabled accurate spot analyses using an electron probe microanalyzer (EPMA) (Model JCMA-733, JEOL, Tokyo, Japan) on the crystals free from inclusions (accelerating voltage, 15 kV; specimen current, 0.012 μA; electron probe diameter, 1 μm). The correction was made by the ZAF routines. The phase constitution was examined by powder X-ray diffractometry (XRD) (Model X'pert, PANalytical, Almelo, The Netherlands).

3. Results and discussion

3.1. Phase constitution and chemical composition

The powder XRD patterns from the tricalcium aluminate solid solutions indicated that the crystals of S-A and S-B are cubic and those of S-D are orthorhombic. These two types of crystals are easily distinguishable using an optical microscope because the cubic crystals remain dark whatever their orientation under crossed polars. With S-C, both the cubic and orthorhombic crystals coexist (Fig. 1). The lath-shaped crystals are orthorhombic, some of which are separated by the cubic crystals. This indicates that the latter crystallized in preference to the former during slow cooling from 1673 K to 1523 K. During subsequent quenching, the intercrystalline liquid crystallized in very small plates, mainly composed of calcium aluminoferrite.

Based on the oxide compositions of the tricalcium aluminate solid solutions determined by EPMA (Table 2), the atomic ratios have been derived on the basis of six oxygen atoms in one formula unit (Table 3). The sum total of the Al, Fe and Si atoms becomes nearly two [10], which implies that all of the Fe and Si atoms exclusively go to the Al sites and these sites are entirely filled by these atoms. The atomic ratios of the individual crystals are plotted with Al + Fe as the ordinate and Si as the abscissa (Fig. 2A) and showed the following excellent correlation (correlation coefficient r=.994):

$$\mathrm{Al} + \mathrm{Fe} = 1.991(1) - 0.950(9)\mathrm{Si} \qquad (6)$$

where the figures in parentheses indicate standard deviations.

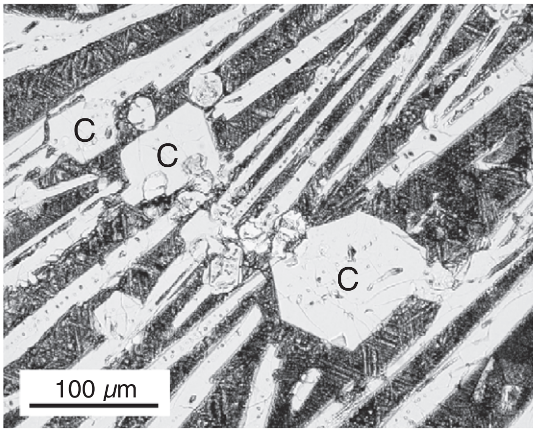

Fig. 1. Optical micrograph of S-C sample. Thin section. Transmitted light. Large transparent crystals are of the calcium aluminate solid solutions. The crystals labeled "C" are cubic, and the lath-shaped crystals are orthorhombic.

Table 2
Chemical composition of calcium aluminate solid solutions

Substance	Chemical composition (mass%)[a]				
	S-A	S-B	S-C		S-D
			Cubic	Orthorhombic	
SiO_2	2.3(1)	3.18(9)	3.8(5)	5.5(3)	4.2(3)
Fe_2O_3	2.9(4)	2.8(3)	3.4(3)	4.0(4)	3.2(4)
Al_2O_3	33.6(3)	33.2(2)	32.2(6)	30.6(6)	32.1(2)
Na_2O	1.01(7)	1.7(1)	1.5(1)	2.6(1)	3.4(1)
CaO	60.1(1)	59.2(1)	59.1(3)	57.3(2)	57.2(2)
Total	100	100	100	100	100

Figures in parentheses indicate standard deviations.

[a] Total is normalized to be 100 mass%.

The sum total of the Na and Ca atoms for S-D is greater than three (Table 3), indicating that the excess Na atoms would occupy sites in the six-membered Al_6O_{18} rings. With S-C, vacancies would be formed in the Ca sites because of $Na + Ca < 3$. For the crystals of S-A and S-B, the Ca sites are almost filled by these atoms. The atomic ratios of Ca and Na + Si are strongly correlated (Fig. 2B), in accord with a previous study [9], as follows:

$$Ca = 3.010(2) - 0.524(5)(Na + Si) \quad (r = .992) \tag{7}$$

Eqs. (6) and (7) are in fair agreement with Eqs. (5) and (3), respectively. This strongly indicates that the constrained chemical variation of the present solid solutions can be expressed by the combination of Eqs. (1) and (4) as follows:

$$Na_{2x}Ca_{3-x-y}[(Al, Fe)_{1-y}Si_y]_2O_6 \tag{8}$$

where x is the amount of Ca substituted by Na ($0 \leq x < 0.158$), and y is the amount of Al substituted by Si ($0 \leq y < 0.136$).

The crystal system changed from cubic to orthorhombic with increasing Na concentration (x value) in the solid solution (Fig. 3). The substitution of Si and Fe for Al extended the solid solution range of the orthorhombic phase to lower the values of x in agreement with a previous study [6]. On the contrary, the substitution effect on the solid solution range of the cubic phase was reversed. Between the regions where the cubic and orthorhombic phases are formed, there is a region consisting of the two-phase mixture.

Table 3
Atomic ratios of calcium aluminate solid solutions

Substance	Atomic ratio				
	S-A	S-B	S-C		S-D
			Cubic	Orthorhombic	
Si	0.106(4)	0.143(4)	0.17(2)	0.25(1)	0.19(1)
Fe	0.10(1)	0.09(1)	0.12(1)	0.14(1)	0.11(1)
Al	1.79(1)	1.76(1)	1.71(3)	1.62(3)	1.70(1)
Na	0.088(6)	0.15(1)	0.128(9)	0.222(9)	0.29(1)
Ca	2.910(7)	2.856(8)	2.85(1)	2.76(1)	2.76(1)
O	6	6	6	6	6
Si + Fe + Al	1.995(3)	1.999(5)	1.999(3)	2.004(4)	1.999(6)
Na + Ca	2.998(6)	3.01(1)	2.98(1)	2.98(1)	3.05(1)

Figures in parentheses indicate standard deviations.

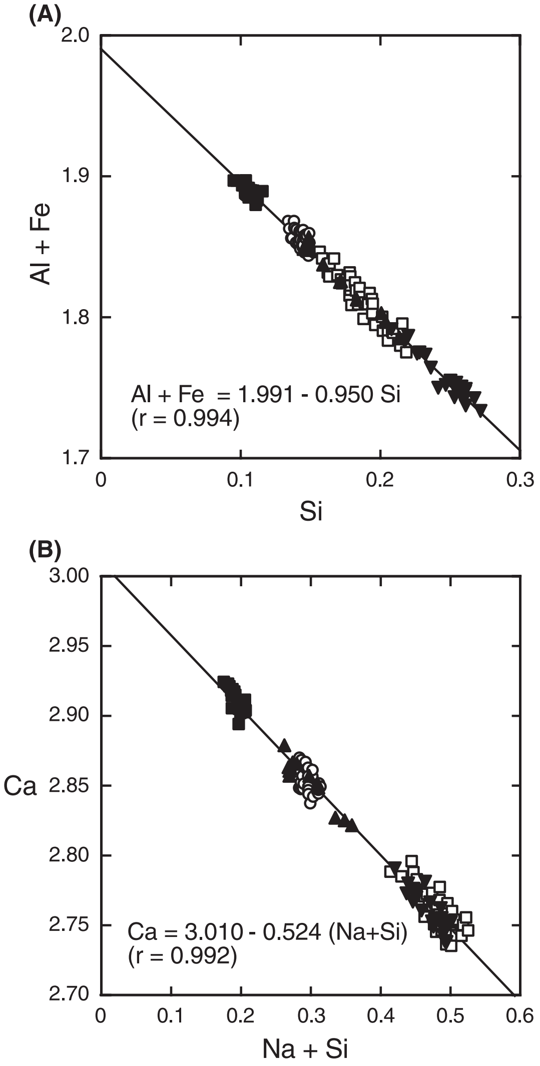

Fig. 2. Variation diagrams for (A) Al + Fe versus Si and (B) Ca versus Na + Si. Crystals of (■) S-A, (○) S-B and (□) S-D. Crystals of S-C in (▲) the cubic system and (▼) the orthorhombic system. The linear fit suggests Al + Fe = 2 − Si in (A) and Ca = 3 − 0.5(Na + Si) in (B).

3.2. General formula for tricalcium aluminate in Portland cement clinkers

In Portland cement clinkers, the crystals of the tricalcium aluminates generally contain K^+ and Mg^{2+} as substituent ions in addition to Na^+, Fe^{3+} and Si^{4+}. Thus, it is necessary to modify Eq. (8) when describing the chemical variation of the clinker aluminates. The replacement mechanism of Ca^{2+} by K^+ would be very similar to that of Ca^{2+} by Na^+ [4], and the substitution of Ca^{2+} by Mg^{2+} would simply occur within the limit of replacement. As a result, the chemical formula of the tricalcium aluminate doped with all of those ions is most probably given as

$$(\mathrm{Na,K})_{2x}(\mathrm{Ca,Mg})_{3-x-y}[(\mathrm{Al,Fe})_{1-y}\mathrm{Si}_y]_2\mathrm{O}_6 \qquad (9)$$

where x is the amount of Ca substituted by Na and K, and y is the amount of Al substituted by Si. This formula leads to Eq. (5) and the following equation:

$$\mathrm{Ca} + \mathrm{Mg} = 3 - 0.5[\mathrm{Na} + \mathrm{K} + \mathrm{Si}] \qquad (10)$$

As pointed out by Hall and Scrivener [11], the aluminate microanalysis in previous studies may be subject to some errors arising from contamination by other phases. In the preset study, Eq. (5) has been confirmed to hold for the tricalcium aluminate doped with Fe_2O_3 and SiO_2. Thus, we have employed it as a criterion for the reliable analyses. The EPMA data that satisfy this requirement were selected from those in previous studies [9–14] and plotted with Al + Fe as the ordinate and Si as the abscissa (Fig. 4A). A linear regression of these atomic ratios is derived as follows:

$$\mathrm{Al} + \mathrm{Fe} = 2.001(4) - 1.03(2)\mathrm{Si} \quad (r = .995) \qquad (11)$$

We then plotted these data with Ca + Mg as the ordinate and Na + K + Si as the abscissa (Fig. 4B) to find a strong correlation between them.

$$\mathrm{Ca} + \mathrm{Mg} = 3.006(4) - 0.51(1)\ [\mathrm{Na} + \mathrm{K} + \mathrm{Si}] \quad (r = .994) \qquad (12)$$

The excellent agreements between Eqs. (10) and (12) as well as Eqs. (5) and (11) justify the validity of the general Eq. (9).

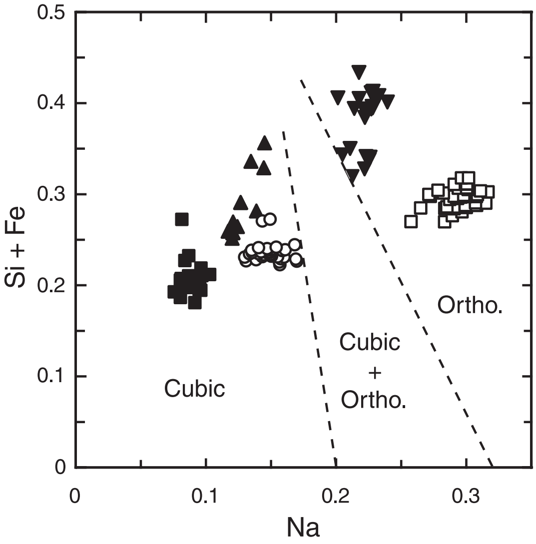

Fig. 3. Si + Fe versus Na variation diagram. Crystals of (■) S-A, (○) S-B and (□) S-D. Crystals of S-C in (▲) the cubic system and (▼) the orthorhombic system. Crystals of $Na_{2x}Ca_{3-x}Al_2O_6$ with $0 \le x \le 0.10$ ($0 \le \mathrm{Na} \le 0.20$) are cubic and those with $0.16 \le x \le 0.20$ ($0.32 \le \mathrm{Na} \le 0.40$) are orthorhombic [6].

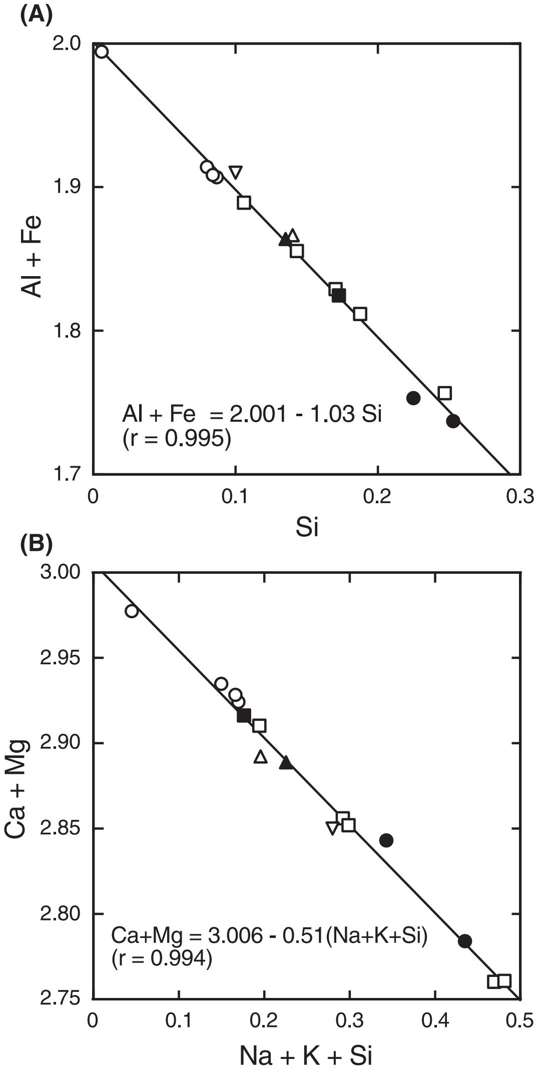

Fig. 4. Variation diagrams for (A) Al + Fe versus Si and (B) Ca + Mg versus Na + K + Si. Different marks denote different references (○ [9], ■ [10], ● [11], ▽ [12], △ [13] and ▲ [14]). (□) Average values for the present study. The data plotted in (A) are those regarded as satisfying equation Al + Fe = 2 − Si. The linear fit in (B) suggests Ca + Mg = 3 − 0.5(Na + K + Si).

How the substitutions of Ca by Mg and that of Al by Fe influence the values of x and y in Eq. (9) is a future subject. The reliable microanalysis of various tricalcium aluminate solid solutions, including clinker aluminates, would enhance our understanding of the extent to which the formula is applicable.

4. Conclusions

(1) The chemical formula of the tricalcium aluminate doped with Na_2O, Fe_2O_3 and SiO_2 was determined as $Na_{2x}Ca_{3-x-y}[(Al,Fe)_{1-y}Si_y]_2O_6$, where x is the amount of Ca substituted by Na ($0 \le x < 0.158$), and y is the amount of Al substituted by Si ($0 \le y < 0.136$).

(2) The crystal system changed from cubic to orthorhombic with increasing x value. The substitution of Si and Fe for Al extended the solid solution range of the orthorhombic phase to lower values of x, while its effect on the solid solution range of the cubic phase was reversed.

(3) A modified general formula, $(Na,K)_{2x}(Ca,Mg)_{3-x-y}[(Al,Fe)_{1-y}Si_y]_2O_6$, has been proposed, which may be applicable to a wide range of chemical variations in solid solutions.

Acknowledgements

Supported by a Grant-in-Aid for Scientific Research (No. 14550799) from the Japan Society for the Promotion of Science and a grant from the NITECH 21st Century COE Program for Environmental Ceramics.

References

[1] Y. Suzukawa, The alkali phases in Portland cement: III. Influence of Na_2O on the mineral composition of Portland cement, Zem.-Kalk-Gips 9 (1956) 433–436.

[2] K.E. Fletcher, H.G. Midgley, A.E. Moore, The binary system $3CaO\cdot Al_2O_3$-$Na_2O\cdot 8CaO\cdot 3Al_2O_3$ within the system CaO-Al_2O_3-Na_2O, Mag. Concr. Res. 17 (1965) 171–176.

[3] M. Regourd, S. Chromy, L. Hjorth, B. Mortureux, A. Guinier, Polymorphism of solid solutions of sodium oxide in tricalcium aluminate, J. Appl. Crystallogr. 6 (1973) 355–364.

[4] I. Maki, Nature of the prismatic dark interstitial material in Portland cement clinker, Cem. Concr. Res. 3 (1973) 295–313.

[5] M. Regourd, A. Guinier, Crystal chemistry of the components of Portland cement clinker, Proceedings of 6th International Congress on the Chemistry of Cement, Moscow, USSR, 1974, vol. 1, Stroiizdat, Moscow, USSR, 1976, pp. 25–51.

[6] Y. Takeuchi, F. Nishi, I. Maki, Crystal–chemical characterization of the $3CaO\cdot Al_2O_3$-Na_2O solid-solution series, Z. Kristallogr. 152 (1980) 259–307.

[7] F.C. Lee, H.M. Banda, F.P. Glasser, Substitution of Na, Fe and Si in tricalcium aluminate and the polymorphism of solid solutions, Cem. Concr. Res. 12 (1982) 237–246.

[8] P. Mondal, J.W. Jeffery, The crystal structure of tricalcium aluminate, $Ca_3Al_2O_6$, Acta Crystallogr. B31 (1975) 689–697.

[9] K. Fukuda, S. Inoue, H. Yoshida, Substitution of sodium and silicon in tricalcium aluminate, J. Am. Ceram. Soc. 86 (1) (2003) 112–114.

[10] P. Terrier, H. Hornain, Composition of tricalcium aluminate (in French), Rev. Mater. Constr. Trav. Publics 666 (1971) 60–64.

[11] C. Hall, K. Scrivener, Oilwell cement clinkers, Adv. Cem. Based Mater. 7 (1998) 28–38.

[12] K.E. Fletcher, The composition of the tricalcium aluminate and ferrite phases in Portland cement determined by the use of an electron-probe microanalyser, Mag. Concr. Res. 21 (66) (1969) 3–14.

[13] M. Kristmann, Portland cement clinker mineralogical and chemical investigations, Cem. Concr. Res. 8 (1978) 93–102.

[14] K. Fukuda, A. Takeda, A. Yamaguchi, S. Hashimoto, H. Yoshida, Characterization of liquid exsolved by remelting reaction of belite, J. Am. Ceram. Soc. 84 (5) (2001) 1155–1160.