

Investigation of The Relationship between Groups and Subgroups in C3S's Structure Transition

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Abstract: In recent years, many studies have been carried out on cement and its phase's to understand the morphology, and to control the mineralogy of this material; due to the great position it has become globally occupied. This material is formed from a synthetic rock called clinker; tricalcium silicate (Ca_3SiO_5 or C3S) its major constituent present a concentration from 40% to 70%, and its solid solution with various impurities is called alite. Impure C3S exhibits seven polymorphs from ambient temperature to 1500°C; three forms triclinic (T1, T2, T3), three monoclinic (M1, M2, M3) and one shape rhombohedral (R). At room temperature, impurities stabilize some of the high temperature forms of the pure compound. Those forms are related by transformation matrix determined in this article. The aim of the present paper is to investigate the structural modulations of alite.

Key words: Cement, clinker Portland, Polymorph, crystal structure, alite, space group, sub-group, matrix and coordinates system.

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I. Introduction

Alite is the most important phase in cement Portland, it forms 60 to 70% of clinker Portland, and it is a solid solution of C3S, modified by substitution or insertion of foreign ions in its crystal structure. In a high temperature, the thermal agitation factor of atomic position will increase and with the effect of atomic interaction, some atoms leave their position, and let a hole, which will be occupied by another atom came from impurities which has the same size of the lifted one; those substitution and/or insertion may be the key of structure transitions. In kiln, using a combination of differential thermal analysis (ATD), optic microscopy and X-ray diffraction (XRD), several transformations were observed of alite polymorphism [1].



It is usually found in clinkers in a monoclinic form (M1, M3 or a mixture of both), and rarely in T2 shape [2]. Among those structures, just 4 polymorphs have a structural model, which are T1, T2, M3 and R; Recently De Noirfontaine has presented M1 form based on group and sub-group relationship [3].

The first study of alite was done by Jeffery [4] on a single crystal, he showed that the three polymorphs T1, R and M3 have a similar structure, and he gives a pseudo one common for the true of the three forms, this structure was confirmed by O'Daniel on single crystal sample. The cell parameters with hexagonal axis ($a_H = b_H = 7\text{Å}$ & $c_H = 25\text{Å}$) and space group (R3m) were determined for the composition of alite: $54(\text{CaO}).16(\text{SiO}_2).\text{Al}_2\text{O}_3.\text{MgO}$ with $Z=9$ formulas by cell (81 atom per cell). The three structures are very close; they are different by the calcium ions and oxygen's atoms of SiO_4 tetrahedra, they are different by the disorder of orientation in tetrahedra SiO_4^{4-} .

II. Space group transformations

Nishi and Takéuchi were solved at the same way the rhombohedral R [5] and the monoclinic M3 [6] polymorphs, this M3 structure characterized by a big number of atoms (228 per cell, table 1) with different and complicated disordered orientation of SiO_4 tetrahedra. In 1995, Mumme determined the substructure of M3 polymorph, similar to that presented by Nishi with an average structure

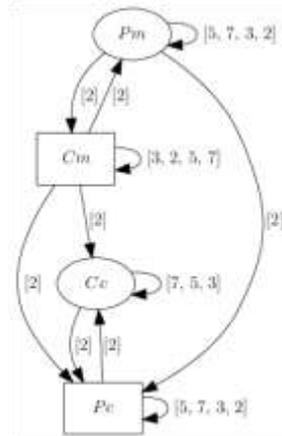


Figure 2: Monoclinic transformations

From Jeffery and Nishi model, The rhombohedral structure R3m has the multiplicity $Z=9$, so for alite (Ca_3SiO_5) we have 72 crystallographically independent sites: 18 Ca atoms all in general position [site $3 \times 9b$]; 9 Si atoms in special position SP (00z) [site of $3 \times 3a$]; and 45 Oxygen atoms: 6 in special position (00z) [site $6 \times 3a$] and 3 in general position [$3 \times 9b$] (Figure 4).

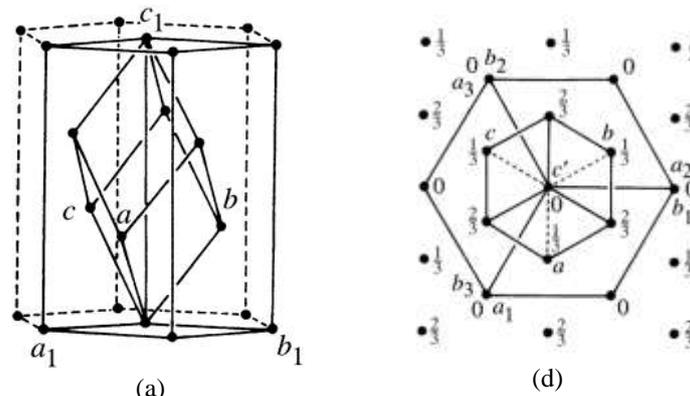


Fig. 3.1.3.6 Unit cells in the rhombohedral lattice; same origin for all cells. The basis of the rhombohedral cell is labeled a, b, c . Two settings of the triple hexagonal cell are possible with respect to a primitive rhombohedral cell. The obverse setting with the lattice points $0, 0, 0; \frac{1}{3}, \frac{1}{3}, \frac{1}{3}; \frac{2}{3}, \frac{2}{3}, \frac{2}{3}; 1, 1, 1$ has been used in International Tables since 1952. Its general reflection condition is $-h + k + l = 3n$. The reverse setting with lattice points $0, 0, 0; \frac{1}{3}, \frac{2}{3}, \frac{2}{3}; \frac{2}{3}, \frac{1}{3}, \frac{1}{3}; 1, 1, 1$ was used in the 1935 edition. Its general reflection condition is $h - k + l = 3n$. (a) Obverse setting of triple hexagonal cell a_1, b_1, c_1 in relation to the primitive rhombohedral cell a, b, c . (b) Reverse setting of triple hexagonal cell a_1, b_1, c_1 in relation to the primitive rhombohedral cell a, b, c . (c) Primitive rhombohedral cell a, b, c in relation to the three triple hexagonal cells in obverse setting $a_1, b_1, c_1; a_2, b_2, c_2; a_3, b_3, c_3$. Projection along c' . (d) Primitive rhombohedral cell a, b, c in relation to the three triple hexagonal cells in reverse setting $a_1, b_1, c_1; a_2, b_2, c_2; a_3, b_3, c_3$. Projection along c' .

Figure 3: Rhombohedral Hexagonal transformation in ITC [12]

2.2 Rhombohedral-monoclinic transformation

There are two main considered transformations in phase transition and group-subgroup relationship, Transformation of the coordinate system and symmetry operations. The matrix of transformation is written as follow:

$$\begin{bmatrix} a' & b' & c' \end{bmatrix}_R = \begin{bmatrix} a & b & c \end{bmatrix} \times P \quad (1)$$

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix}_R = P^{-1} \times \begin{bmatrix} x \\ y \\ z \end{bmatrix} \quad (2)$$

To study the transformation from R3m to Cm, we have first to change the basis of rhombohedral system to hexagonal axis to facilitate the calculation. According to figure 3 and figure 5a, the transformation can be written as:

$$a_R = \frac{2}{3}a_H + \frac{1}{3}b_H + \frac{1}{3}c_H$$

$$b_R = \frac{-1}{3}a_H + \frac{1}{3}b_H + \frac{1}{3}c_H$$

$$c_R = \frac{-1}{3}a_H - \frac{2}{3}b_H + \frac{1}{3}c_H$$

$$[a \ b \ c]_R = [a \ b \ c]_H \times P \quad (3)$$

$$[a \ b \ c]_R = [a \ b \ c]_H \times \begin{bmatrix} \frac{2}{3} & \frac{-1}{3} & \frac{-1}{3} \\ \frac{1}{3} & \frac{1}{3} & \frac{-2}{3} \\ \frac{1}{3} & \frac{1}{3} & \frac{1}{3} \end{bmatrix}$$

With

$$P = \begin{bmatrix} \frac{2}{3} & \frac{-1}{3} & \frac{-1}{3} \\ \frac{1}{3} & \frac{1}{3} & \frac{-2}{3} \\ \frac{1}{3} & \frac{1}{3} & \frac{1}{3} \end{bmatrix} \quad (4)$$

We can calculate even the inverse transformation Q using the identity matrix by:

$$\Rightarrow Q = P^{-1} = \begin{bmatrix} 1 & 0 & 1 \\ -1 & 1 & 1 \\ 0 & -1 & 1 \end{bmatrix} \quad (5)$$

Equations (3) and (5) give the matrix of transformation P from the old basis, where the inverse matrix Q transforms the coordinates. So we can say that after defining the matrix P of rhombohedral ----> hexagonal transformation, calculation or finding all parameters information became easier. For atomic position, we have the Equation (6) below[11]:

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix}_R = \begin{bmatrix} x \\ y \\ z \end{bmatrix}_H \times Q = \begin{bmatrix} x \\ y \\ z \end{bmatrix}_H \times \begin{bmatrix} 1 & 0 & 1 \\ -1 & 1 & 1 \\ 0 & -1 & 1 \end{bmatrix} \quad (6)$$

So based on those calculations, we can calculate or find metric unit cell (equation 3), miller indices (Equation 7) and atomic positions (equation 6), just from the matrix of transformation[11]:

$$[h \ k \ l]_R = [h \ k \ l]_H \times P$$

$$[h \ k \ l]_R = [h \ k \ l]_H \times \begin{bmatrix} \frac{2}{3} & \frac{-1}{3} & \frac{-1}{3} \\ \frac{1}{3} & \frac{1}{3} & \frac{-2}{3} \\ \frac{1}{3} & \frac{1}{3} & \frac{1}{3} \end{bmatrix} \quad (7)$$

The same as before for hexagonal-Monoclinic transformation, all matrixes are confirmed by ITC after calculated;

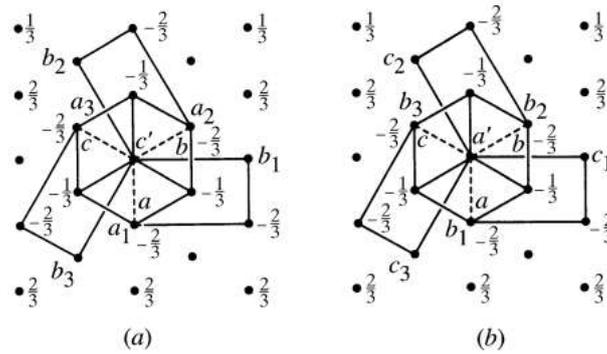


Fig. 5.1.3.10. Rhombohedral lattice with primitive rhombohedral cell a, b, c and the three centered monoclinic cells. (a) C-centered cells C_1 with a_1, b_1, c' ; C_2 with a_2, b_2, c' ; and C_3 with a_3, b_3, c' . The unique monoclinic axes are b_1, b_2 and b_3 , respectively. Origin for all four cells is the same. (b) A-centered cells A_1 with a', b_1, c_1 ; A_2 with a', b_2, c_2 ; and A_3 with a', b_3, c_3 . The unique monoclinic axes are c_1, c_2 and c_3 .

Figure 4: Rhombohedral monoclinic transformation in ITC [12]

From the figure 4 we can write:

$$\begin{aligned} a_H &= \frac{3}{2}a_M - \frac{1}{2}b_M + c_M \\ b_H &= b_M \\ c_H &= c_M \end{aligned}$$

So :

$$\begin{aligned} [a \ b \ c]_H &= [a \ b \ c]_M \times P' \\ [a \ b \ c]_H &= [a \ b \ c]_M \times \begin{bmatrix} \frac{3}{2} & 0 & 0 \\ -\frac{1}{2} & 1 & 0 \\ 1 & 0 & 1 \end{bmatrix} \end{aligned} \quad (8)$$

In this way from equation (3) and (8) we can calculate:

$$\begin{aligned} [a \ b \ c]_R &= [a \ b \ c]_H \times P = [a \ b \ c]_M \times P' \times P \\ [a \ b \ c]_R &= [a \ b \ c]_M \times \begin{bmatrix} \frac{3}{2} & 0 & 0 \\ -\frac{1}{2} & 1 & 0 \\ 1 & 0 & 1 \end{bmatrix} \times \begin{bmatrix} \frac{2}{3} & -\frac{1}{3} & -\frac{1}{3} \\ \frac{1}{3} & \frac{1}{3} & -\frac{2}{3} \\ \frac{1}{3} & \frac{1}{3} & \frac{1}{3} \end{bmatrix} \end{aligned} \quad (9)$$

These calculations give the matrix of Rhombohedra- monoclinic transformation P''.

$$[a \ b \ c]_R = [a \ b \ c]_M \times \begin{bmatrix} 1 & -\frac{1}{2} & -\frac{1}{2} \\ 0 & \frac{1}{2} & -\frac{1}{2} \\ 1 & 0 & 0 \end{bmatrix} \quad (10)$$

$$P'' = \begin{bmatrix} 1 & -1/2 & -1/2 \\ 0 & 1/2 & -1/2 \\ 1 & 0 & 0 \end{bmatrix} \Rightarrow Q'' = P''^{-1} = \begin{bmatrix} 0 & 0 & 1 \\ -1 & 1 & 1 \\ -1 & -1 & 1 \end{bmatrix} \quad (11)$$

$$\begin{bmatrix} h' & k' & l' \end{bmatrix}_R = \begin{bmatrix} h & k & l \end{bmatrix}_M \times P''$$

$$\begin{bmatrix} h' & k' & l' \end{bmatrix}_R = \begin{bmatrix} h & k & l \end{bmatrix}_M \times \begin{bmatrix} 0 & 0 & 1 \\ -1 & 1 & 1 \\ -1 & -1 & 1 \end{bmatrix} \quad (12)$$

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix}_R = \begin{bmatrix} x \\ y \\ z \end{bmatrix}_M \times Q'' = \begin{bmatrix} x \\ y \\ z \end{bmatrix}_M \times \begin{bmatrix} 0 & 0 & 1 \\ -1 & 1 & 1 \\ -1 & -1 & 1 \end{bmatrix} \quad (13)$$

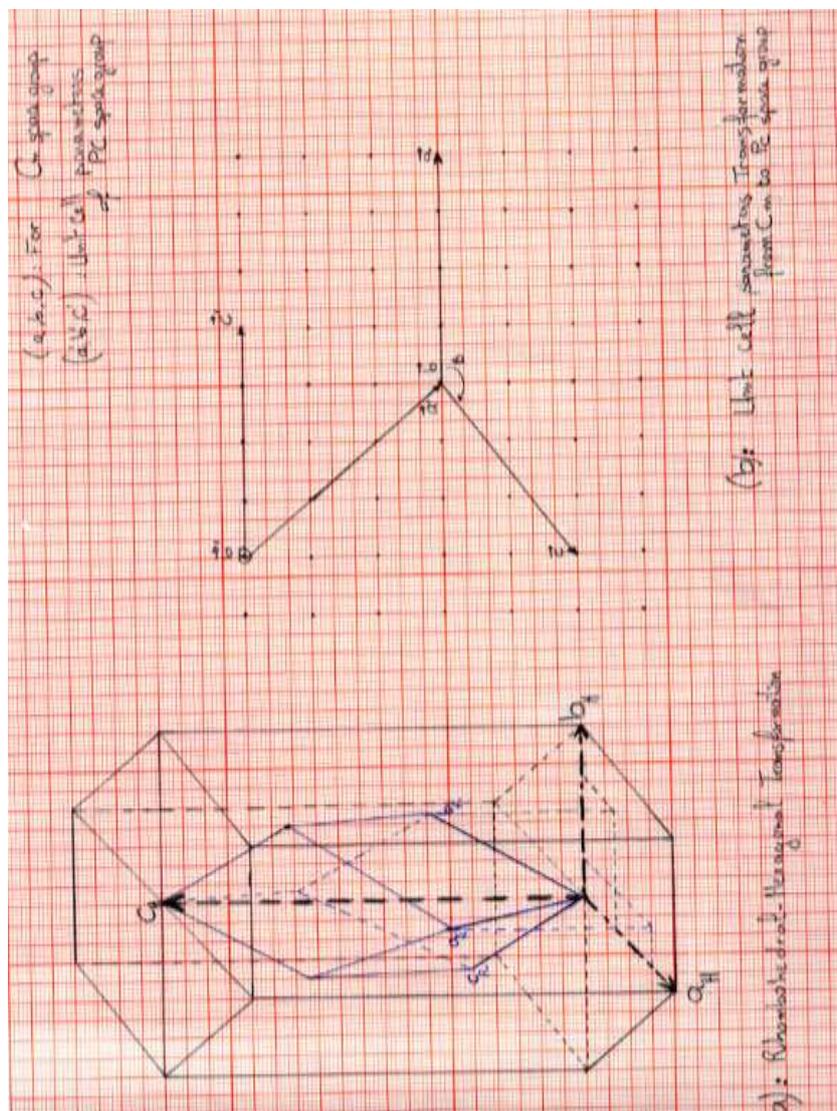


Figure 5: Unit cell parameters transformation

Those matrixes are confirmed by International Tables of Crystallography VA[12] for the choice1 in obverse setting (figure 6);

Primitive rhombohedral cell → triple hexagonal cell R_1 , obverse setting (Fig. 5.1.3.6c)	$\begin{pmatrix} 1 & 0 & 1 \\ \bar{1} & 1 & 1 \\ 0 & \bar{1} & 1 \end{pmatrix}$	$\begin{pmatrix} \frac{2}{3} & \frac{1}{3} & \frac{1}{3} \\ \frac{1}{3} & \frac{1}{3} & \frac{2}{3} \\ \frac{1}{3} & \frac{2}{3} & \frac{1}{3} \end{pmatrix}$	Rhombohedral space groups (cf. Section 4.3.5)
Triple hexagonal cell R , obverse setting → C-centred monoclinic cell, unique axis b , cell choice 1 (Fig. 5.1.3.9a) c and b axes invariant	$\begin{pmatrix} \frac{2}{3} & 0 & 0 \\ \frac{1}{3} & 1 & 0 \\ \frac{2}{3} & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \frac{2}{3} & 0 & 0 \\ \frac{1}{3} & 1 & 0 \\ 1 & 0 & 1 \end{pmatrix}$	Rhombohedral space groups (cf. Section 4.3.5)
Primitive rhombohedral cell → C-centred monoclinic cell, unique axis b , cell choice 1 (Fig. 5.1.3.10a) $[111]_r \rightarrow c_m$	$\begin{pmatrix} 0 & 0 & 1 \\ \bar{1} & 1 & 1 \\ \bar{1} & \bar{1} & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & \frac{1}{3} & \frac{1}{3} \\ 0 & \frac{1}{3} & \frac{2}{3} \\ 1 & 0 & 0 \end{pmatrix}$	Rhombohedral space groups (cf. Section 4.3.5)

Figure 6: Selected 3×3 transformation matrices P and $Q = P^{-1}$ [12]

Taking the graph below (Figure 7), the $C1m1$ is considered as non-isomorphic subgroup of $R3m$ which is a special kind of klassengleiche subgroups (subgroup belongs to the same crystal class; it has lost translation symmetry; its primitive cell larger than that of G) and belong to the same space group type (Hermann-Mauguin symbol) [12]; type “I”, it preserve the position 1 and number 4 plus those obtained by centering translation.

CONTINUED	No. 160	$R3m$
Generators selected (1); $r(1,0,0)$; $r(0,1,0)$; $r(0,0,1)$; $r(\frac{2}{3},\frac{1}{3},\frac{1}{3})$; (2); (4)		
Positions	Coordinates	Reflection conditions
Multiplicity		
Wyckoff letter	$(0,0,0)+$ $(\frac{1}{3},\frac{1}{3},\frac{1}{3})+$ $(\frac{2}{3},\frac{2}{3},\frac{2}{3})+$	General:
Site symmetry		hkl : $-h+k+l=3n$
18 c 1	(1) x,y,z (2) $\bar{y},x-\bar{y},z$ (3) $\bar{x}+y,\bar{x},z$	$hk0$: $-h+k=3n$
	(4) \bar{y},\bar{x},z (5) $\bar{x}+y,y,z$ (6) $x,x-\bar{y},z$	$h\bar{h}0$: $l=3n$
		$h00$: $h+l=3n$
		$00l$: $l=3n$
		$h\bar{h}00$: $h=3n$
		Special: no extra conditions
9 b m	x,\bar{x},z $x,2x,z$ $2\bar{x},z$	
3 a $3m$	$0,0,z$	
Symmetry of special projections		
Along $[001]$ $p31m$	Along $[100]$ $p1$	Along $[210]$ $p1m1$
$a' = \frac{1}{2}(2a+b)$ $b' = \frac{1}{2}(-a+b)$	$a' = \frac{1}{2}(a+2b)$ $b' = \frac{1}{2}(-a-2b+c)$	$a' = \frac{1}{2}b$ $b' = \frac{1}{2}c$
Origin at $0,0,z$	Origin at $x,0,0$	Origin at $x,\frac{1}{2},0$
Maximal non-isomorphic subgroups		
I	$[2]R31(R3,146)$ (1; 2; 3)+	
	$[3]R1m(Cm,8)$ (1; 4)+	
	$[3]R1m(Cm,8)$ (1; 5)+	
	$[3]R1m(Cm,8)$ (1; 6)+	
IIa	$[3]P3m1(156)$ 1; 2; 3; 4; 5; 6	
IIb	$[2]R3c(a' = -a, b' = -b, c' = 2c)(161)$	
Maximal isomorphic subgroups of lowest index		
IIc	$[2]R3m(a' = -a, b' = -b, c' = 2c)(160)$; $[4]R3m(a' = -2a, b' = -2b)(160)$	
Minimal non-isomorphic supergroups		
I	$[2]R3m(166)$; $[4]P43m(215)$; $[4]F43m(216)$; $[4]I43m(217)$	
II	$[3]P31m(a' = \frac{1}{2}(2a+b), b' = \frac{1}{2}(-a+b), c' = 4c)(157)$	

Figure 7: Rhombohedral space group in ITC [12]

2.3 Monoclinic transformation

Monoclinic system for C3S has 3 forms, M1, M2, and M3; the known structures are for M3 and M1, we will study one form which is M3 superstructure of Angeles De La Torre [8], the multiplicity is equal to 36, so it found:

M3-Ca3SiO57 → the monoclinic structural description has 155 crystallographically independent sites: 54 Calcium atoms [18 atom in special position (x0z) and 36 in general position]; 18 Silicon atoms all are in special position; and 83 Oxygen atoms [56 atoms in special position (x0z) and 27 in general positions].

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The graph thereafter (figure 8), and the figure 2, shows the relation between Cm (M3 space group) and Pc, the space group of M1 superstructure proposed by De Noirfontaine [2].

First, before talking about matrix transformation, we need to take a look on ITC for Cm space group (Figure 8):

CONTINUED	No. 8	<i>Cm</i>
Generators selected (1): $x(1,0,0)$; $y(0,1,0)$; $z(0,0,1)$; $x(\frac{1}{2}, \frac{1}{2}, 0)$; (2)		
Position:		
Multiplicity:	Coordinates	
Wyckoff letter:	(0,0,0)+ (b, b, 0)+	
Site symmetry:	(1) x, y, z (2) x, \bar{y}, z	
4 - b - 1		
Reflection conditions:		
General:		
A01 : $b + k = 2n$		
A02 : $k = 2n$		
A03 : $k = 2n$		
A04 : $b + k = 2n$		
A05 : $k = 2n$		
A06 : $k = 2n$		
Special: no extra conditions		
Symmetry of special projections:		
Along [001] $c m$ $a = a_c$ $b = b_c$ Origin at 0,0,0	Along [100] $a m$ $a = a_c$ $b = a_c$ Origin at x,0,0	Along [010] $b m$ $a = c$ $b = 2a$ Origin at 0, y, 0
Maximal non-isomorphic subgroups		
I [2] C1 (P1, 1) 1+		
II [2] P1a1 (Pc, 7) 1; 2 + (1, 1, 0)		
[2] P1m1 (Pmc, 6) 1; 2		
IIb [2] C1c1 (C' = 2C) (C', 9) [2] P1c1 (C' = 2C) (C', 9)		
Maximal isomorphic subgroups of lowest index		
IIc [2] C1m1 (C' = 2C or a' = a + 2c, C' = 2C) (Cm, 8); [3] C1m1 (B = 3b) (Cm, 8)		
Minimal non-isomorphic supergroups		
I [2] C2/m (12); [2] Cmc2 (35); [2] Cmc2, (38); [2] Amc2 (38); [2] Amc2 (39); [2] Fmc2 (42); [2] Fmc2 (44); [2] Fmc2 (46); [3] P3m1 (156); [3] P31m1 (157); [3] R3m (160)		
II [2] P1m1 (C' = 2a, B = 2b) (Pmc, 6)		

Figure 8: Monoclinic space group in ITCA [12]

The present section gives a brief summary, of the sub- and supergroup data in the space group Cm; the select subgroup P1a1 (conventional group is P1c1) has been classed in non-isomorphic subgroup of C1m1; type II which is a klassengleiche transformation or called “k subgroup”; that means that the transformation is accompanied with preserve of the same crystalline class and losing all centric translation; and the letter “a” means that C1m1 and P1c1 have the same conventional cells. We keep the positions: (x y z) and (x+1/2, -y+1/2, z) (Figure 8).

C_2^3	<i>C1m1</i>	No. 8	<i>Cm</i>
UNIQUE AXIS <i>b</i> , CELL CHOICE I			
Generators selected (1): $x(1,0,0)$; $y(0,1,0)$; $z(0,0,1)$; $x(\frac{1}{2}, \frac{1}{2}, 0)$; (2)			
General position			
Coordinates			
Multiplicities:		(0,0,0)+ $(\frac{1}{2}, \frac{1}{2}, 0)$ +	
Wyckoff letter:			
Site symmetry:		(1) x, y, z (2) x, \bar{y}, z	
4 - b - 1			
I Maximal translationengleiche subgroups			
[2] C1 (1, P1) 1+		$1/2(a-b), 1/2(a+b), c$	
II Maximal klassengleiche subgroups			
• Loss of centring translations			
[2] P1a1 (7, P1c1) 1; 2 + $(\frac{1}{2}, \frac{1}{2}, 0)$		$-a - c, b, a$	
[2] P1m1 (6) 1; 2		$0, 1/4, 0$	

Figure 9: Monoclinic space group in ITC A1[13]

Figure 9, present the same space group Cm in International tables for crystallography volume A1 [13], this edition of tables are specify for symmetry relations between space groups, from this figure and figure 5b we can extract the relation between P1a1 and C1m1, where we have:

$$\begin{aligned}
 a_{Pc} &= -a_{Cm} - c_{Cm} \\
 b_{Pc} &= b_{Cm} \\
 c_{Pc} &= a_{Cm}
 \end{aligned}
 \tag{14}$$

So the matrix P here and the inverse Q could be written as:

$$P = \begin{bmatrix} -1 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{bmatrix} \Rightarrow Q = P^{-1} = \begin{bmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ 1 & 0 & -1 \end{bmatrix} \quad (15)$$

For general transformation of coordinate system, both the basis and the origin have to be transformed; with p, which is the translation matrix or coordinate system of the new origin O' in the old one [14].

$$P = \begin{bmatrix} -1 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{bmatrix} \Rightarrow p = \begin{bmatrix} 0 \\ 1/4 \\ 0 \end{bmatrix}$$

$$[P, p] = \begin{bmatrix} -1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1/4 \\ -1 & 0 & 0 & 0 \end{bmatrix} \quad (16)$$

$$p' = -P^{-1} \times p = \begin{bmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ 1 & 0 & 1 \end{bmatrix} \times \begin{bmatrix} 0 \\ 1/4 \\ 0 \end{bmatrix} \quad (17)$$

p' corresponds to the position of the old origin in the new coordinate system [15].

Combined with the origin shift, the new coordinates result from the old ones according to:

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix}_{Pc} = \begin{bmatrix} P^{-1} & p' \end{bmatrix} \times \begin{bmatrix} x \\ y \\ z \end{bmatrix}_{Cm}$$

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix}_{Pc} = \begin{bmatrix} 0 & 0 & -1 & 0 \\ 0 & 1 & 0 & -1/4 \\ 1 & 0 & 1 & 0 \end{bmatrix} \times \begin{bmatrix} x \\ y \\ z \end{bmatrix}_{Cm} \quad (19)$$

So from equation (14) and (18) we find the atomic position and unit cell parameters transformed from Cm to Pc space group.

$$x_{Pc} = z_{Cm}$$

$$y_{Pc} = y_{Cm} - \frac{1}{4}$$

$$z_{Pc} = x_{Cm} - z_{Cm}$$

Those calculations are explained in ITC Vol A [12] and using the same calculations of rhombohedral-monoclinic transformation, we can confirm the result mentioned above in figure 10 and figure 11:

Cell choice 1 → cell choice 2: $\begin{cases} P \rightarrow P \\ C \rightarrow A \end{cases}$ Cell choice 2 → cell choice 3: $\begin{cases} P \rightarrow P \\ A \rightarrow I \end{cases}$ Cell choice 3 → cell choice 1: $\begin{cases} P \rightarrow P \\ I \rightarrow C \end{cases}$ (Fig. 5.1.3.2a)	Unique axis b invariant	$\begin{pmatrix} 1 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 1 \end{pmatrix}$	Monoclinic (cf. Section 2.2.16)
Cell choice 1 → cell choice 2: $\begin{cases} P \rightarrow P \\ A \rightarrow B \end{cases}$ Cell choice 2 → cell choice 3: $\begin{cases} P \rightarrow P \\ B \rightarrow I \end{cases}$ Cell choice 3 → cell choice 1: $\begin{cases} P \rightarrow P \\ I \rightarrow A \end{cases}$ (Fig. 5.1.3.2b)	Unique axis c invariant	$\begin{pmatrix} 0 & 1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	Monoclinic (cf. Section 2.2.16)
Cell choice 1 → cell choice 2: $\begin{cases} P \rightarrow P \\ B \rightarrow C \end{cases}$ Cell choice 2 → cell choice 3: $\begin{cases} P \rightarrow P \\ C \rightarrow I \end{cases}$ Cell choice 3 → cell choice 1: $\begin{cases} P \rightarrow P \\ I \rightarrow B \end{cases}$ (Fig. 5.1.3.2c)	Unique axis a invariant	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 1 \\ 0 & 1 & 0 \end{pmatrix}$	Monoclinic (cf. Section 2.2.16)

Figure 10: Selected 3 × 3 transformation matrices P and Q = P⁻¹ [12]

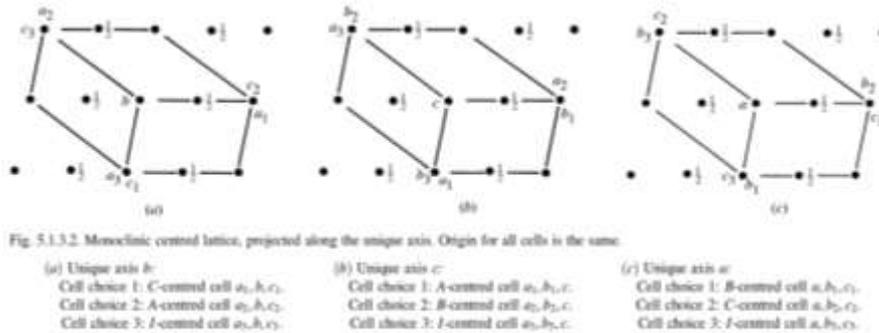


Figure 11: Monoclinic transformation equivalent[12]

2.4 Triclinic structure

To find the metric and positions relationship between known polymorphs is not easy, especially for triclinic structure which is characterized by its low symmetry, it has one axis order 1 rotated in the inverse direction; the triclinic structure which is likely found in commercial clinker is the shape T2 [13]; this structure was solved by Peterson who gives 83 crystallographic sites: 29 Calcium atom [25 atoms in general position and 4 in special position (0 0 0); (0 1/2 0); (1/2 0 1/2) and (1/2 1/2 1/2)]; 9 Silicon atom in general positions; and 45 Oxygen all are occupied general positions.

And for structural description of De La Torre [1] model for T3 form, he has the same 83 crystallographically independent sites: 29 Calcium [4 in special position (x0z) and 25 in general position]; 9 Silicon all in general position; and 45 Oxygen in general position.

CONTINUED	No. 2	$P\bar{1}$
Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2)		
Positions	Coordinates	Reflection conditions
Multiplicity, Wyckoff letter, Site symmetry		General: no conditions Special: no extra conditions
2 1 1	(1) x, y, z (2) $\bar{x}, \bar{y}, \bar{z}$	

Figure 12: Triclinic space group in ITC[12]

III. Conclusions

This article is a bibliographic review on the polymorphism of C3S; it discusses the matrix transformations based on group sub-groups relationship. This work reports a study of the crystallographic structure of alite polymorphs and involves information concerning the mechanism of transitions between all forms. The calculation and determination of matrix transformation in C3S transitions will facilitate solving structures. This work will be supported after; by another article which applied those matrices to find atomic positions of alite in industrial samples.

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Tableau 1: Cell parameters of known polymorphs of C3S

Form	Chemical composition	Space group	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Z	V (Å ³)	References
M3	$\text{Ca}_{2.96}\text{Na}_{0.01}(\text{Si}_{10.90}\text{Al}_{10.04}\text{Fe}_{0.02}\text{F}_{0.03}\text{Mg}_{0.03})\text{O}_5$	Cm	12,235	7,073	9,298	90	116,31	90	6	721.3	[7]
	$\text{Ca}_{2.98}\text{Mg}_{0.01}(\text{Si}_{10.98}\text{Al}_{10.01}\text{Fe}_{0.01}\text{O}_5)$	Cm	33,083	7,027	18,499	90	94,1	90	36	4289	[6]
	$\text{Ca}_{2.94}\text{Mg}_{0.01}\text{Si}_{10.94}\text{Al}_{10.01}\text{O}_5$	Cm	33,1078	7,0355	18,5211	90	94,137	90	36	4302.9	[8]
M1	-	Pc	27.87438	7.0591	12.2578	90	116.031	90	18	2167	[8]
R	$\text{Ca}_{2.98}\text{Si}_{10.98}\text{Al}_{10.04}\text{O}_5$	R3m	7,135	7,135	25,586	90	90	120	9	1128	[5]
	$\text{Ca}_3(\text{SiO}_3)_2\text{O}$	R3m	7	7	25	90	90	120	9	1060.9	[4]
T1	$\text{Ca}_3(\text{SiO}_3)_2\text{O}$	P ⁻¹	11.67	14.24	13.72	105.5	94.3	90	18	2190	[9]
T2	Ca_3SiO_5	P ⁻¹	11.7416	14.2785	13.7732	105.129	94.415	89.889	18	2222.02	[10]
T3	$\text{Ca}_{2.96}\text{Mg}_{0.03}\text{Al}_{10.01}(\text{Si}_{10.99}\text{Al}_{10.01})\text{O}_5$	P ⁻¹	11.6389	14.1716	13.6434	104.982	94.622	90.107	18	2166.228	[1]