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THE STRUCTURE AND QUANTUM CHEMISTRY STUDIES OF $3CaO \bullet 3Al_2O_3 \bullet SrSO_4$

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ABSTRACT

The $3CaO \bullet 3Al_2O_3 \bullet SrSO_4$ single crystals are prepared and defined with $PbCl_2$ as a flux. By means of structure analyzing the overall crystal parameters are obtained. The space group is $I\bar{4}3m$, and unit cell parameter is a = 9.210(4)Å. Atomic coordinates, bond lengths and angles are refined. By a SCC-DV-X_α method of quantum chemistry the molecular structures of $3CaO \bullet 3Al_2O_3 \bullet SrSO_4$ and $3CaO \bullet 3Al_2O_3 \bullet BaSO_4$ are discussed in detail. The Fermi energy, bond order, population, net charge and covalent bond order of molecular structures are obtained. Possessing higher net charge of Ba atoms, lower atomic bond order and covalent bond order of Ba and Ba-O bond than those of Sr and Sr-O bond in $3CaO \bullet 3Al_2O_3 \bullet SrSO_4$, $3CaO \bullet 3Al_2O_3 \bullet BaSO_4$ has higher hydration activity and initial rate of hydration.

Introduction

$3CaO \bullet 3Al_2O_3 \bullet SrSO_4$ has higher hydration strength than $3CaO \bullet 3Al_2O_3 \bullet CaSO_4$(1,2), The studies about $3CaO \bullet 3Al_2O_3 \bullet CaSO_4$ have been done a good lot, but the work about $3CaO \bullet 3Al_2O_3 \bullet SrSO_4$ is not too many in which the data of single crystal is unknown. In this paper we try to prepare and refine $3CaO \bullet 3Al_2O_3 \bullet SrSO_4$ single crystals for the advanced work on it.

Quantum chemistry is a new science studying chemical problems with quantum mechanics. Having been used to explore the structure of substances at the level of molecules, atoms and electrons, it can solve some problems those are not settled with conventional theories and methods. There are considerable senses to materials science. Feng Xiuji(3) first used quantum chemistry to the field of cement chemistry in which the structure and performance of β-$C_2S(Ca_2SiO_4)$ and γ-C_2S are studied. The fundamental reason is that the hydration activity of

TABLE 1
Final Coordinates, Occupancy Factors (K) and Isotropic Temperature Factors of Atoms (U_{11})

Atoms	X/A	Y/B	Z/C	K	U_{11}
S	0.0000(0)	0.0000(0)	0.0000(0)	0.0417(0)	0.1057(161)
Al	0.2500(0)	0.5000(0)	0.0000(0)	0.2500(0)	0.0142(36)
Ca_1	0.1900(17)	0.1900(17)	0.1900(17)	0.0721(26)	0.0048(39)
Sr_1	0.1900(17)	0.1900(17)	0.1900(17)	0.0213(9)	0.0048(39)
Ca_2	0.2237(27)	0.2237(27)	0.2237(27)	0.0529(26)	0.0568(135)
Sr_2	0.2237(27)	0.2237(27)	0.2237(27)	0.0204(9)	0.0568(135)
O_1	0.3988(49)	0.3988(49)	0.3988(49)	0.1667(0)	0.1849(201)
O_2	0.1547(17)	0.1547(17)	0.4519(22)	0.5000(0)	0.0268(78)

β-C_2S is higher than that of γ-C_2S is that the Ca-O bond of β-C_2S is weaker than that of γ-C_2S to lead to the hydration reaction easily.

In this paper, the authors try to synthesis the single crystals of $3CaO \cdot 3Al_2O_3 \cdot SrSO_4$ by $PbCl_2$ as a flux for the advanced work on this field. furthermore, the $3CaO \cdot 3Al_2O_3 \cdot SrSO_4$ and $3CaO \cdot 3Al_2O_3 \cdot BaSO_4$, another cementitious mineral, are studied with SCC-DV-X_α method. The relation between structure and performance is uncovered at the level of molecules, atoms and electrons.

Preparation and Refinement of the Single Crystals

The single crystal of $3CaO \cdot 3Al_2O_3 \cdot SrSO_4$ is prepared by the melted method. Fine powder of $3CaO \cdot 3Al_2O_3 \cdot SrSO_4$ synthesized by heating the stoichiometric mixture of $CaCO_3$, Al_2O_3, $SrSO_4$ at 1350 °C for 2hrs, is mixed with $PbCl_2$ flux at the ratio 1:20 to 1:50. The mix mentioned above is transferred to a Pt crucible and heated in an electric furnace at the given temperatures from 800 to 1000 °C for 1 to 40 hours, and then the flux is vaporized and the crystals of $3CaO \cdot 3Al_2O_3 \cdot SrSO_4$ are remained. The single crystals are 60-120μm in diameter, and large enough for x-ray single crystal studies. Its chemical composition is verified by chemical

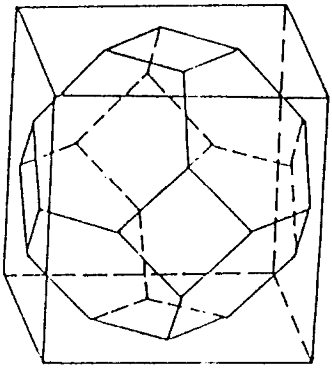

FIG. 1.
Cage building by $[AlO_4]$.

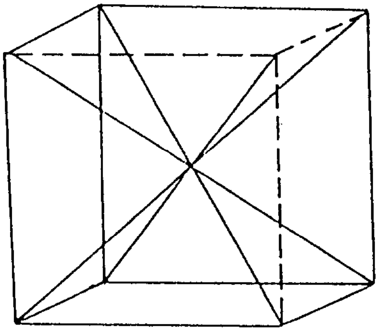

FIG. 2.
Passage position.

analysis, EPMA and XRD. Under a polarization microscope the extinction is found, and refractive index is 1.573. Under a solid microscope the crystals are regular rhombus twelve-face bodies.

A single crystal with 0.1 × 0.1 × 0.1 cm^3 in sizes is analyzed by a Rigaku RASA-5RD four-cycles single crystal x-ray diffractometry. The space group and unit cell parameters are I43m, a = 9.210(4) Å respectively. The final R factor is 0.070. The final coordinates, occupancy factors and isotropic factors of atoms are listed in Table 1.

The structure frames of $3CaO \cdot 3Al_2O_3 \cdot SrSO_4$ are formed of six tetragonal rings(parallel to [100], [010], [001] per two faces) and eight hexagonal rings (parallel to [111], $[\bar{1}11]$, $[1\bar{1}1]$, $[11\bar{1}]$ per two faces) composed of Al-O tetrahedrons (Fig.1), and the "passage" position is determined along the normal direction of hexagonal rings (Fig.2). This passage parallels L^3, and is distributed along the body diagonal of the unit cell. Fig.3 shows a part projection of the crystal structure along the c axis. Main bond lengths and angles are listed in Tables 2 and 3 respectively.

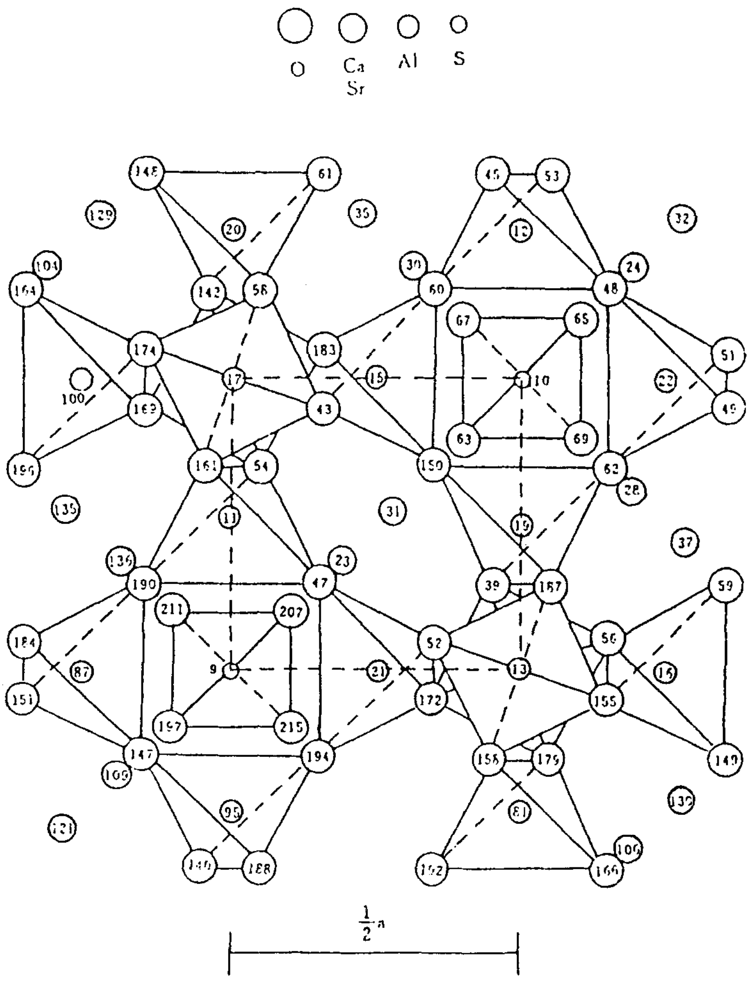

FIG. 3.
Projection of $3CaO \cdot 3Al_2O_3 \cdot SrSO_4$ structure along c axis.

TABLE 2
Main Bond Lengths (Å)

Atom - Atom	Bond length	Atom - Atom	Bond length
$Ca(Sr)_{23}$ -O_{47}	2.45553	$Ca(Sr)_{31}$ -O_{63}	2.79323
$Ca(Sr)_{23}$ -O_{43}	2.45553	$Ca(Sr)_{31}$ -O_{172}	2.96226
$Ca(Sr)_{23}$ -O_{39}	2.45553	$Ca(Sr)_{31}$ -O_{161}	2.96226
$Ca(Sr)_{23}$ -O_{215}	2.92072	$Ca(Sr)_{31}$ -O_{150}	2.96226
$Ca(Sr)_{23}$ -O_{207}	2.92072	Al_{11} -O_{190}	1.73108
$Ca(Sr)_{23}$ -O_{211}	2.92072	Al_{11} -O_{47}	1.73108
$Ca(Sr)_{23}$ -O_{150}	2.98335	Al_{11} -O_{54}	1.73108
$Ca(Sr)_{23}$ -O_{172}	2.98335	Al_{11} -O_{161}	1.73108
$Ca(Sr)_{23}$ -O_{161}	2.98335	S_9 -O_{215}	1.61436
$Ca(Sr)_{31}$ -O_{47}	2.28581	S_9 -O_{211}	1.61436
$Ca(Sr)_{31}$ -O_{43}	2.28581	S_9 -O_{207}	1.61436
$Ca(Sr)_{31}$ -O_{39}	2.28581	S_9 -O_{197}	1.61436

Quantum Chemistry Computation and Discussions

The SCC-DV-X_α method used in this paper was advanced by D.Ellis(4). In this method the dispersed points are selected in potential space, and the error functions are determined by the approximate solutions of relevant equations of single particles. Evaluating the variations calculus of proper parameters in the error functions to all the points, the secular equation is obtained. The question is exchanged to solve this equation that is easy to be resolved relatively.

TABLE 3
Main Bond Angles (deg.)

Atom - Atom - Atom	Angles	Atom - Atom - Atom	Angles
O_{215} - S_9 - O_{211}	109.4712	O_{215} - $Ca(Sr)_{23}$ - O_{150}	111.6331
O_{215} - S_9 - O_{207}	109.4712	O_{215} - $Ca(Sr)_{23}$ - O_{161}	111.6331
O_{215} - S_9 - O_{197}	109.4712	O_{215} - $Ca(Sr)_{23}$ - O_{172}	66.0175
O_{211} - S_9 - O_{207}	109.4712	O_{211} - $Ca(Sr)_{23}$ - O_{150}	111.6331
O_{211} - S_9 - O_{197}	109.4712	O_{211} - $Ca(Sr)_{23}$ - O_{172}	111.6331
O_{207} - S_9 - O_{197}	109.4712	O_{211} - $Ca(Sr)_{23}$ - O_{161}	66.0175
O_{190} - Al_{11} - O_{47}	119.0674	O_{211} - $Ca(Sr)_{23}$ - O_{207}	53.6542
O_{190} - Al_{11} - O_{54}	104.8969	O_{207} - $Ca(Sr)_{23}$ - O_{172}	111.6331
O_{190} - Al_{11} - O_{161}	104.8969	O_{207} - $Ca(Sr)_{23}$ - O_{161}	111.6331
O_{47} - Al_{11} - O_{161}	104.8969	O_{207} - $Ca(Sr)_{23}$ - O_{150}	66.0175
O_{47} - Al_{11} - O_{54}	104.8969	O_{150} - $Ca(Sr)_{23}$ - O_{161}	118.3563
O_{161} - Al_{11} - O_{54}	119.0674	O_{172} - $Ca(Sr)_{23}$ - O_{161}	118.3563
O_{47} - $Ca(Sr)_{23}$ - O_{43}	104.0393	O_{150} - $Ca(Sr)_{23}$ - O_{172}	118.3563
O_{47} - $Ca(Sr)_{23}$ - O_{39}	104.0393	O_{47} - $Ca(Sr)_{31}$ - O_{39}	115.7190
O_{47} - $Ca(Sr)_{23}$ - O_{215}	96.6851	O_{47} - $Ca(Sr)_{31}$ - O_{63}	77.8878
O_{47} - $Ca(Sr)_{23}$ - O_{211}	96.6851	O_{47} - $Ca(Sr)_{31}$ - O_{172}	61.4809
O_{47} - $Ca(Sr)_{23}$ - O_{207}	145.8796	O_{47} - $Ca(Sr)_{31}$ - O_{161}	61.4809
O_{47} - $Ca(Sr)_{23}$ - O_{150}	148.1029	O_{47} - $Ca(Sr)_{31}$ - O_{150}	170.8305
O_{47} - $Ca(Sr)_{23}$ - O_{172}	59.6822	O_{47} - $Ca(Sr)_{31}$ - O_{43}	115.7190
O_{215} - $Ca(Sr)_{23}$ - O_{207}	53.6542		

Quantum chemistry computation and discussions

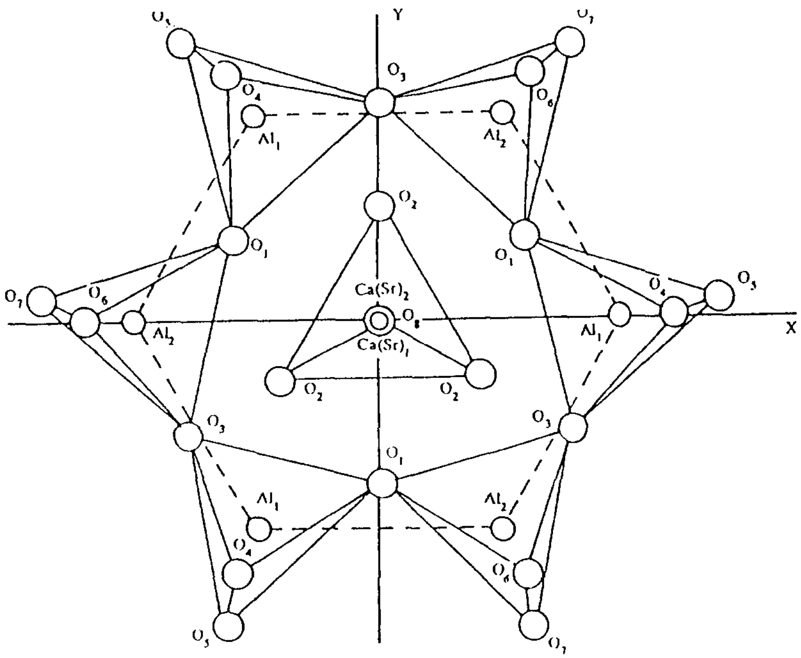

FIG. 4.
Positions of atoms in the coordinate system for computation.

Based on the structure of $3CaO \cdot 3Al_2O_3 \cdot SrSO_4$ the model is designed for the computation of quantum chemistry. Presenting the structure, the hexagonal ring is used as the prime unit of the model. Through coordinate transformation the projection of the model along the z axis with C_{3V} symmetry is shown in Fig.4. The atomic coordinates of the model are shown in Table 4. Since $Ca(Sr)_1$ and $Ca(Sr)_2$ do not exist in one hexagonal ring, they are divided into two computational systems. The first is composed of $Ca(Sr)_1$, Al_1, Al_2, O_1, O_2,O_3, O_4 and O_5, and the second is $Ca(Sr)_2$, Al_1, Al_2, O_1, O_2, O_4, O_5 and O_8 being closer to $Ca(Sr)_2$ than O_4. $3CaO \cdot 3Al_2O_3 \cdot BaSO_4$ is considered the same with $3CaO \cdot 3Al_2O_3 \cdot SrSO_4$ in structure, and adopted to the same models. The question to be studied is mainly on the difference caused by the replacing of Ba in $3CaO \cdot 3Al_2O_3 \cdot SrSO_4$. The computational systems composed of Sr_1, Sr_2,Ba_1 and Ba_2 are expressed as $Sr(1)Al_6O_{15}$, $Sr(2)Al_6O_{13}$, $Ba(1)Al_6O_{15}$ and $Ba(2)Al_6O_{13}$, respectively.

TABLE 4
Atom Coordinates for Computation (a.u.)

Atoms	x	y	z
$Sr_1(Ba_1)$	0.0000	0.0000	5.7295
$Sr_2(Ba_2)$	0.0000	0.0000	6.7458
Al_1	-3.0777	-5.3308	7.5388
Al_2	-6.1554	0.0000	7.5388
O_1	0.0000	-4.2199	7.6524
O_2	2.4918	-1.4380	1.0172
O_3	0.0000	5.5923	6.4582
O_4	-3.6590	6.5110	10.5352
O_5	-3.8090	-7.7914	5.5094
O_8	0.0000	0.0000	12.0261

TABLE 5

Bond Order, Population and Net Charge of $Sr(1)Al_6O_{15}$

Atoms	Bond order	Population	Net charge
Sr_1	0.4178	0.8163	1.1837
Al_1	1.4736	2.1775	0.8225
Al_2	0.2933	2.5387	0.4613
O_1	0.7545	2.5913	-0.5913
O_2	0.0532	2.1745	-0.1745
O_3	0.1619	2.4892	-0.4892
O_4	0.5321	2.2871	-0.2871
O_5	0.1024	2.1363	-0.1363

TABLE 6

Bond Order, Population and Net Charge of $Sr(2)Al_6O_{13}$

Atoms	Bond order	Population	Net charge
Sr_2	0.4272	1.8995	0.1005
Al_1	1.4366	2.1239	0.8761
Al_2	0.3110	2.5049	0.4951
O_1	0.6591	2.5299	-0.5299
O_2	0.1182	2.0772	-0.0772
O_3	0.1620	2.5172	-0.5172
O_5	0.4989	2.2643	-0.2643
O_8	0.3428	2.0485	-0.0485

TABLE 7

Bond Order, Population and Net Charge of $Ba(1)Al_6O_{15}$

Atoms	Bond order	Population	Net charge
Ba_1	0.3340	0.5173	1.4827
Al_1	1.4890	2.1824	0.8176
Al_2	0.3428	2.5666	0.4334
O_1	0.6129	2.6538	-0.6538
O_2	0.0529	2.0571	-0.0571
O_3	0.2127	2.6209	-0.6209
O_4	0.4360	2.3662	-0.3662
O_5	0.0967	2.0473	-0.0473

According to the regulations of computational program, the atomic coordinates above and some parameters of atoms are imported into a CYBER-930 computer. After computing 50 repeating times the convergence is made. The details of results are as follows:

The bond order, population and net charge of atoms in $Sr(1)Al_6O_{15}$, $Sr(2)Al_6O_{13}$, $Ba(1)Al_6O_{15}$ and $Ba(2)Al_6O_{13}$ are in Table 5 to Table 8, respectively.The covalent bond orders in $3CaO \bullet 3Al_2O_3 \bullet SrSO_4$ and $3CaO \bullet 3Al_2O_3 \bullet BaSO_4$ are in Tables 9 and 10, respectively.

In Tables 5 and 10, the atomic and average covalent bond order of Al-O bond in $Sr(1)Al_6O_{15}$, $Sr(2)Al_6O_{13}$, $Ba(1)Al_6O_{15}$ and $Ba(2)Al_6O_{13}$ are almost the same, and the average covalent bond orders of Al-O are higher than those of Sr-O and Ba-O. So these demonstrate that the influence

TABLE 8

Bond Order, Population and Net Charge of $Ba(2)Al_6O_{13}$

Atoms	Bond order	Population	Net charge
Ba_2	0.3229	0.5077	1.4923
Al_1	1.4396	2.1806	0.8194
Al_2	0.3371	2.5648	0.4352
O_1	0.5905	2.6799	-0.6799
O_2	0.0477	2.1199	-0.1199
O_3	0.2039	2.6065	-0.6065
O_5	0.3885	2.3421	-0.3421
O_8	0.0667	2.0112	-0.0112

TABLE 9

Covalent Bond Order of $Sr(1)Al_6O_{16}$ and $Sr(2)Al_6O_{13}$

$Sr(1)Al_6O_{15}$		$Sr(2)Al_6O_{13}$	
$Sr\text{-}O_1$ (3)	0.2376	$Sr\text{-}O_1$ (3)	0.1156
$Sr\text{-}O_2$ (3)	0.1624	$Sr\text{-}O_2$ (3)	0.0071
$Sr\text{-}O_3$ (3)	0.0439	$Sr\text{-}O_8$ (3)	0.3045
Ave.	0.0493	Ave.	0.0610
$Al_1\text{-}O_1$ (1)	0.2223		
$Al_1\text{-}O_3$ (1)	0.0233		
$Al_1\text{-}O_4$ (1)	0.1710		
$Al_1\text{-}O_5$ (1)	0.0214		
Ave.	0.1095		

(1)-one bond (3)-three bonds

TABLE 10

Covalent Bond Order of $Ba(1)Al_6O_{15}$ and $Ba(2)Al_6O_{13}$

$Ba(1)Al_6O_{15}$		$Ba(2)Al_6O_{13}$	
$Ba\text{-}O_1$ (3)	0.1813	$Ba\text{-}O_1$ (3)	0.2083
$Ba\text{-}O_2$ (3)	0.1201	$Ba\text{-}O_2$ (3)	0.0503
$Ba\text{-}O_3$ (3)	0.0676	$Ba\text{-}O_8$ (3)	0.0535
Ave.	0.0410	Ave.	0.0446
$Al_1\text{-}O_1$ (1)	0.2169		
$Al_1\text{-}O_3$ (1)	0.0328		
$Al_1\text{-}O_4$ (1)	0.1705		
$Al_1\text{-}O_5$ (1)	0.0195		
Ave.	0.1099		

(1)-one bond (3)-three bonds

of Al on $3CaO \cdot 3Al_2O_3 \cdot SrSO_4$ and $3CaO \cdot 3Al_2O_3 \cdot BaSO_4$ is not considerable compared with Sr and Ba, and that the bond of Sr-O and Ba-O are broken to react with water more easily than that of Al-O. What determines the performance of two minerals is mainly the difference of Sr and Ba in the structure. P.Yan(2) has considered that the initial hydration of $3CaO \cdot 3Al_2O_3 \cdot$

$BaSO_4$ is faster than $3CaO \cdot 3Al_2O_3 \cdot SrSO_4$ by experiments. According to the computational results (Table 5 to 8) the net charge(1.4829 and 1.4923) of Ba_1 and Ba_2 are higher than those(1.1837 and 0.1005) of Sr_1 and Sr_2.The atoms with higher net charge can easily react with the lone-pair electrons of water molecule. In addition, the atomic bond orders(0.3340 and 0.3229) and covalent bond orders(0.041 and 0.0446) of Ba_1-O and Ba_2-O are lower than those (0.4178 and 0.4242, 0.0493 and 0.0610) of Sr_1-O and Sr_2-O, respectively. Atoms with lower atomic bond orders and covalent bond orders can be broken more easily to react with water.

Conclusions

The single crystals of $3CaO \cdot 3Al_2O_3 \cdot SrSO_4$ are prepared by melted method with $PbCl_2$ as a flux. By the structure analysis, the space group, unit cell parameters, final atomic coordinates, bond lengths and bond angles are obtained.

Through quantum chemistry computation, the energy lever of molecule, atomic bond order, population, net charge and covalent bond order of $3CaO \cdot 3Al_2O_3 \cdot SrSO_4$ and $3CaO \cdot 3Al_2O_3 \cdot BaSO_4$ are gained.

Atomic bond order and average covalent bond order of Al-O in two minerals are almost the same, and the Ba-O and Sr-O bonds are weaker than Al-O bonds to be broken easily to react with water.

The reason that the initial hydration of $3CaO \cdot 3Al_2O_3 \cdot BaSO_4$ is faster than $3CaO \cdot 3Al_2O_3 \cdot SrSO_4$ is: (1) the net charge of Ba in $3CaO \cdot 3Al_2O_3 \cdot BaSO_4$ is higher than that of Sr in $3CaO \cdot 3Al_2O_3 \cdot SrSO_4$ to lead to react with water easily. (2) $3CaO \cdot 3Al_2O_3 \cdot BaSO_4$ with lower bond order and average bond order of Ba-O can be broken more easily to react with water than $3CaO \cdot 3Al_2O_3 \cdot SrSO_4$.

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