Crystal Structures of Wollastonite $Ca(Ge_x,Si_{1-x})O_3$

F. Nishi[a], Y. Matsumoto[b], R. Miyawaki[c]

[a]*Saitama Institute of Technology, Fusaiji 1690, Okabe, Ohsato-gun, Saitama, JAPAN,* [b]*Tohoku University, Aoba-ku, Sendai, Miyagi, JAPAN,* [c]*Dept. of Geology and paleontology, Shinjuku Branch of National Science Museum, 3-23-1 Hyakunincho, Shinjuku, Tokyo, JAPAN*

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Four crystals which have wollastonite structures were studied. They are shown as Ca(Gex, Si1-x)O3 (X=0.25, 0.40, 0.85, 1.0). They were synthesized from CaCl2, SiO2 and GeO2 at about 1500K. The lattice constants are: (angstrom, degree)

X=0.25 a=7.970(1) , b=7.369(1), c=7.114(1), alpha=90.07(1) , beta=95.07(1) , gamma=103.43(1)

X=0.40 a=7.983(2), b=7.382(1), c=7.128(1), alpha=90.07(1) , beta=95.06(1) , gamma=103.43(1)

X=0.85 a=8.076(1), b=7.494(1), c=7.232(1), alpha=90.10(1) , beta=94.65(1) , gamma=103.48(1)

X=1.0 a=8.125(2) , b=7.554(1), c=7.292(2), alpha=90.11(3) , beta=94.40(3) , gamma=103.48(1)

It can be observed that the lattice constants increase with increasing Ge contents in their structures. The R factors of these structures are 4.2%, 4.3%, 3.6% and 4.8% for X=0.25, 0.40, 0.85 and 1.0, respectively. There are three independent tetrahedral sites(T1, T2 and T3) in which Ge and Si atoms can be located on the basis of crystallographic consideration. The occupancies of Ge and Si atoms and the average bond lengths for each T site are:

X=0.25 T1=Ge 15.3(2)% + Si 84.7(2)%, T2=Ge 15.4(2)% + Si 84.6(2)%, T3=Ge 44.2(2)% + Si 55.8(2)% Ave. bond length (angstrom): T1=1.637(3), T2=1.637(3), T3=1.681(3)

X=0.40 T1=Ge 29.0(3)% + Si 71.0(3)%, T2=Ge 28.1(3)% + Si 71.9(3)%, T3=Ge 62.9(3)% + Si 37.1(3)% Ave. bond length(angstrom): T1=1.643(4), T2=1.643(4), T3=1.684(4)

X=0.85 T1=Ge 79.1(2)% + Si 20.9(2)%, T2=Ge 79.4(2)% + Si 20.6(2)%, T3=Ge 96.5(2)% + Si 3.5(2)% Ave. bond length(angstrom): T1=1.703(3), T2=1.702(3), T3=1.739(3)

It can be observed that T3 site among three T sites includes the largest amount of Ge occupancies in three different compounds. In addition, it can be observed that T1 and T2 sites have almostly same amount of Ge occupancies. The reason why T3 site includes the largest amount of Ge occupancies may be explained as follows: The O5 and O6 atoms coordinate only two Ca atoms (Ca1 and Ca2) and one T atom whereas the other O atoms coordinate three Ca atoms and one T atom. Accordingly, not only the bond lengths of O5-Ca and O6-Ca but also O5-T1 and O6-T2 are fairly short in order to gain much bond valences from Ca and T atoms. The bonds of O5-T1 and O6-T2 are strongly fixed and their lengths can not be easily changed. On the contarary, there is no such a restriction in T3 tetrahedron and a large amount of Ge atom can occupy T3 site.

There are three independent Ca sites in each structure. Ca1 and Ca2 are coordinated by six oxygens and Ca3 coordinated by seven. Accordingly, the average bond lengths of Ca1-O and Ca2-O (2.385-2.401angstrom) are shorter than those of Ca3-O (2.427-2.443 angstrom). However, it is noted that each average bond length of Ca1-O, Ca2-O and Ca3-O is almostly same through the four wollastonite structures (X=0.25, X=0.40, X=0.85 and X=1.0) and there is no significant errors of them through the four structures.