

s5.m15.p10 **Twins vs. cell-twins.** Massimo Nespolo^a and Giovanni Ferraris^b, ^aLCM3B CNRS-UMR 7036 UHP Nancy 1, France, and ^bDSMP University Torino, Italy. E-mail: massimo.nespolo@lcm3b.uhp-nancy.fr

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The concept of cell-twin can be traced back to Ito [1], in his pioneer studies of what nowadays we describe as a special case of modular structures at the unit-cell level [2]. Ito's type of compounds is isochemical and substantially corresponds to polytypes: their structure can be described as built by the juxtaposition of modules, smaller than the final unit cell, related by a local symmetry operation which may have a gliding component. The module itself may also give rise to its own structure, in which it represents the full unit cell. Later on, modular structures were discovered, where the chemistry is not kept constant in going from the building modules to the final structure. Whereas in some cases (heterochemical modular structures), which substantially correspond to members of homologous and polysomatic series, these changes in the chemistry are essential to the structure-building mechanism (tropochemical cell-twinning, non-conservative twinning), sometimes they simply represent a convenient way to accommodate impurity atoms down to a very low concentration (chemical twinning) [3]. This fine classification is not only a matter of terminology, but has a direct connection with the problem of establishing the boundaries between cell-twins (modular structures *at the unit-cell level*) and twins, which are classified as modular structures *at the crystal level* in [2]. The mentioned boundaries, as shown by studies at nanoscale, cannot be simply a matter of size, because the formation of twins may occur at a very early stage of crystal growth. To establish a conceptual boundary, we propose the following criteria. The edifice of a twin is heterogeneous (*i.e.* modular at crystal level) because it does not correspond to a uniquely oriented crystal structure but consists of at least two crystallographically, oriented individuals. Consequently, such *edifice* cannot be described by a space group and does not possess a structural unit cell extending to the whole volume and describing its whole structure. It instead possesses a (chromatic) point group [4] where the "chromatic" elements (symmetry elements which do not belong to the individual) relate the different individuals in the twin; the twin operations are external to any structural unit cell. On the contrary, the *edifice* of an Ito's cell-twin is homogeneous, is described by a space group, and possesses a structural unit cell: the cell-twin operations act within this cell, putting in relation modules that may correspond to a unit cell of a (hypothetic) end-member structure. With the exception of class I twins (in which the twin operation is equivalent to an inversion centre [5]), the twin law has to be known to solve, or at least to refine the structure, whereas the modular structure of all kinds of unit-cell level modular structures is often discovered once the structure has been refined (its modular nature can be usefully exploited to obtain a model of the structure, but in principle the structure can be solved even without knowledge of its modular nature).

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- [5] Catti, M. and Ferraris, G. (1976). *Acta Crystallogr.* **A32**, 163-165.

s5.m15.p11 **Crystal Structures of Wollastonite** $\text{Ca}(\text{Ge}_x\text{Si}_{1-x})\text{O}_3$. F. Nishi^a, Y. Matsumoto^b, R. Miyawaki^c, ^aSaitama Institute of Technology, Fusaiji 1690, Okabe, Ohsato-gun, Saitama, Japan, ^bTohoku University, Aoba-ku, Sendai, Miyagi, Japan, ^cDept. of Geology and paleontology, Shinjuku Branch of National Science Museum, 3-23-1 Hyakunincho, Shinjuku, Tokyo, Japan. E-mail: nishi@sit.ac.jp

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Four crystals which have wollastonite structures were studied. They are shown as $\text{Ca}(\text{Ge}_x\text{Si}_{1-x})\text{O}_3$ ($X=0.25, 0.40, 0.85, 1.0$). They were synthesized from CaCl_2 , SiO_2 and GeO_2 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 contrary, 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.