Hardystonite from Franklin Furnace: A natural modulated melilite

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ABSTRACT

Natural hardystonite, (Ca1.85Na0.14Pb0.01)(Zn0.85Al0.07Mg0.03Mn3+0.02Fe3+)2Si2.00O7 (X2T1(T2)2O7 (X = Ca, Sr, Pb, Ba, Na,Y, Er,Yb; T1 = Be, Mg, Mn2+, Fe2+, Co, Cu, Zn, Cd, Al, Fe3+, Ga, Si; T2 = Si, Ge, Al, Fe2+, Ga, Be) have been synthesized either from a melt, by solid-solution between gehlenite, Ca2Al2SiO7, and åkermanite, Ca2MgSi2O7. These phases are found in both plutonic and volcanic rocks, in blast-furnace slags, and in aluminum-rich chondrules of meteorites (Deer et al. 1986). Many melilite-type compounds with the general formula X2T1(T2)2O7 (X = Ca, Sr, Pb, Ba, Na,Y, Er,Yb; T1 = Be, Mg, Mn2+, Fe2+, Co, Cu, Zn, Cd, Al, Fe3+, Ga, Si; T2 = Si, Ge, Al, Fe2+, Ga, Be) have been synthesized either from a melt, by sintering, or under hydrothermal conditions (Röthlisberger et al. 1990). Several crystal structure refinements on synthetic compounds with a wide range of chemical compositions have been published (Bartram 1969; Louisnathan 1970; Kimata and Li 1981, 1982; Kimata and Ohashi 1982; Kimata 1983a, 1983b, 1984, 1985; Armbruster et al. 1990; Shimizu et al. 1995; Yang et al. 1997). However, comparatively, few natural melilitides have been studied (Bartram 1969; Louisnathan 1970; Kimata and Ii 1990, 1991). Several crystal structure refinements on synthetic compounds with a wide range of chemical compositions have been published (Bartram 1969; Louisnathan 1970; Kimata and Li 1981, 1982; Kimata and Ohashi 1982; Kimata 1983a, 1983b, 1984, 1985; Armbruster et al. 1990; Shimizu et al. 1995; Yang et al. 1997). However, comparatively, few natural melilitides have been studied (Warren 1930; Smith 1953; Louisnathan 1971; Cruciani and Vaccaro 1996; Giuli et al. 2000).

Hemingway et al. (1986) observed satellite reflections and thermal behavior anomalies in synthetic Ca2MgSi2O7. Seifert et al. (1987) reported electron diffraction patterns and TEM images of synthetic iron-bearing åkermanites exhibiting two-dimensional incommensurately modulated structure. They also suggested that the formation of the incommensurate phase is due to a structural misfit between tetrahedral sheet and the X-polyhedral layer. Röthlisberger et al. (1990) pointed out the role of the chemical composition in the stabilization of the incommensurate phase. By means of an electron diffraction and electron microscopy study of synthetic Ca2ZnGe2O7, Van Heurck et al. (1992) showed the structure to be modulated by the formation of microdomains involving different orientations of the T1 and T2 tetrahedra. According to Seifert and Röthlisberger (1993) the modulation amplitude is temperature-dependent and the dynamic disorder of the X cations may lead to the stabilization of the unmodulated melilite structure at high temperatures only. From the theoretical principles of the incommensurability in crystals (Janssen and Janner 1987), the incommensurate phases are intermediate between a commensurate high-temperature phase (unmodulated structure) and a low-temperature commensurate superstructure (the so called “lock-in phase”). Riester and Böhm (1997) found the “lock-in phase” of Co-åkermanite to occur at 130 K. The result is a nearly commensurate phase (3a × 3a × c supercell), with clusters of 6- and 7-fold coordinated calcium arranged in octagons (Riester et al. 2000). On the basis of a five-dimensional refinement of the modulated phase, Hagiya et al. (1993) and Kusaka et al. (1998) concluded that modulation in synthetic compounds [Co-åkermanite and Ca2(Mg1.33Fe1.67)SiO7] results from static displacement of the constituent atoms from their dynamically-averaged positions, that is, modulation arises from positional and not substitutional disorder. In contrast, Jiang et al. (1998) postulated that occupational modulation makes a contribution to the overall modulation characteristics, as a consequence of an ordered distribution of Sr in (Ca0.9Ca0.1)2MgSi2O7. Occupancy modulation of Sr and Ca was observed also by Bagautdinov et al. (2000) who refined the incommensurately modulated structure of (Sr0.1Ca0.87)2CoSi2O7. A formal solution to the problem of the modulated structure in melilites was provided by

INTRODUCTION

The melilite group of minerals consists mainly of solid-solutions between gehlenite, Ca2Al2SiO7, and åkermanite, Ca2MgSi2O7. These phases are found in both plutonic and volcanic rocks, in blast-furnace slags, and in aluminum-rich chondrules of meteorites (Deer et al. 1986). Many melilite-type compounds with the general formula X2T1(T2)2O7 (X = Ca, Sr, Pb, Ba, Na,Y, Er,Yb; T1 = Be, Mg, Mn2+, Fe2+, Co, Cu, Zn, Cd, Al, Fe3+, Ga, Si; T2 = Si, Ge, Al, Fe2+, Ga, Be) have been synthesized either from a melt, by sintering, or under hydrothermal conditions (Röthlisberger et al. 1990). Several crystal structure refinements on synthetic compounds with a wide range of chemical compositions have been published (Bartram 1969; Louisnathan 1970; Kimata and Li 1981, 1982; Kimata and Ohashi 1982; Kimata 1983a, 1983b, 1984, 1985; Armbruster et al. 1990; Shimizu et al. 1995; Yang et al. 1997). However, comparatively, few natural melilitides have been studied (Warren 1930; Smith 1953; Louisnathan 1971; Cruciani and Vaccaro 1996; Giuli et al. 2000).

Hemingway et al. (1986) observed satellite reflections and thermal behavior anomalies in synthetic Ca2MgSi2O7. Seifert et al. (1987) reported electron diffraction patterns and TEM images of synthetic iron-bearing åkermanites exhibiting two-dimensional incommensurately modulated structure. They also suggested that the formation of the incommensurate phase is due to a structural misfit between tetrahedral sheet and the X-polyhedral layer. Röthlisberger et al. (1990) pointed out the role of the chemical composition in the stabilization of the incommensurate phase. By means of an electron diffraction and electron microscopy study of synthetic Ca2ZnGe2O7, Van Heurck et al. (1992) showed the structure to be modulated by the formation of microdomains involving different orientations of the T1 and T2 tetrahedra. According to Seifert and Röthlisberger (1993) the modulation amplitude is temperature-dependent and the dynamic disorder of the X cations may lead to the stabilization of the unmodulated melilite structure at high temperatures only. From the theoretical principles of the incommensurability in crystals (Janssen and Janner 1987), the incommensurate phases are intermediate between a commensurate high-temperature phase (unmodulated structure) and a low-temperature commensurate superstructure (the so called “lock-in phase”). Riester and Böhm (1997) found the “lock-in phase” of Co-åkermanite to occur at 130 K. The result is a nearly commensurate phase (3a × 3a × c supercell), with clusters of 6- and 7-fold coordinated calcium arranged in octagons (Riester et al. 2000). On the basis of a five-dimensional refinement of the modulated phase, Hagiya et al. (1993) and Kusaka et al. (1998) concluded that modulation in synthetic compounds [Co-åkermanite and Ca2(Mg1.33Fe1.67)SiO7] results from static displacement of the constituent atoms from their dynamically-averaged positions, that is, modulation arises from positional and not substitutional disorder. In contrast, Jiang et al. (1998) postulated that occupational modulation makes a contribution to the overall modulation characteristics, as a consequence of an ordered distribution of Sr in (Ca0.9Ca0.1)2MgSi2O7. Occupancy modulation of Sr and Ca was observed also by Bagautdinov et al. (2000) who refined the incommensurately modulated structure of (Sr0.1Ca0.87)2CoSi2O7. A formal solution to the problem of the modulated structure in melilites was provided by

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