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Low-temperature study of natural melilite ($\text{Ca}_{1.89}\text{Sr}_{0.01}\text{Na}_{0.08}\text{K}_{0.02}$) ($\text{Mg}_{0.92}\text{Al}_{0.08}$)($\text{Si}_{1.97}\text{Al}_{0.03}$) O_7 : towards a commensurate value of the q vector

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Abstract As is usual for peculiar chemical compositions, melilite-type compounds exhibit a two-dimensional incommensurately modulated structure which can be described with two wave vectors: $\mathbf{q}_1 = \alpha(\mathbf{a}^* + \mathbf{b}^*)$ and $\mathbf{q}_2 = \alpha(-\mathbf{a}^* + \mathbf{b}^*)$, where \mathbf{a}^* and \mathbf{b}^* are the tetragonal reciprocal axes of the basic cell. The low-temperature dependence of the modulation wave vector of a natural melilite crystal with chemical composition $(\text{Ca}_{1.89}\text{Sr}_{0.01}\text{Na}_{0.08}\text{K}_{0.02})(\text{Mg}_{0.92}\text{Al}_{0.08})(\text{Si}_{1.97}\text{Al}_{0.03})\text{O}_7$ has been studied by X-ray single-crystal diffraction methods in the temperature range 298–100 K. The value of the α coefficient shows a continuous linear increase, ranging from 0.281(1) at 298 K to 0.299(1) at 100 K. No plateau-like temperature dependence was observed throughout the temperature studied, thus indicating that no independent phase with a specific q stabilizes in this natural crystal. A comparison with the low-temperature behaviour of synthetic $\text{Ca}_2\text{MgSi}_2\text{O}_7$ is given.

Keywords Åkermanite · Melilite · Incommensurate structures · Low temperature · q vector

Introduction

The melilite group minerals mainly consist of a solid solution between gehlenite, $\text{Ca}_2\text{Al}_2\text{SiO}_7$ and åkermanite, $\text{Ca}_2\text{MgSi}_2\text{O}_7$. Melilite-type compounds exhibit the general formula $\text{X}_2\text{T}^1\text{T}^2\text{O}_7$ ($\text{X} = \text{Ca}, \text{Sr}, \text{Pb}, \text{Ba}, \text{Na}, \text{K}, \text{Y}$; $\text{T}^1 = \text{Be}, \text{Mg}, \text{Fe}^{2+}, \text{Cu}, \text{Co}, \text{Zn}, \text{Mn}, \text{Cd}, \text{Al}, \text{Fe}^{3+}, \text{Ga}, \text{Si}$; $\text{T}^2 = \text{Si}, \text{Ge}, \text{Al}, \text{B}, \text{Fe}^{3+}, \text{Ga}, \text{Be}$). The structure, space group $P4_2/m$, was first determined by Warren (1930) and subsequently refined by Smith (1953). It consists of a linkage of T^1 and T^2 tetrahedra forming

sheets parallel to (001). The eight-coordinated X cations provide the connection between adjacent layers.

As with peculiar chemical compositions ($\text{T}^1 = \text{Mg}, \text{Fe}^{2+}, \text{Co}, \text{Zn}$; $\text{T}^2 = \text{Si}$; $\text{X} = \text{Ca}$), at room temperature, the set of strong main reflections is accompanied by weak satellite reflections indicating a two-dimensional incommensurately modulated structure. This feature, observed first by Hemingway et al. (1986) and Seifert et al. (1987), has been the subject of a number of further studies (Merwin et al. 1989; Armbruster et al. 1990; Iishi et al. 1990; Röthlisberger et al. 1990; Van Heurck et al. 1992; Seifert and Röthlisberger 1993; Iishi et al. 1994; Tamura et al. 1996; Yang et al. 1997; Jiang et al. 1998; Schosnig et al. 2000; Bindi et al. 2001a; Schaper et al. 2001). The modulation in melilites can be described with two wave vectors: $\mathbf{q}_1 = \alpha(\mathbf{a}^* + \mathbf{b}^*)$ and $\mathbf{q}_2 = \alpha(-\mathbf{a}^* + \mathbf{b}^*)$, where \mathbf{a}^* and \mathbf{b}^* are the tetragonal reciprocal axes of the basic cell. In recent years, the modulated structure of several melilite-type compounds was refined by means of a five-dimensional model in the superspace group $P4_2m:p4mg$ on both synthetic (Hagiya et al. 1993; Kusaka et al. 1998; Bagautdinov et al. 2000; Kusaka et al. 2001) and natural (Bindi et al. 2001b) crystals.

According to the theoretical principles of the incommensurability in crystals (Janssen and Janner 1987), the incommensurate phases can be regarded as transitional structural states between a commensurate high-temperature phase (unmodulated structure) and a low-temperature commensurate superstructure (the so-called lock-in phase). Riester and Böhm (1997) observed a nearly commensurate superstructure ($3a \times 3a \times c$; $\alpha = 0.324$) of Co-åkermanite to occur at 130 K. The structure of this lock-in phase, refined by Riester et al. (2000) in the space group $P4$, exhibits clusters of sixfold- and sevenfold-coordinated Ca atoms arranged in octagons. On the other hand, a twinned orthorhombic model ($P2_12_12$) for the commensurate structure of $\text{Ca}_2\text{CoSi}_2\text{O}_7$ ($\alpha = 0.333$) was proposed by Hagiya et al. (2001). The same supercell ($3a \times 3a \times c$) for Co-åkermanite was also observed by means of transmission electron microscopy by Schaper et al. (2001) at 100 K. More recently,

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Bagautdinov et al. (2002) showed that there is no evidence for the stabilization of the commensurate lock-in phase for the synthetic compounds $\text{Ca}_2\text{MgSi}_2\text{O}_7$ and $\text{Ca}_2\text{ZnSi}_2\text{O}_7$. However, they observed a moderate change in the modulation wavelength with decreasing temperature in the synthetic åkermanite, whereas in the synthetic hardystonite the value of the \mathbf{q} vector changes noticeably, with a plateau-like region in the temperature range 60–169 K.

Until now, in natural melilites, strong IC (incommensurate) satellites have been observed only for the åkermanite from San Venanzo, Italy (Bindi et al. 2001b), and to a lesser extent, for the hardystonite from Franklin Furnace, New Jersey (Bindi et al. 2001a). However, no investigation was performed to study a low-temperature lock-in phase transition. For this reason, we examined a crystal of melilite from San Venanzo (Italy) by low-temperature single-crystal X-ray diffraction.

Experimental

A transparent crystal ($120 \times 130 \times 100 \mu\text{m}$) of melilite was mounted on a Nonius Mach-3 single-crystal diffractometer equipped with an N_2 cooling device, using $\text{MoK}\alpha$ radiation ($50 \text{ kV} \times 28 \text{ mA}$). Unit-cell parameters, determined by centring a list of 25 main reflections ($13 < \theta < 20^\circ$) at room temperature are: $a = 7.831(1)$, $c = 5.009(1) \text{ \AA}$, $V = 307.17(2) \text{ \AA}^3$. To estimate α , 40 satellite reflections were centred at room temperature and an average value of $\alpha = 0.281(1)$ was obtained. Subsequently, the temperature was lowered to 100 K with a cooling rate of 50 K h^{-1} , and both main and satellite reflections were centred again. The same procedure was then repeated at 130, 160, 190, 220 and 250 K (heating rate 50 K h^{-1}). Before each measurement the sample was held at the specified temperature for about 30 min. The corresponding values of the α coefficient, together with the unit-cell parameters, are reported in Table 1. As a check, the crystal was cooled again at 160 K. The α value obtained did not reveal significant variation from the previous one, thus indicating that no hysteresis occurs within the temperature range examined.

In order to control the role of the kinetics in reaching equilibrium, the crystal was kept at arbitrary temperatures (100 and 160 K) for 48 h, and the α value was determined again. Although Riester et al. (2000) pointed out that the slow kinetics of the low-temperature phase transition was accounted for by a long equilibration time, no appreciable time-dependent change in intensities and/or positions of the reflections was observed.

The same crystal used for the X-ray experiment was analyzed by means of a Jeol JXA-8600 electron microprobe. Major and minor elements were determined at a 15-kV accelerating voltage and a 10-nA beam current, with variable counting times: 10 s were used for Na, 15 s for the other major elements, and 40 s for the minor

Table 1 Unit-cell parameters together with the α values for the selected crystal at different temperatures

T(K)	a (Å)	c (Å)	V (Å ³)	α
298	7.831(1)	5.009(1)	307.17(8)	0.281(1)
250	7.829(1)	5.009(1)	307.02(8)	0.2853(9)
220	7.827(1)	5.010(1)	306.92(8)	0.2883(6)
190	7.825(2)	5.010(1)	306.8(1)	0.2910(6)
160	7.822(2)	5.011(1)	306.6(1)	0.2931(9)
130	7.818(3)	5.012(2)	306.3(2)	0.2957(7)
100	7.815(4)	5.013(2)	306.2(3)	0.299(1)

elements Sr and K. Replicate analyses on different spots were performed and the crystal was found to be homogeneous within the analytical uncertainty. On the basis of the chemical data given in Table 2, the following empirical formula was obtained: $(\text{Ca}_{1.89}\text{Sr}_{0.01}\text{Na}_{0.08}\text{K}_{0.02})(\text{Mg}_{0.92}\text{Al}_{0.08})(\text{Si}_{1.97}\text{Al}_{0.03})\text{O}_7$.

Results and discussion

It is well known that in the case of two-dimensional modulated structures all the reflections can be indexed by five integers, $hklmn$, corresponding to the five-dimensional base (de Wolff 1974) $\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}_1 + n\mathbf{q}_2$, where \mathbf{a}^* , \mathbf{b}^* and \mathbf{c}^* are the reciprocal axes of the basic structure. In Fig. 1 the intensity of the satellite reflection $4300\bar{1}$, normalized to the value measured at 100 K, is plotted against the temperature. The intensity of the satellite increases with decreasing temperature, and a linear trend is clearly observed. The relative increase (22%) of the value measured at room temperature compares favourably with the variation observed by Bagautdinov et al. (2002) for the synthetic åkermanite (18%). Likewise, the \mathbf{q} vector observed at room temperature [$\alpha = 0.281(1)$] is in agreement with the value [0.2815(5)] determined by

Table 2 Electron microprobe analyses (means, ranges and standard deviations in wt% of oxides) and atomic ratios (on the basis of five cations) for the selected crystal

Oxide	wt%	Range	σ (%)	Atom	Atomic ratios
SiO_2	43.59	43.49–43.71	0.09	Si	1.973
Al_2O_3	2.01	1.85–2.08	0.05	Al	0.107
MgO	13.64	13.55–13.71	0.05	Mg	0.920
CaO	39.02	38.67–39.14	0.01	Ca	1.892
SrO	0.51	0.42–0.55	0.04	Sr	0.013
Na_2O	0.90	0.88–1.05	0.05	Na	0.080
K_2O	0.26	0.22–0.34	0.04	K	0.015
Total	99.93			Σ_{ch}	13.958

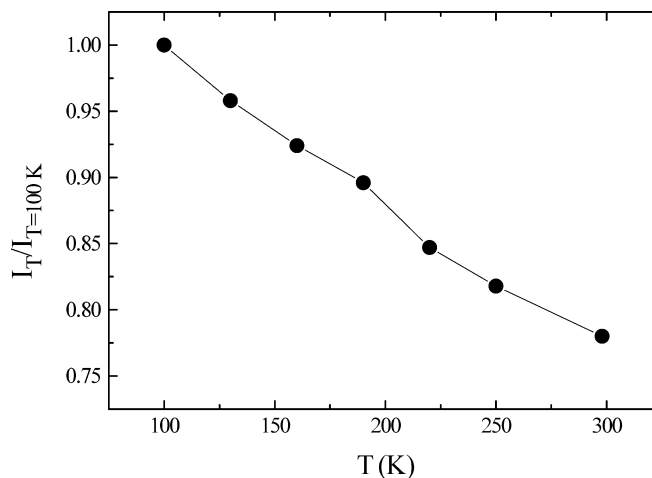


Fig. 1 Temperature dependence of the relative intensity of the satellite reflection $4300\bar{1}$ normalized to the value measured at 100 K

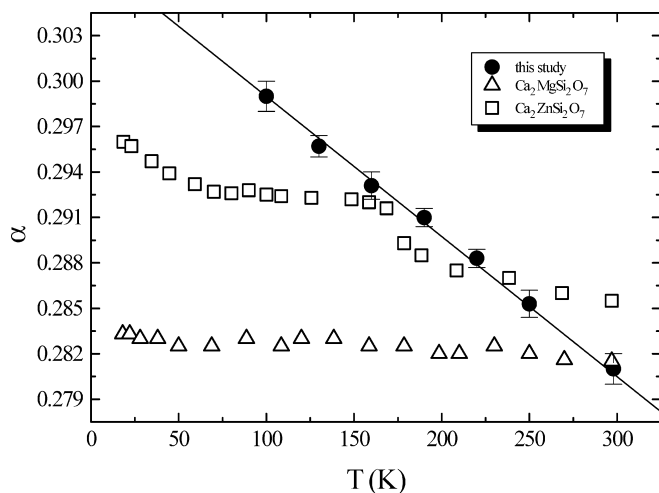


Fig. 2 Temperature dependence of the α coefficient. *Solid symbols* refer to the natural melilite studied here. *Empty symbols* refer to data from literature (Bagautdinov et al. 2002); *squares* synthetic $\text{Ca}_2\text{ZnSi}_2\text{O}_7$; *up-triangles* synthetic $\text{Ca}_2\text{MgSi}_2\text{O}_7$

Bagautdinov et al. (2002). The fact that the basic results are similar to those reported by Bagautdinov et al. (2002) is not surprising, the chemical composition being close to that of the $\text{Ca}_2\text{MgSi}_2\text{O}_7$ end member. On the contrary, as shown in Fig. 2, strong differences with respect to synthetic åkermanite are found when the temperature dependence of the α value is considered. Within the temperature range examined, the α value obtained here increases linearly (regression line: $\alpha = 0.3076(4) - 0.00009(2) [T(\text{K})]$; $r = -0.999$), from 0.281(1) at 298 K to 0.299(1) at 100 K (Table 1), without plateau-like regions. This increase (0.018) is considerably greater than the (0.001) observed by Bagautdinov et al. (2002) for the synthetic $\text{Ca}_2\text{MgSi}_2\text{O}_7$ within a comparable temperature range (from 0.2815 at 297 K to 0.2825 at 108.5 K; M. Ohmasa, personal communication). Considering the linear equation obtained, and hypothesizing that the linear trend also extends down to 0 K, one can speculate that a value of $\alpha = 0.333$ is never reached in this crystal. Since the variations of the \mathbf{q} vector are strictly related to the incommensurate–commensurate phase transition, it can be supposed that in the natural melilite studied here a low-temperature commensurate structural state is never stabilized. Additional work at ultralow temperatures (helium-cryostat) will be necessary to confirm this hypothesis. Furthermore, the continuous variation of the \mathbf{q} vector with decreasing temperature, without plateau-like regions, indicates that in the natural $(\text{Ca}_{1.89}\text{Sr}_{0.01}\text{Na}_{0.08}\text{K}_{0.02})(\text{Mg}_{0.92}\text{Al}_{0.08})(\text{Si}_{1.97}\text{Al}_{0.03})\text{O}_7$ no independent phase with a specific \mathbf{q} is stabilized within the temperature range investigated.

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