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Incommensurate–normal phase transition in natural melilite: an in situ high-temperature X-ray single-crystal study

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Abstract The structure of a natural melilite with chemical composition $(\text{Ca}_{1.87}\text{Sr}_{0.02}\text{Na}_{0.10}\text{K}_{0.02})_{\Sigma 2.01}(\text{Mg}_{0.96}\text{Al}_{0.07})_{\Sigma 1.03}(\text{Si}_{1.98}\text{Al}_{0.02})_{\Sigma 2.00}\text{O}_7$ has been investigated by X-ray single-crystal diffraction methods within the temperature range 298–773 K. The values of the α coefficient of the modulation wave vector were determined at 298 K, 323 K, 348 K, and 358 K. These values show a continuous linear decrease from 0.2833(6) at 298 K to 0.2763(9) at 358 K. The incommensurate phase undergoes a phase transition to the normal phase at 359 K. The refinements of the structure, carried out at 298 K, 348 K, 359 K, 373 K, 413 K, 463 K, 513 K, 573 K, 673 K, and 773 K, showed that the normal phase (high-temperature phase) does not significantly differ from the basic structure (the average structure of the incommensurate structure). This study confirms that in natural melilites with chemical composition close to that of åkermanite the wavelength of the incommensurate modulation increases when the temperature rises. The different behaviour of the $\mathbf{q}$ -vector as a function of temperature in natural and synthetic åkermanite is discussed.

Keywords åkermanite · Melilite · Incommensurate structures · High temperature diffraction data · $\mathbf{q}$ Vector

Introduction

The melilite group of minerals mainly consists 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 ex-

hibit the general formula $\text{X}_2\text{T}^1\text{T}^2_2\text{O}_7$ ($\text{X} = \text{Ca}, \text{Sr}, \text{Pb}, \text{Ba}, \text{Na}, \text{K}, \text{Y}$; $\text{T}^1 = \text{Be}, \text{Mg}, \text{Fe}^{2+}, \text{Cu}, \text{Co}, \text{Zn}, \text{Mn}, \text{Cd}, \text{Al}, \text{Fe}^{3+}, \text{Ga}, \text{Si}$; $\text{T}^2 = \text{Si}, \text{Ge}, \text{Al}, \text{B}, \text{Fe}^{3+}, \text{Ga}, \text{Be}$). The structure, space group $P4_21m$, 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.

The presence of a two-dimensional incommensurately modulated structure (usually indicated as IC structure) at room temperature and the transition to a non-modulated high-temperature phase (normal phase, usually indicated as N phase) in melilite were discovered independently by Hemingway et al. (1986) and Seifert et al. (1987), and have 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 two-dimensional incommensurate 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 unit cell. As a consequence, 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. The recent availability of automated programs for multidimensional crystal structure refinement (i.e., REMOS 82.1, Yamamoto 1984; JANA2000, Petricek and Dusek 2000) allowed to describe the modulated structure of both synthetic (Hagiya et al. 1993; Kusaka et al. 1998; Bagautdinov et al. 2000; Kusaka et al. 2001) and natural (Bindi et al. 2001b) melilite-type compounds with a five-dimensional model in the superspace group $P4_21m:p4mg$.

According to the theoretical principles of incommensurability in crystals (Janssen and Janner 1987), the

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IC phases can be regarded as transitional structural states between a high-temperature commensurate phase (normal phase) and a low-temperature commensurate superstructure (the so called “lock-in phase”). The variation of the q value throughout the temperature range of the stability of the incommensurate phase has been the subject of a number of studies in the recent years (Riester and Böhm 1997; Riester et al. 2000; Hagiya et al. 2001; Kusaka et al. 2001; Schaper et al. 2001; Bagautdinov et al. 2002; Bindi and Bonazzi 2003). Most of these studies focused on the determination of the low-temperature lock-in phase (Riester and Böhm 1997; Riester et al. 2000; Hagiya et al. 2001; Schaper et al. 2001); the only structural work dealing with the high-temperature IC–N phase transition, however, is that reported by Kusaka et al. (2001). These authors, studying the synthetic $\text{Ca}_2\text{CoSi}_2\text{O}_7$, $\text{Ca}_2\text{MgSi}_2\text{O}_7$ and $\text{Ca}_2(\text{Mg}_{0.55}\text{Fe}_{0.45})\text{Si}_2\text{O}_7$ melilite-type compounds within the temperature range 297–773 K, showed that the IC phase undergoes a transition to the N phase at 493 K for $\text{Ca}_2\text{CoSi}_2\text{O}_7$, at 360 K for $\text{Ca}_2\text{MgSi}_2\text{O}_7$, and at 510 K for $\text{Ca}_2(\text{Mg}_{0.55}\text{Fe}_{0.45})\text{Si}_2\text{O}_7$. Kusaka et al. (2001) pointed out that the modulated structure is characterized by the presence of six-, seven-, and eight-coordinated Ca cations forming arrays along the [001] axis, as well as complete bundles consisting of four arrays of the six-coordinated Ca ions around an array of T^1O_4 tetrahedra. Moreover, these authors showed that the normal phase (high-temperature phase) does not significantly differ from the basic structure (the average structure of the incommensurate structure).

Until now, strong IC satellites in natural melilites have been observed only in the case of the åkermanite from San Venanzo, Italy (Bindi et al. 2001b), and, to a lesser extent, of the hardystonite from Franklin Furnace, New Jersey (Bindi et al. 2001a). However, no investigation was carried out to study the IC–N phase transition and the high temperature behaviour of the structure of a natural sample. As Kusaka et al. (2004) pointed out, the in situ temperature studies are very important to clarify the structural variations accompanying a change of the q value. In addition, strong differences in the temperature dependence of the q value at low temperatures were found in the natural åkermanite with respect to the synthetic analogue (Bindi and Bonazzi 2003). For

these reasons, it seemed relevant to examine a crystal of melilite from San Venanzo (Italy) by means of single-crystal X-ray diffraction within the temperature range 298–773 K.

Experimental

A crystal (100×100×150 μm) of melilite was mounted on a Bruker-P4 single-crystal diffractometer equipped with a heating device. After each measurement, carried out using Mo $K\alpha$ radiation (50 kV×26 mA), the temperature of the heater was controlled with a chromel-alumel thermocouple (K-type) placed at the same position where the crystal was located. The temperature fluctuations were less than ± 1.5 K throughout the temperature range. It cannot be excluded, however, that slightly higher temperature variations had occurred during the data collection due to the movement of the χ -circle. Unit-cell parameters, determined by centring 40 main reflections ($12 < \theta < 18^\circ$) at room temperature, were: $a = 7.826(1)$, $c = 5.004(1)$ Å, $V = 306.48(8)$ Å³. To estimate the value of the α coefficient, 40 satellite reflections (4300 $\bar{1}$, 21010, 520 $\bar{1}$ 0 and 311 $\bar{1}$ 0, together with their tetragonal equivalent reflections) were centred at room temperature, obtaining an average value of $\alpha = 0.2833(6)$. In order to analyse the basic structure, intensity data were collected up to $\theta = 35^\circ$ with ω -scan mode and variable scan speed (Table 1). Subsequently, the temperature was raised to 323 K with a heating rate of 15 K/h, both main and satellite reflections were centred again, and the α coefficient was calculated (Table 2). The same procedure was then repeated at 348 K and 358 K. At 359 K, the intensities of the first-order satellites became too low to be measured, and only the main reflections were centred up to 773 K. The unit-cell parameters are reported in Table 2. The whole intensity data collection was carried out also at 348 K, 359 K, 373 K, 413 K, 463 K, 513 K, 573 K, 673 K and 773 K (Table 1). Before each measurement the sample was maintained at the specified temperature for about 30 min. As a check, the crystal was cooled at 323 and 298 K. The α value obtained did not reveal significant variations from the previous one [0.2831(9) and 0.2810(9) vs 0.2833(6) and 0.2809(8) at 298 K and 323 K, respectively], thus indicating that no hysteresis

Table 1 Experimental details of the data collections

Temperature (K)	298	348	359	373	413	463	513	573	673	773
Scan width ($^\circ$)	2.5	2.8	3.0	3.0	3.0	3.1	3.1	3.1	3.1	3.1
Scan speed ($^\circ/\text{min}$)	3.5–10.0	3.5–10.0	3.5–10.0	3.5–8.0	3.5–8.0	3.0–8.0	3.0–8.0	3.0–7.0	3.0–6.0	2.5–5.5
Independent refl.	437	437	437	437	438	441	441	442	447	447
Refl. with $F_o > 4\sigma(F_o)$	373	370	375	374	378	400	388	416	365	363
R_{merge}	0.094	0.095	0.094	0.092	0.092	0.093	0.092	0.067	0.089	0.089
R_{obs}	0.065	0.064	0.063	0.064	0.067	0.061	0.072	0.052	0.063	0.062
R_{all}	0.070	0.069	0.071	0.070	0.071	0.065	0.076	0.054	0.069	0.069

Table 2 Unit-cell parameters together with the α values for the selected crystal at different temperatures

$T(K)$	a (Å)	c (Å)	Vol. (Å ³)	α
298	7.826(1)	5.004(1)	306.48(8)	0.2833(6)
323	7.826(1)	5.004(1)	306.48(8)	0.2809(8)
348	7.830(1)	5.002(1)	306.67(8)	0.2782(8)
358	7.833(1)	5.004(1)	307.02(8)	0.2763(9)
359	7.832(1)	5.003(1)	306.89(8)	—
373	7.833(2)	5.004(1)	307.0(1)	—
398	7.836(2)	5.006(1)	307.4(1)	—
413	7.838(2)	5.006(1)	307.5(1)	—
438	7.843(2)	5.009(1)	308.1(1)	—
463	7.845(2)	5.011(1)	308.4(1)	—
488	7.849(1)	5.017(1)	309.08(8)	—
513	7.852(1)	5.019(1)	309.44(8)	—
573	7.857(2)	5.022(2)	310.0(2)	—
673	7.868(2)	5.027(1)	311.2(1)	—
773	7.879(2)	5.032(2)	312.4(2)	—

occurs within the temperature range examined. All the collected intensity data were treated for Lorentz-polarization effects and subsequently corrected for absorption following the semi-empirical method of North et al. (1968). The full-matrix least-squares program SHELXL-97 (Sheldrick 1997) was used for the refinement of the structure done on F^2 . The positional parameters of the synthetic åkermanite $\text{Ca}_2\text{MgSi}_2\text{O}_7$ (Yang et al. 1997) were used as starting parameters in the refinement of the structure. As expected for a chemical composition very close to that of a pure åkermanite, no improvement was achieved allowing the site-occupancy factors to vary. Therefore all refinements were done using the scattering curves of neutral Ca, Mg, Si, O (Ibers and Hamilton 1974) for X, T¹, T² and anion sites, respectively.

The same crystal used for the X-ray experiment was analysed 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 elements, Sr and K. Replicate analyses on different spots were performed and the crystal was found to be homogeneous within the analytical limits. On the basis of the chemical data given in Table 3, the following

Table 3 Electron microprobe analyses (means, ranges and standard deviations in wt% of oxides) and atomic ratios (on the basis of seven oxygens) for the selected crystal

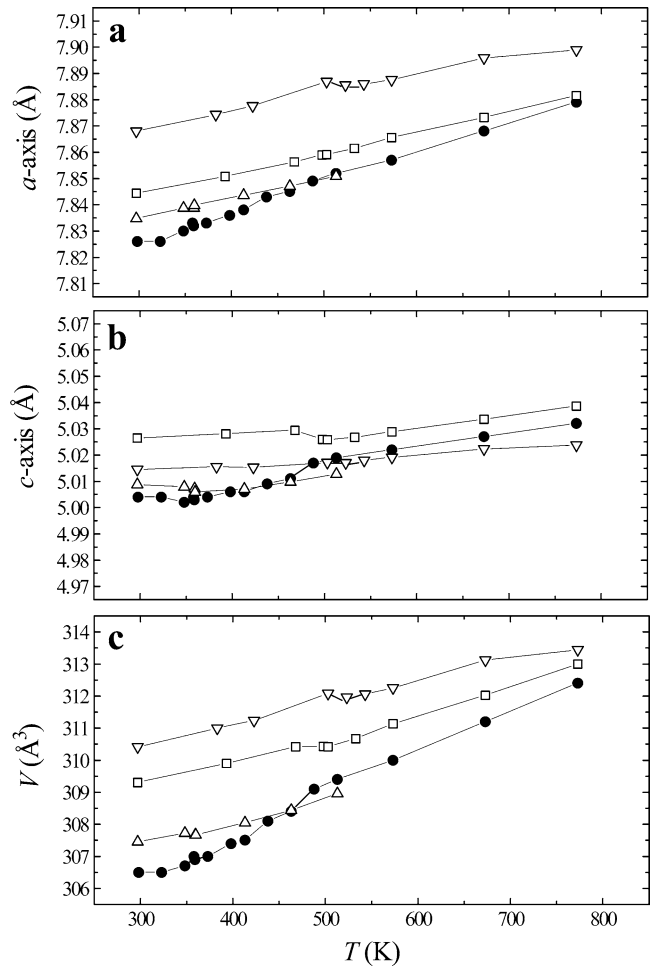
Oxide	wt%	Range	σ (%)	Atom	Atomic ratios
SiO ₂	43.30	43.11–43.76	0.09	Si	1.98
Al ₂ O ₃	1.68	1.40–2.01	0.05	Al	0.09
MgO	14.08	13.59–14.71	0.05	Mg	0.96
CaO	38.35	38.02–39.22	0.01	Ca	1.87
SrO	0.76	0.46–0.88	0.04	Sr	0.02
Na ₂ O	1.15	0.89–1.24	0.05	Na	0.10
K ₂ O	0.35	0.25–0.41	0.04	K	0.02
Total	99.67			Σ_{ch}	14.01

empirical formula was obtained: $(\text{Ca}_{1.87}\text{Sr}_{0.02}\text{Na}_{0.10}\text{K}_{0.02})\Sigma_{2.01}(\text{Mg}_{0.96}\text{Al}_{0.07})\Sigma_{1.03}(\text{Si}_{1.98}\text{Al}_{0.02})\Sigma_{2.00}\text{O}_7$.

Results and discussion

Unit-cell parameters

The variations of the unit-cell parameters with the heating temperature for the crystal examined are compared with those observed by Kusaka et al. (2001) for synthetic $\text{Ca}_2\text{CoSi}_2\text{O}_7$, $\text{Ca}_2\text{MgSi}_2\text{O}_7$, and $\text{Ca}_2(\text{Mg}_{0.55}\text{Fe}_{0.45})\text{Si}_2\text{O}_7$ (Fig. 1a–c). As shown in Fig. 1a, the a parameter shows a similar behaviour for all the samples without any remarkable discontinuity around the IC–N transition temperature. Nonetheless, the increment with temperature is higher for the natural crystal: at 513 K the a value obtained [7.852(1) Å] matches closely the value that was found for the

**Fig. 1** Variation of the unit-cell parameters with temperature. *Solid symbols* refer to the natural melilite studied here. *Empty symbols* refer to data from literature (Kusaka et al. 2001); *squares* synthetic $\text{Ca}_2\text{CoSi}_2\text{O}_7$; *upward triangles* synthetic $\text{Ca}_2\text{MgSi}_2\text{O}_7$; *downward triangles* synthetic $\text{Ca}_2\text{Mg}_{0.55}\text{Fe}_{0.45}\text{Si}_2\text{O}_7$

synthetic $\text{Ca}_2\text{MgSi}_2\text{O}_7$ [7.8509(5) Å], whereas at 773 K the value measured [7.879(2) Å] approaches the value that was observed for the synthetic Co-åkermanite [7.8815(5) Å]. On the other hand, the c parameter (Fig. 1b) shows the typical depression around the transition temperature (Fig. 1a–d in Kusaka et al. 2001), but an enhanced thermal expansion in the natural crystal with respect to synthetic åkermanite is clearly evident, thus causing a higher slope in the unit-cell volume versus temperature plot (Fig. 1c). In addition, a small but detectable change in slope in the expansion curve of the c axis is apparent between 463 K and 488 K. No significant structural change, however, seems to account for this feature.

q Modulation vector

The value of the coefficient α measured at room temperature [$\alpha = 0.2833(6)$] is close to the values determined for the synthetic åkermanite [0.2815(5) Bagautdinov et al. (2002); 0.280(2) Kusaka et al. (2001)]. This feature 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, strong differences with respect to synthetic åkermanite are found when the temperature dependence of the α value is considered. For the natural melilite, indeed, α decreases from 0.2833(6) at room temperature down to 0.2763(9) at 358 K. On the contrary, within a comparable temperature range, α increases from 0.280(2) to 0.283(8) in the synthetic $\text{Ca}_2\text{MgSi}_2\text{O}_7$ (Kusaka et al. 2001). Recently Bindi and Bonazzi (2003) reported a low-temperature study of a natural melilite with a chemical composition close to that of the crystal studied here. They found that the α value decreases linearly from 0.299(1) at 100 K to 0.281(1) at 298 K, and outlined the strong differences in the low-temperature behaviour of the $\mathbf{q}$ -vector with respect to the synthetic $\text{Ca}_2\text{MgSi}_2\text{O}_7$ (Bagautdinov et al. 2002). When low- and high-temperature data for both the natural (Bindi and Bonazzi 2003; this study) and synthetic åkermanite (Bagautdinov et al. 2002; Kusaka et al. 2001) are plotted together (Fig. 2), a different structural response of the modulated structure as a function of temperature is clearly evident. In particular, in the 100–358 K temperature range, the decrease of the α value for the natural crystal can be modelled by the linear regression $\alpha = 0.3067(7) - 0.000080(3) T \text{ (K)}$ ($r = -0.995$), whereas the corresponding data for both synthetic $\text{Ca}_2\text{MgSi}_2\text{O}_7$ and $\text{Ca}_2\text{CoSi}_2\text{O}_7$ compounds do not exhibit any significant trend to change with temperature. On the other hand, for the synthetic $\text{Ca}_2(\text{Mg}_{0.55}\text{Fe}_{0.45})\text{Si}_2\text{O}_7$ (Kusaka et al. 2001), α changes as a function of temperature with a decreasing rate very similar to that of the natural crystal. The reason for such differences remains unclear.

A different distribution of either XO_6 arrays and complete bundles composed of four XO_6 arrays and a central array of $\text{T}^{\text{I}}\text{O}_4$ tetrahedra may play a crucial role

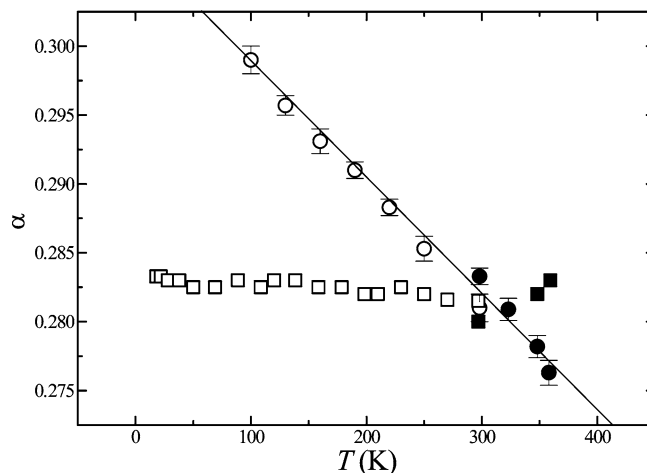


Fig. 2 Temperature dependence of the α coefficient of the modulation vector. Circles refer to natural melilite (open Bindi and Bonazzi 2003; solid this study). Squares refer to synthetic åkermanite (open Bagautdinov et al. 2002; solid Kusaka et al. 2001)

in the stabilisation of diverse IC modulated structures at different temperatures. Kusaka et al. (2001), indeed, found that the percentage of the six-coordinated Ca in $\text{Ca}_2(\text{Mg}_{0.55}\text{Fe}_{0.45})\text{Si}_2\text{O}_7$ decreases from 17.8% at 297 K to 3.8% at 423 K. Nevertheless, it was demonstrated by simulation methods (Kusaka et al. 2004) that the number of XO_6 arrays does not change sensibly as a function of the α value, whereas the number of complete bundles increases slightly with an increase of α .

Satellite intensities and transition temperature

As the temperature increases, the satellite intensities gradually decrease, and at 348 K the values are almost half of those initially observed at 298 K. At 358 K, satellite intensities were found to be very weak but still detectable and to fall to levels close to the background at 359 K. The IC–N transition temperature was consequently determined to be 359 K. This result is in excellent agreement with either the $T_{\text{IC–N}}$ value (360 K) found by Kusaka et al. (2001) or that (358 K) resulted from heat-capacity measurements (Hemingway et al. 1986) for the synthetic åkermanite.

Basic and normal structures

Fractional atomic coordinates and isotropic temperature parameters are given in Table 4. Selected bond distances and angles are in Table 5. On the whole, the structural arrangement of the basic structure of the incommensurate phase remains unchanged in the normal phase, apart from the thermal expansion. The most remarkable change observed with the increase of temperature concerns the $\langle \text{X–O} \rangle$ bond length, which remains almost constant up to the IC–N transition

Table 4 Fractional atomic coordinates and isotropic displacement parameters for the selected crystal

<i>T</i> (K)	298	348	359	373	413	463	513	573	673	773
X										
<i>x/a</i>	0.3316(1)	0.3320(1)	0.3320(1)	0.3320(1)	0.3319(1)	0.3321(1)	0.3319(1)	0.3321(1)	0.3317(1)	0.3317(1)
<i>z/c</i>	0.5065(2)	0.5059(2)	0.5057(3)	0.5055(2)	0.5057(2)	0.5058(3)	0.5055(2)	0.5057(3)	0.5058(3)	0.5058(3)
<i>U</i> _{eq}	0.0354(4)	0.0340(4)	0.0515(5)	0.0351(4)	0.0372(4)	0.0380(4)	0.0429(4)	0.0314(5)	0.0481(4)	0.0482(4)
T¹										
<i>U</i> _{eq}	0.0267(6)	0.0272(6)	0.0450(7)	0.0276(6)	0.0293(6)	0.0290(5)	0.0326(6)	0.0207(6)	0.0362(6)	0.0361(6)
T²										
<i>x/a</i>	0.1399(2)	0.1400(2)	0.1401(2)	0.1401(1)	0.1401(1)	0.1397(1)	0.1399(2)	0.1395(1)	0.1397(1)	0.1397(2)
<i>z/c</i>	0.9359(3)	0.9349(3)	0.9345(3)	0.9349(3)	0.9347(3)	0.9350(3)	0.9352(3)	0.9347(3)	0.9351(3)	0.9351(3)
<i>U</i> _{eq}	0.0259(4)	0.0257(4)	0.0434(5)	0.0265(4)	0.0277(4)	0.0276(4)	0.0318(4)	0.0181(4)	0.0336(4)	0.0337(4)
O1										
<i>z/c</i>	0.1805(9)	0.1828(9)	0.1832(9)	0.1829(9)	0.1813(9)	0.1787(9)	0.1831(9)	0.1799(9)	0.1791(9)	0.1795(9)
<i>U</i> _{eq}	0.0401(9)	0.0355(9)	0.0552(9)	0.0355(9)	0.0387(9)	0.0381(9)	0.0446(9)	0.0343(9)	0.0512(9)	0.0507(9)
O2										
<i>x/a</i>	0.1408(5)	0.1407(5)	0.1407(6)	0.1409(5)	0.1411(5)	0.1405(5)	0.1408(5)	0.1406(6)	0.1412(6)	0.1412(6)
<i>z/c</i>	0.2558(9)	0.2536(9)	0.2537(9)	0.2546(9)	0.2542(9)	0.2550(9)	0.2542(9)	0.2531(9)	0.2527(9)	0.2527(9)
<i>U</i> _{eq}	0.0367(9)	0.0372(9)	0.0550(9)	0.0379(9)	0.0412(9)	0.0422(9)	0.0484(9)	0.0376(9)	0.0551(9)	0.0558(9)
O3										
<i>x/a</i>	0.0795(6)	0.0805(6)	0.0814(7)	0.0806(6)	0.0804(6)	0.0811(6)	0.0805(6)	0.0812(7)	0.0799(6)	0.0799(6)
<i>y/b</i>	0.1868(5)	0.1871(5)	0.1874(6)	0.1861(4)	0.1873(4)	0.1873(4)	0.1866(5)	0.1877(5)	0.1876(5)	0.1872(5)
<i>z/c</i>	0.7864(6)	0.7859(5)	0.7869(8)	0.7855(6)	0.7862(6)	0.7863(7)	0.7861(6)	0.7867(7)	0.7871(7)	0.7872(7)
<i>U</i> _{eq}	0.0397(8)	0.0363(7)	0.0542(9)	0.0367(7)	0.0380(7)	0.0404(8)	0.0450(8)	0.0334(8)	0.0489(8)	0.0485(8)

T¹: (0, 0, 0); X, T² and O2: (*x*, 1/2−*x*, *z*); O1: (0, 1/2, *z*)

Table 5 Selected bond distances (Å) and angles (°) for the crystal examined

<i>T</i> (K)	298	348	359	373	413	463	513	573	673	773
T ¹ –O3 ^{a, e, f, g}	1.915(3)	1.921(3)	1.923(4)	1.917(3)	1.923(3)	1.926(3)	1.923(4)	1.931(4)	1.929(4)	1.928(4)
X–O1 ^a	2.477(4)	2.465(5)	2.463(6)	2.464(5)	2.472(5)	2.481(5)	2.471(5)	2.481(5)	2.491(5)	2.493(5)
X–O2 ^b	2.456(5)	2.466(5)	2.465(6)	2.462(5)	2.461(5)	2.470(5)	2.468(6)	2.478(6)	2.472(6)	2.475(6)
X–O2 ^{a, c}	2.705(4)	2.709(4)	2.709(5)	2.709(4)	2.714(4)	2.708(4)	2.718(4)	2.718(5)	2.730(4)	2.733(4)
X–O3 ^{b, d}	2.424(4)	2.421(4)	2.419(5)	2.421(4)	2.424(4)	2.424(4)	2.429(4)	2.430(5)	2.438(4)	2.442(4)
X–O3 ^{a, c}	2.682(5)	2.684(4)	2.691(5)	2.687(4)	2.686(4)	2.692(4)	2.694(5)	2.697(5)	2.696(4)	2.701(4)
<X–O>	2.569	2.570	2.571	2.570	2.573	2.575	2.578	2.581	2.586	2.590
T ² –O1 ^b	1.654(3)	1.659(3)	1.660(4)	1.660(3)	1.658(3)	1.651(3)	1.663(3)	1.654(3)	1.657(3)	1.660(3)
T ² –O2 ^h	1.600(4)	1.594(5)	1.597(5)	1.600(4)	1.600(5)	1.604(5)	1.601(5)	1.599(5)	1.597(5)	1.598(5)
T ² –O3 ^{b, d}	1.620(4)	1.614(4)	1.607(4)	1.621(3)	1.613(3)	1.615(4)	1.623(4)	1.614(4)	1.619(4)	1.624(4)
<T ² –O>	1.624	1.620	1.618	1.626	1.621	1.621	1.628	1.620	1.623	1.627
T ² –O1–T ²	138.77(6)	138.44(6)	138.43(6)	138.41(7)	139.02(7)	139.62(7)	138.16(8)	139.26(8)	139.46(8)	139.36(8)
T ¹ –O3–T ²	117.68(6)	118.48(7)	118.80(6)	118.35(7)	118.60(8)	118.58(7)	118.47(8)	118.73(8)	118.83(9)	118.85(9)
σ ² _{T1}	4.19	4.50	6.04	3.57	4.96	5.26	4.25	5.87	5.80	5.54
σ ² _{T2}	53.59	53.58	51.56	52.82	51.80	50.09	53.07	49.59	49.34	48.82
λ _{T2}	1.0123	1.0122	1.0118	1.0120	1.0119	1.0115	1.0120	1.0113	1.0112	1.0111

Symmetry codes are: ^a*y*, −*x*, 1−*z*; ^b*x*, *y*, *z*; ^c1/2+*x*, 1/2−*y*, 1−*z*; ^d1/2−*y*, 1/2−*x*, *z*; ^e*x*, *y*, −1+*z*; ^f−*x*, −*y*, −1+*z*; ^g−*y*, *x*, 1−*z*; ^h*x*, *y*, 1+*z*

temperature but increases linearly from 2.571 Å at 359 K to 2.590 Å at 773 K (Fig. 3). A moderate thermal expansion is observed for T¹ and, to a lesser extent, for T² tetrahedra.

As previously noted (Giuli et al. 2000; Bindi et al. 2001a, c), the modulated character of a melilite-type structure can be monitored by the analysis of the T² distortion parameters (i.e., σ² and λ, Robinson et al. 1971). Indeed, the highest values are observed for compounds having satellites with strong intensities (i.e., Ca₂CoSi₂O₇ and Ca₂ZnGe₂O₇) whereas the lowest ones

are observed for unmodulated melilites (i.e., okayama-lite Ca₂SiB₂O₇). This is related to the structural misfit between the tetrahedral sheet and the X-polyhedral layer; such a structural strain and the consequent deformation of the tetrahedral sheet increase with the average size of tetrahedral cations with respect to the size of X-cations. Since, with increasing temperature, the X polyhedron expands more than both T¹ and T² tetrahedra, the tetrahedral sheet becomes more regular and, consequently, the values of σ²_{T2} and λ_{T2} slightly decrease as a function of temperature (Table 5).

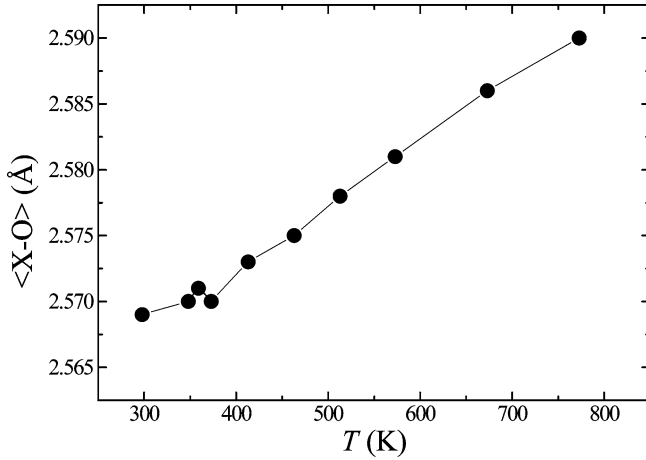


Fig. 3 Variation of the $\langle X-O \rangle$ bond length with temperature in natural melilite

Analysis of thermal displacement ellipsoids

As it is well known, an incommensurate modulation is also made evident by the analysis of the size and the shape of the displacement ellipsoids in the average structures. According to Armbruster et al. (1990), the strong anisotropy of the displacement ellipsoids of O1 and O3 oxygens in the average structure of melilites is related to the incommensurate modulation. This feature indicates wide disorder in the orientation of the tetrahedra on the scale of the basic unit cell. Therefore, $d_{\max O1}$ and $d_{\max O3}$ were calculated according to the formulae proposed by Armbruster et al. (1990),

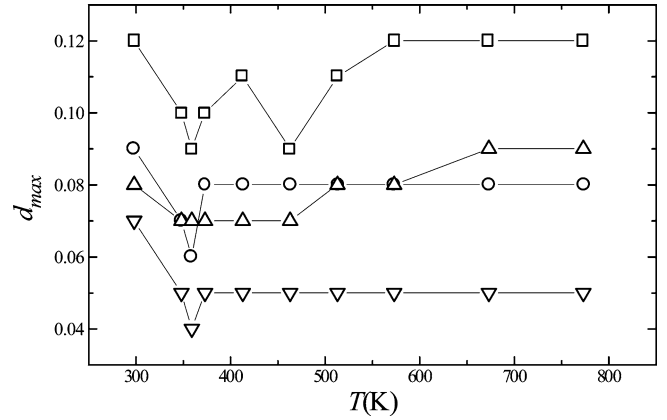


Fig. 4 Temperature dependence of the $d_{\max}$ values for X (downward triangles), O1 (squares), O2 (upward triangles), and O3 (circles) in the basic and normal structures

using the root mean square displacements reported in Table 6. In addition, analogous parameters were obtained also for O2 and X atoms (Fig. 4), while T^1 and T^2 were not taken into account due to their negligible anisotropy. As the heating temperature increased from 298 K to 359 K, the $d_{\max}$ values deeply decreased, in particular those of X, O1 and O3. Since the $d_{\max}$ value parameters are a substantial measure of anisotropy, this feature could reasonably be related to the progressive reduction of the modulated character of the fine structure. Probably due to a compensational effect related to the increase of the atomic thermal vibrations, the $d_{\max}$ values increase again after the IC–N transition temperature, reaching almost constant val-

Table 6 Root-mean square displacements of atoms in basic and normal structures for the natural melilite

T (K)	298	348	359	373	413	463	513	573	673	773
T^1										
Axis 1	0.175	0.174	0.218	0.175	0.180	0.174	0.186	0.148	0.197	0.196
Axis 2	0.175	0.174	0.218	0.175	0.180	0.174	0.186	0.148	0.197	0.196
Axis 3	0.138	0.145	0.200	0.147	0.152	0.162	0.169	0.141	0.176	0.177
X										
Axis 1	0.148	0.148	0.199	0.149	0.155	0.164	0.170	0.134	0.174	0.174
Axis 2	0.177	0.181	0.225	0.186	0.193	0.192	0.207	0.179	0.223	0.223
Axis 3	0.230	0.218	0.253	0.220	0.224	0.224	0.239	0.210	0.253	0.254
T^2										
Axis 1	0.133	0.132	0.189	0.136	0.139	0.148	0.155	0.124	0.154	0.155
Axis 2	0.169	0.167	0.215	0.170	0.174	0.171	0.186	0.135	0.191	0.191
Axis 3	0.177	0.178	0.219	0.179	0.183	0.177	0.192	0.144	0.201	0.201
O1										
Axis 1	0.134	0.134	0.184	0.135	0.141	0.160	0.164	0.124	0.164	0.164
Axis 2	0.169	0.169	0.222	0.167	0.165	0.165	0.176	0.146	0.186	0.188
Axis 3	0.272	0.246	0.287	0.246	0.262	0.248	0.276	0.257	0.304	0.299
O2										
Axis 1	0.137	0.140	0.188	0.142	0.145	0.154	0.158	0.126	0.160	0.159
Axis 2	0.185	0.190	0.232	0.194	0.204	0.201	0.216	0.198	0.239	0.237
Axis 3	0.239	0.237	0.276	0.237	0.248	0.250	0.271	0.240	0.288	0.293
O3										
Axis 1	0.150	0.148	0.202	0.151	0.152	0.169	0.183	0.146	0.181	0.182
Axis 2	0.178	0.180	0.220	0.173	0.179	0.171	0.184	0.154	0.199	0.197
Axis 3	0.255	0.234	0.271	0.240	0.242	0.252	0.260	0.235	0.272	0.271

ues approximately at the same level observed in the basic structure. As expected, O2, which usually exhibits the smallest anisotropy among the oxygen atoms in the melilite-type structures, shows a smoothed curve. These observations are in keeping with the results obtained by Kusaka et al. (2001), who observed the longest axes of the atoms in each basic structure to shorten in the proximity of transition temperatures.

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