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Twinning in natural melilite simulating a fivefold superstructure

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Additional reflections seemingly leading to a tetragonal fivefold supercell have been observed in a number of melilites. A careful examination of the collected intensity data reveals that this feature is due to the coexistence of two twin domains related by a $(1\bar{2}0)$ twin plane. Reflections of the first domain (I) with $h_{\rm b}^2 + k_{\rm b}^2 = 5n$ overlap those of the second domain (II) when both the following additional conditions are verified: $-h_{\rm b} + 2k_{\rm b} = 5n$ and $2h_{\rm b} + k_{\rm b} = 5n$. Indices of the superimposed reflections are $h_{\rm b,I}\ k_{\rm b,I}\ l_{\rm b,I}$ for the first domain, and $h_{\rm b,II} = \frac{3}{5}h_{\rm b,I} + \frac{4}{5}k_{\rm b,I}$, $k_{\rm b,II} = \frac{4}{5}h_{\rm b,I} - \frac{3}{5}k_{\rm b,I}$, $l_{\rm b,II} = l_{\rm b,I}$ for the second domain. The non-crystallographic pseudosymmetry in the melilite structure is discussed.

1. Introduction

The melilite group of minerals mainly consists of a solid solution between gehlenite, $Ca_2Al_2SiO_7$, and åkermanite, $Ca_2MgSi_2O_7$. Melilite-type compounds exhibit the general formula $X_2T^1T^2_2O_7$ (X = Ca, Sr, Pb, Ba, Na, Y; T^1 = Be, Mg, Fe^{2+}, Cu, Co, Zn, Mn, Cd, Al, Fe^{3+}, Ga, Si; T^2 = Si, Ge, Al, B, Fe^{3+}, Ga, Be). The structure, space group $P\bar{4}2_1m$, consists of a linkage of T^1 and T^2 tetrahedra forming sheets parallel to (001). Large cations occur in irregular eight-coordinated X sites between the sheets.

Melilite-type compounds have received much attention in recent years because of the presence of additional satellite reflections in the *hk*0 plane leading to a two-dimensional incommensurately modulated structure (Bindi, Bonazzi, Dusek *et al.*, 2001, and references therein). The formation of the incommensurate phase appears to be chemically controlled, being due to a structural misfit between the tetrahedral sheet and the layer of X-polyhedra (Seifert *et al.*, 1987). The lock-in phase transition into the commensurately modulated structure ($3a_{\rm b} \times 3a_{\rm b} \times c_{\rm b}$, where the index b indicates the basic unit cell of melilite) occurs in the temperature range 100–160 K (Riester *et al.*, 2000; Hagiya *et al.*, 2001; Schaper *et al.*, 2001). A melilite-related superstructure ($a = a_{\rm b}$, $b = a_{\rm b}$, $c = 3c_{\rm b}$; space group $P2_1$) was found for the low form of the synthetic $Ca_2ZnGe_2O_7$ compound (Armbruster *et al.*, 1990). In addition, a number of minerals exhibiting structures topologically very similar to that of melilite show different supercells, owing to the complex isomorphic substitutions. In particular, Ca–Na ordering in meliphanite (Dal Negro *et al.*, 1967) and in leucophanite (Cannillo *et al.*, 1967; Grice & Hawthorne, 1989) leads to supercells with $a = 2^{1/2}a_{\rm b}$, $c = 2c_{\rm b}$ (space group $I\bar{4}$) and $a = a_{\rm b}$, $b = a_{\rm b}$, $c = 2c_{\rm b}$ (space group $P2_12_12_1$), respectively. According to Grice & Robinson (1984), the superstructure in jeffreyite ($a = 2a_{\rm b}$; $b = 2a_{\rm b}$, $c = 8c_{\rm b}$; space group $C222_1$) is also probably due to the ordering of some or all of the minor constituents Na, Al and OH^- into distinct atomic positions.

In the course of a research project on the crystal chemistry of natural melilites (Giuli *et al.*, 2000; Bindi, Czank *et al.*, 2001; Bindi *et al.*, 2001; Bindi, 2001), several crystals of a wide range of chemical compositions showed additional reflections seemingly leading to a $5^{1/2}a_{\rm b} \times 5^{1/2}a_{\rm b} \times c_{\rm b}$ supercell. In this communication we report how this superstructure is not an actual state but a twinning artefact.

2. Experimental

A transparent crystal (80 × 110 × 120 µm) of melilite picked up from a haüynophyric rock from Monte Vulture, Italy (Melluso *et al.*, 1996), was selected for the X-ray analysis. A search routine, carried out with a Bruker-P4 single-crystal diffractometer, produced a list of 50 reflections yielding the following tetragonal unit cell: $a_{\rm s}$ = 17.388 (3), $c_{\rm s}$ = 5.031 (1) Å, $V_{\rm s}$ = 1520.9 (4) Å^3 ($5^{1/2}a_{\rm b} \times 5^{1/2}a_{\rm b} \times c_{\rm b}$). An intensity data collection ($5^\circ < \theta < 33^\circ$) was carried out by means of an Oxford Diffraction 'Xcalibur 2' single-crystal diffractometer (Enhance X-ray source, X-ray radiation Mo $K\alpha$, λ = 0.71073 Å) fitted with a Sapphire 2 CCD detector. A total of 2321 'frames' of data were collected at room temperature as 12 sets of ω runs with an exposure time of 30 s per frame and a frame width of 0.75°. This afforded an overall data collection of 11 003 reflections (590 unique). Data frames were processed using the *CrysAlis* software package (Oxford Diffraction, 2002) running on the Xcalibur 2 control PC.

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 an accelerating voltage of 15 kV and a beam current of 10 nA, 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 uncertainty. On the basis of five cations, the following empirical formula was obtained: $(Ca_{1.70}Sr_{0.07}Na_{0.20}K_{0.03})(Mg_{0.70}Fe^{2+}_{0.04}Al_{0.25}Fe^{3+}_{0.01})(Si_{1.92}Al_{0.08})O_{7.00}$.

3. Results and discussion

The reciprocal lattice projection reconstructed using the collected intensity data[1] showed easily visible additional reflections that could not be indexed with the basic unit cell of melilite. Indeed, all the reflections were consistent with a tetragonal supercell with $a_s = 5^{1/2}a_b$, $c_s = c_b$. An examination of the collected intensity data, however, revealed that only reflections having $h_s^2 + k_s^2 = 5n$ with $n = m^2 + p^2$ (where m and p are integers) are present. Such a typical warning sign indicated that the possibility of twinning had to be taken into consideration. In fact, the reflections can be sorted into two sets. The first set can be indexed according to the basic unit cell of melilite by the transformation matrix: $[\frac{2}{5}\,-\frac{1}{5}\,0,\ \frac{1}{5}\,\frac{2}{5}\,0,\,0\,0\,1]$. Analogously, the second set yielded the basic unit cell by the transformation matrix: $[\frac{2}{5}\,\frac{1}{5}\,0,\ \frac{1}{5}\,-\frac{2}{5}\,0,\,0\,0\,1]$. However, some reflections of both sets can be indexed by both transformations (overlapped reflections). The unit-cell parameters obtained for the two sets are a = 7.775 (2), c = 5.029 (1) Å, V = 304.00 (9) Å^3 and a = 7.777 (1), c = 5.032 (1) Å, V = 304.34 (7) Å^3, respectively. This is consistent with the coexistence of two crystal domains related by a $(1\bar{2}0)$ twin plane (basic orientation). The twin fraction was computed from the intensities of non-superimposed twin-related pairs. The resulting value $[I_I/(I_I + I_{II}) = 0.52\,(1)]$ was found to be constant within the analytical uncertainty, thus confirming the model proposed.

Fig. 1 reports a portion of the $hk0$ layer of the reciprocal lattice due to the whole twinned melilite crystal. There are three fundamentally different categories of reflections: the first one from domain I only (black), the second one from domain II only (white), and the third one grouping the overlapped reflections (black–white). The conditions for reflection overlapping are: $h_b^2 + k_b^2 = 5n$ with $-h_b + 2k_b = 5n$ and $2h_b + k_b = 5n$. The Miller indices of the overlapped reflections are $h_{b,I}\,k_{b,I}\,l_{b,I}$ for the first domain, and $h_{b,II} = \frac{3}{5}h_{b,I} + \frac{4}{5}k_{b,I}$, $k_{b,II} = \frac{4}{5}h_{b,I} - \frac{3}{5}k_{b,I}$, $l_{b,II} = l_{b,I}$ for the second domain of the twin. Overlapped reflections are surrounded by four ditetragonal clusters of alternating diffraction peaks of the two individual domains.

As shown in Fig. 2, the theoretical $(1\bar{2}0)$-twinned reciprocal lattice matches very well the distribution of the experimental intensities. The observed diffraction pattern has point symmetry in the same crystal class $\bar{4}2m$, but in a different orientation. In particular, the $\bar{4}$ axes of both I and II domains are superimposed, while the twofold rotations and reflections through a plane are oriented differently. Depending on the twin-fraction value, there are two different scenarios that must be taken into account. In a crystal with twin-fraction different from one-half $[I_I/(I_I + I_{II}) \neq 0.50]$, such a non-merohedral twinning does not involve an increase of symmetry: only the intersection of the point groups of domains I and II is maintained ($\bar{4}$ axis). On the contrary, a twinned crystal consisting of 0.50 domain I + 0.50 domain II will have the same point symmetry ($\bar{4}2m$) but in a different orientation. The symmetry exhibited by the observed diffraction pattern confirms the twin-fraction to be nearly equal to one-half.

It is well known that for twinning to occur a portion of the structure must be coherent with both twin-related orientations (I, II), so that the free energy at the twin boundary is at a minimum. In melilite this portion can be

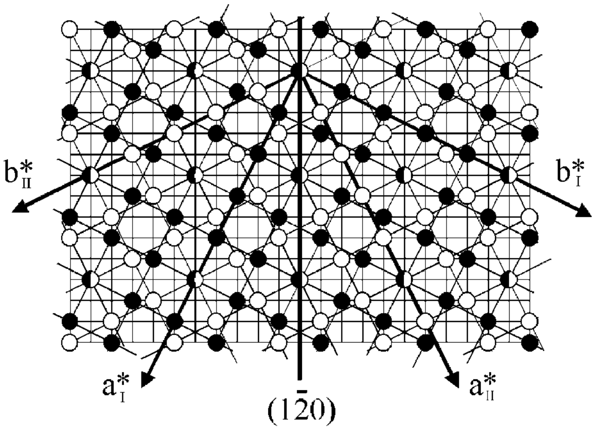

Figure 1
The $hk0$ layer of the reciprocal lattice of the twinned melilite crystal. The black-dotted lattice belongs to the first domain (I) and the open-circled lattice to the second domain (II). The thin-lined grid refers to the fivefold superlattice. The $(1\bar{2}0)$ twin-plane is indicated.

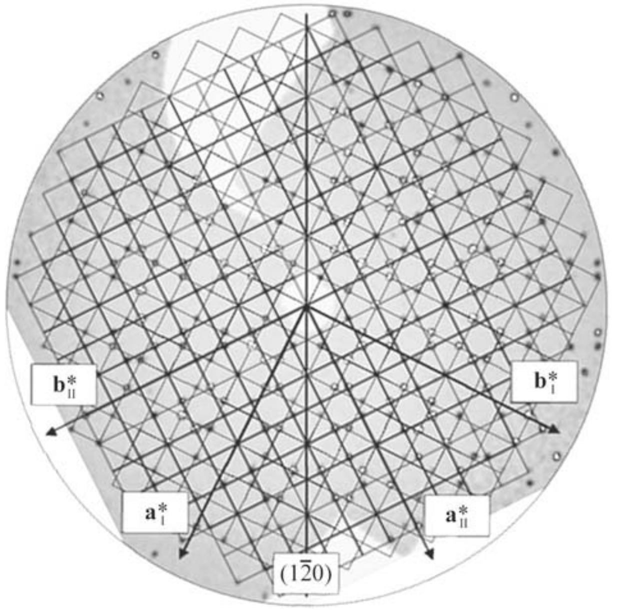

Figure 2
Experimental image of the twinned melilite crystal ($[001]_b$ projection) reconstructed using the *CrysAlis* software package (Oxford Diffraction, 2002). The grids refer to the reciprocal lattices of both twin domains. The $(1\bar{2}0)$ twin-plane is indicated.

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[1] The reciprocal lattice projection has been deposited and is available from the IUCr electronic archive (Reference: BK0126).

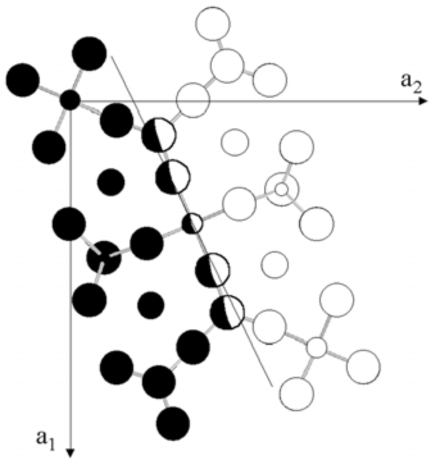

Figure 3
Structural sketch indicating pseudosymmetry in the structure of melilite (see text). Circles with increasing size represent T^2, T^1, X and O.

recognized in the structural motif sketched in Fig. 3. A pseudomirror parallel to the $(1\bar{2}0)$ twin-plane, in fact, transforms a part of it (black in Fig. 3) into its symmetry-related (white in Fig. 3). It should be stressed that such a non-crystallographic pseudosymmetry works with more or less pronounced tetrahedral rotations in the different portions of the twin boundary.

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References

Armbruster, T., Röthlisberger, F. & Seifert, F. (1990). *Am. Mineral.* **75**, 847–858.

Bindi, L. (2001). Doctoral thesis, University of Florence, Italy.

Bindi, L., Bonazzi, P., Dusek, M., Petrícek, V. & Chapuis, G. (2001). *Acta Cryst.* B**57**, 739–746.

Bindi, L., Bonazzi, P. & Fitton, J. G. (2001). *Eur. J. Mineral.* **13**, 121–125.

Bindi, L., Czank, M., Röthlisberger, F. & Bonazzi, P. (2001). *Am. Mineral.* **86**, 747–751.

Cannillo, E., Giuseppetti, G. & Tazzoli, V. (1967). *Acta Cryst.* **23**, 255–259.

Dal Negro, A., Rossi, G. & Ungaretti, L. (1967). *Acta Cryst.* **23**, 260–264.

Giuli, G., Bindi, L. & Bonazzi, P. (2000). *Am. Mineral.* **85**, 1512–1515.

Grice, J. D. & Hawthorne, F. C. (1989). *Can. Mineral.* **27**, 193–197.

Grice, J. D. & Robinson, G. W. (1984). *Can. Mineral.* **22**, 443–446.

Hagiya, K., Kusaka, K., Ohmasa, M. & Iishi, K. (2001). *Acta Cryst.* B**57**, 271–277.

Melluso, L., Morra, V. & Di Girolamo, P. (1996). *Mineral. Petrol.* **56**, 225–250.

Oxford Diffraction (2002). *CrysAlis CCD and RED*. Version 1.70. Oxford Diffraction Ltd, Oxford, UK.

Riester, M., Böhm, H. & Petricek V. (2000). *Z. Kristallogr.* **215**, 102–109.

Schaper, A. K., Schosnig, M., Kutoglu, A., Treutmann, W. & Rager, H. (2001). *Acta Cryst.* B**57**, 443–448.

Seifert, F., Czank, M., Simons, B. & Schmahl, W. (1987). *Phys. Chem. Miner.* **14**, 26–35.