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Twinning in pyromorphite: The first documented occurrence of twinning by merohedry in the apatite supergroup

Stuart J. Mills,[1,2,*] Giovanni Ferraris,[3] Anthony R. Kampf,[2] and Georges Favreau[4]

[1]Geosciences, Museum Victoria, GPO Box 666, Melbourne 3001, Australia
[2]Mineral Sciences Department, Natural History Museum of Los Angeles County, 900 Exposition Boulevard, Los Angeles, California 90007, U.S.A.
[3]Dipartimento di Scienze Mineralogiche e Petrologiche, Università degli Studi di Torino, Via Valperga Caluso 35, I-10125 Torino, Italy
[4]421 Avenue Jean Monnet, 13090 Aix-en-Provence, France

Abstract

We describe the first documented case of {10$\bar{1}$0} twinning by reflection (or by twofold rotation about [100]) or merohedry (class II) in a member of the apatite supergroup. Twinning about [100] had previously been noted for the apatite supergroup but not confirmed. Pyromorphite crystals from Puech de Compolibat, Combret, Aveyron, France, were studied by single-crystal X-ray diffraction [a = 10.0017(19), c = 7.3413(16) Å, and V = 636.0(2) Å^3, in $P6_3/m$], where twinning was confirmed with the approximate twin fraction 62:38. Subsequent inspection of the morphology confirmed the nature of the twinning. The pyromorphite crystals are typically elongate and show the faces: (2$\bar{1}\,\bar{1}$0), ($\bar{2}$110), (0001), (000$\bar{1}$), (10$\bar{1}$0), ($\bar{1}$010), (10$\bar{1}\,\bar{2}$), and ($\bar{1}$01$\bar{2}$).

Keywords: Twinning by merohedry class II, pyromorphite, Puech de Compolibat, apatite supergroup, crystal structure

Introduction

Twinning is the oriented association of two or more individuals that are related by a twin operation belonging to the point group either of the lattice (twinning by merohedry) or of a sublattice (twinning by reticular merohedry), but not to the point group of the individual. The twin operation can be either exact or approximate; in the latter case the specification *pseudo-merohedry* is applied. The twinned individuals (i.e., the twin) share a common lattice (twin lattice) and contribute to all (twinning by merohedry) or part (twinning by reticular merohedry) of the common nodes. The diffraction pattern of a twin is the weighted image in the reciprocal space of the twin lattice; accordingly, all or part of the diffraction spots are contributed by the two (or more) individuals forming the twin. In case of pseudo-merohedry, splitting of the spots is a clear indication of twinning and the contribution of each individual can be separated either mechanically, aligning only one individual on the diffractometer, or with the help of ad hoc software able to deconvolute the diffraction pattern. Instead, detection of twinning by merohedry is more sophisticated and nowadays usually depends on software that analyzes the intensity distributions of the diffraction pattern.

Catti and Ferraris (1976) classified twins by merohedry into twins of *class I* (the twin operation belongs to the Laue group of the individual) and *class II* (the twin operation does not belong to the Laue group of the individual). In class I [e.g., crystal point group $\bar{6}$, Laue group 6/m, twin operation (0001) plane], the twin operation always superimposes Laue-equivalent lattice nodes and the center of symmetry $\bar{1}$ may always be considered as twin law. In class II twins, instead, the superimposed lattice nodes (and the corresponding superimposed diffracted intensities) are not equivalent in the Laue group [e.g., crystal point group 6/m, Laue group 6/m, twin operation (10$\bar{1}$0) plane]. Apart from minor problems (cf. Catti and Ferraris 1976; Nespolo and Ferraris 2000; Ferraris et al. 2008), the diffraction pattern of class I twins corresponds to that of the individual and the structure solution follows the usual path. For class II twins, instead, the structure solution is subordinated to the identification of the twin law and subsequent deconvolution of the diffraction pattern.

A large part of the natural and synthetic compounds with an apatite-type structure crystallize in space group $P6_3/m$ (e.g., White et al. 2005; Pasero et al. 2010) and, according to the previous discussion, can in principle twin by merohedry class II via a twin element belonging to the lattice point group 6/mmm, but not to the crystal point group 6/m. For apatite, {10$\bar{1}$3}, {11$\bar{2}$3}, {11$\bar{2}$1}, and {10$\bar{1}$0} twinning is reported by Palache et al. (1951) and only {11$\bar{2}$2} was listed for pyromorphite. The first two types of twinning have been described as hybrid twins by Nespolo and Ferraris (2009) according to their recent theory (Nespolo and Ferraris 2005); {11$\bar{2}$1} twinning is by reticular pseudo-merohedry with twin index 3 and obliquity 2.06° (Nespolo and Ferraris 2009). The presence of {10$\bar{1}$0} (or [100]) twinning by merohedry in apatite was considered doubtful by Donnay et al. (1973), who reported it in synthetic "cadmium chloroapatite," $Cd_5(PO_4)_3Cl$, structurally studied by Sudarsanan et al. (1973). In this paper we report the first confirmed case of {10$\bar{1}$0} twinning by merohedry observed both morphologically and structurally in a mineral of the apatite supergroup, namely pyromorphite, $Pb_5(PO_4)_3Cl$.

* E-mail: smills@museum.vic.gov.au

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Location and geology

The Villefranche-de-Rouergue horst (Aveyron, France) is a large Pb-Zn-Ag district with 100 recognized veins, mostly located in the vicinity of the Villefranche fault (e.g., Falgayrolles). The Villefranche horst is built around two granitic units (porphyroid granite of Peyrusse-le-Roc and granodiorite of Sanvensa) intruding the metamorphic series of Lower Rouergue (orthogneiss, chlorite-bearing gneiss, and micaschists). The rim around the Villefranche granites is rich in Pb-Zn-Ag hydrothermal veins. Two localities with tin and tungsten were discovered at the Puech de Compolibat, east of the Combret hamlet in the 1970s (Fortuné and Tollon 1976). Both anomalies were investigated using trenches and drilling, however, these workings are no longer visible. The Puech is cross-cut by E–W trending quartz veins, which range in size between 1 and 2 m, and contain a Pb- and W-rich assemblage including pyromorphite.

Morphology and occurrence

The pyromorphite crystals occur as honey-colored, translucent to opaque crystals up to about 3 mm long. Understanding the unusual morphology of the pyromorphite crystals was possible after discovering the relationship between the two twin components (see below). The crystals are dominated by the opposing pair of faces $(2\bar{1}\,\bar{1}0)$ and $(\bar{2}110)$, producing the long tabular nature of the crystals (Figs. 1 and 2). The $(0001)/(000\bar{1})$ and $(10\bar{1}0)/(\bar{1}010)$ pairs are also prominent, while $(10\bar{1}\,\bar{2})/(\bar{1}012)$ may be present in some crystals. $\{10\bar{1}0\}$ twinning—equivalent to twinning by rotation about [100]—can also be observed macroscopically, although it might readily be mistaken for parallel growth unless confirmed via crystal structure determination (Fig. 3). The specimen used in this study is registered in the collections of Museum Victoria, catalog number M51647.

Pyromorphite occurs with stolzite, raspite, wulfenite, beudantite, galena, cerussite, anglesite, wolframite, mimetite, chalcopyrite, malachite, pseudomalachite, cuprite, brochantite, and native silver (Gayraud et al. 2011). Pierrot et al. (1977) also noted centimeter-size cassiterite crystals, amethyst, and wolframite uncovered during a Bureau de Recherches Géologiques et Minières (BRGM) survey of the location.

Crystal structure

Five tabular crystals of pyromorphite were studied using a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer utilizing monochromatized Mo$K\alpha$ radiation. The Rigaku CrystalClear software package (Rigaku 2002) was used for processing the structure data, including the application of an empirical absorption correction. A hexagonal unit cell corresponding to $a \sim 10.0$ and $c \sim 7.35$ Å was found by the software. Processing of the data indicated that twinning was present. Inspection of the data using PLATON, as well as using the various twin laws known for apatite supergroup minerals in SHELXL (Sheldrick 2008), confirmed the twinning by rotation about [100]. Subsequent analyses of all the crystals confirmed [100] twinning in all cases with a constant ~62:38 ratio. The structure was then solved by direct methods and then compared to that of Dai and Hughes (1989). The SHELXL-97 software was used, with neutral atom scattering factors, for the refinement of the structure from the complete set of twinned data. The data collection and structure refinement details are provided in Table 1, atomic coordinates and displacement parameters in Table 2, and selected bond distances in Table 3.

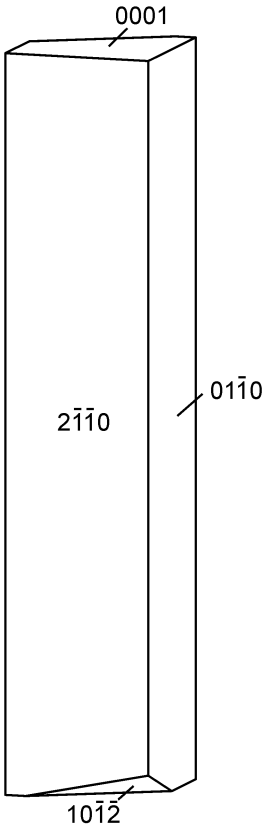

Figure 1. Crystal drawing of pyromorphite (clinographic projection in standard orientation). Note the prominent $(2\bar{1}\,\bar{1}0)$ face, responsible for the tabular morphology.

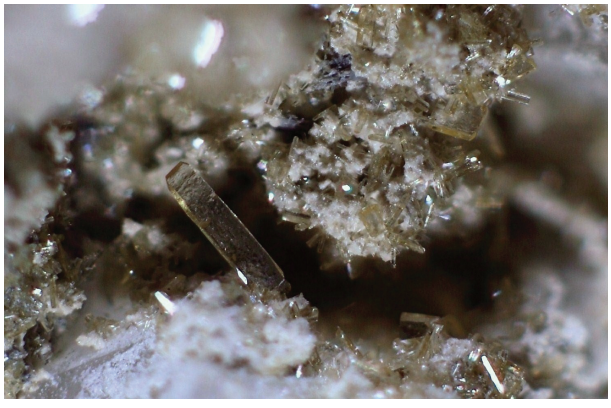

Figure 2. Long tabular pyromorphite crystal exhibiting the faces $(10\bar{1}0)$, $(\bar{1}010)$, $(2\bar{1}\,\bar{1}0)$, $(\bar{2}110)$, (0001), $(000\bar{1})$, $(10\bar{1}\,\bar{2})$, and $(\bar{1}01\bar{2})$ (center), with intergrown pyromorphite crystals (right). Field of view 1 mm across. Laurent Gayraud photograph. (Color online.)

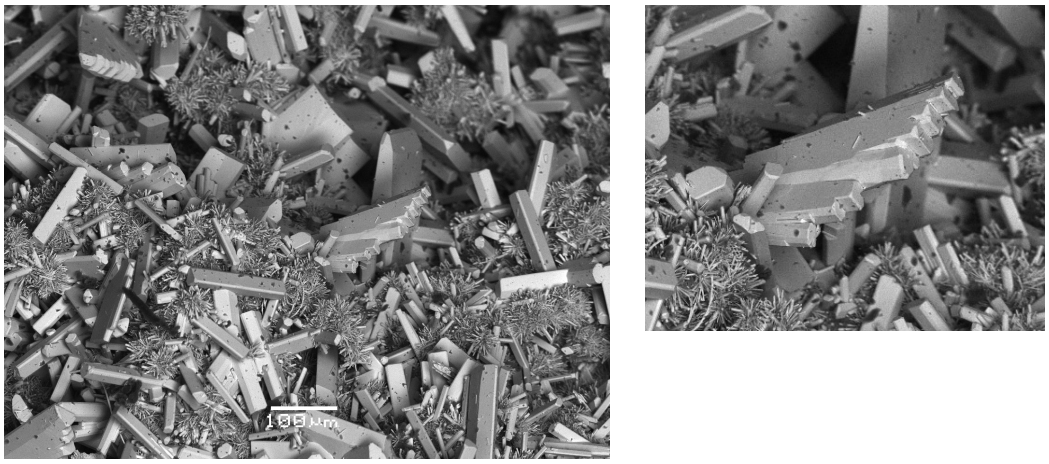

FIGURE 3. Intergrown pyromorphite crystals exhibiting {10$\bar{1}$0} twinning (**left**), with a close-up of a twinned crystal (**right**). Jean-Claude Boulliard and Vincent Bourgoin image.

TABLE 1. Data collection and structure refinement details for pyromorphite

Crystal data	
Cell parameters	a = 10.0017(19) Å
	c = 7.3413(16) Å
	V = 636.0(2) Å^3
	Z = 2
Space group	$P6_3/m$
Data collection	
Temperature (K)	293(2)
λ (Mo$K\alpha$)	0.71075
Crystal shape, size	tabular, 200 × 80 × 70 µm
2θmax (°)	54.98
Reflection range	$-12 \le h \le 12$; $-12 \le k \le 12$; $-9 \le l \le 9$
Total no. reflections	9288
No. unique reflections	529
No. reflections, $F > 4\sigma(F)$	462
Absorption coefficient	µ = 66.604 mm^{-1}
R_{merg} on F^2	0.0968
Refinement	
No. parameters refined	40
R_1, $F > 4\sigma(F)$	0.0340
R_1, all data	0.0386
wR_2 (F^2)*, all data	0.0905
Extinction coefficient	0.0014(3)
Twin fractions	62:38
GOF	1.114
$\Delta\sigma_{min}$, $\Delta\sigma_{max}$ (e/Å^3)	−1.71, 3.39

* $w = 1/[\sigma^2(F_o^2) + (0.0495P^2 + 4.3712P)]$, $P = [2F_c^2 + \mathrm{Max}(F_o^2,0)]/3$.

The average bond lengths obtained for the data (Table 3) are virtually indistinguishable from those of Dai and Hughes (1989). <P-O> is 1.543 Å, while <Pb1-O> is 2.709 Å and <Pb2-O,Cl> is 2.774 Å, compared to 1.54, 2.71, and 2.78 Å, from Dai and Hughes (1989).

DISCUSSION

This is the first documented case of {10$\bar{1}$0} twinning by reflection (or by twofold rotation about [100]) or merohedry in a member of the apatite supergroup and confirms the report by Palache et al. (1951) for twinning in the group. It should be noted that this is a new twin law for pyromorphite. Having confirmed the presence of merohedral {10$\bar{1}$0} twinning from the X-ray diffraction study of pyromorphite, multiple parallel growths of crystals that are observed in SEM (Fig. 3) and optical images (Fig. 2) can be readily interpreted as resulting from multiple {10$\bar{1}$0} twinning. Modern software often allows one to solve crystal structures using diffraction data collected on twinned crystals. If the twin law has not yet been morphologically described, the traditional (but still valid) characterization of a mineral species would greatly benefit if the nanometric information obtained from the diffraction could be complemented by a "guided" inspection of morphological pictures that nowadays can be easily obtained even at the micrometric scale.

TABLE 2. Atomic coordinates and displacement parameters (Å^2) for pyromorphite

Atom	x/a	y/b	z/c	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb1	⅓	−⅓	−0.00478(9)	0.0247(3)	0.0263(4)	0.0263(4)	0.0215(5)	0	0	0.01314(18)
Pb2	0.25475(6)	0.00601(6)	−¼	0.0244(3)	0.0176(4)	0.0209(4)	0.0344(5)	0	0	0.0093(3)
Cl1	0	0	½	0.0236(13)	0.0204(18)	0.0204(18)	0.030(3)	0	0	0.0102(9)
P1	0.4104(4)	−0.6215(4)	−¼	0.0156(7)	0.0125(16)	0.0163(17)	0.0176(16)	0	0	0.0069(14)
O1	−0.1437(11)	−0.6554(12)	¼	0.028(2)	0.017(5)	0.033(6)	0.024(6)	0	0	0.006(5)
O2	0.5248(11)	0.1154(11)	−¼	0.022(2)	0.018(5)	0.015(5)	0.024(5)	0	0	0.002(4)
O3	0.3616(9)	−0.7250(9)	−0.0802(11)	0.0286(17)	0.031(4)	0.032(4)	0.029(4)	0.012(4)	0.013(3)	0.020(4)

Now that the $\{10\bar{1}0\}$ twinning is understood, inspection of pyromorphite from other localities is possible, to find other such cases. Visual inspection of some crystals from the Les Farges mine, Ussel, Limousin, France (e.g., Brousse 1982), show some similar characteristics to those from Puech de Compolibat, indicating $\{10\bar{1}0\}$ twinning may be present. Further analysis is required, however, to confirm this twinning.

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