Zeitschrift für Kristallographie 201, 223–234 (1992)

Reppiaite, $Mn_5(OH)_4(VO_4)_2$, a new mineral from Val Graveglia (Northern Apennines, Italy)

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Received: June 25, 1991; revised: October 8, 1991

Reppiaite / New mineral / Physical and chemical data / Powder pattern / Structure refinement

Abstract. Reppiaite occurs in manganese ores at the Gambatesa Mine, near Reppia village (Val Graveglia, Italy), mainly associated with a Mn-sheet silicate and Mn–Ca-carbonates. It was found in small amounts of very minute tabular crystals, (100) flattened, grown in fracture. Reppiaite, with ideal formula $Mn_5(OH)_4(VO_4)_2$, crystallizes in $C2/m$ space group with $a =$ 9.604(2) Å, $b = 9.558(2)$ Å, $c = 5.393(1)$ Å and $\beta = 98.45(1)°$. The strongest lines in the X-ray powder pattern are $d_{13\bar{1}} = 2.68$ Å and $d_{200} = 4.76$ Å. It is orange-red in colour, transparent, biaxial negative with 2 V large and slightly pleochroic. Microprobe analyses reveal a partial As substitution for V, leading to the empirical formula $Mn_{5.01}(OH)_{3.98}[(V_{1.65}As_{0.35})O_{8.02}]$. The crystal structure of reppiaite is constructed of a quasi cubic close-packing of oxygens and hydroxyl groups, whose layers are stacked parallel to (100). The structure, refined to $R = 0.038$, consists of Mn octahedral layers bound together by isolated (V,As) tetrahedra and hydrogen bonds. Among the minerals, whose chemical formula has the same atomic proportions of reppiaite, only cornubite shows very similar structural features.

Introduction

A systematic study on manganiferous mineralizations in ophiolitic sequences of Eastern Liguria (Italy) led to identify a new manganese vanadate mineral. Its chemical features are related to different natural compounds, such as turanite, $Cu_5(VO_4)_2(OH)_4$ (Guillemin, 1956), cornubite, $Cu_5(AsO_4)_2(OH)_4$ (Claringbull, Hey and Davis, 1959; Tillmanns, Hofmeister and Petitjean, 1985), cornwallite, $Cu_5(AsO_4)_2(OH)_4$ (Berry, 1951; Claringbull et al., 1959), arsenoclasite, $Mn_5(AsO_4)_2(OH)_4$ (Moore, 1967; Moore and Molin-Case, 1971) and the three natural polymorphs of $Cu_5(PO_4)_2(OH)_4$: pseudomalachite (Ghose, 1963; Shoemaker, Anderson and Kostiner, 1977), reichenbachite (Sieber, Tillmanns and Medenbach, 1987) and ludjibaite (Piret and Deliens, 1988). Also the analogous synthetic polymorphs of $Cu_5(PO_4)_2(OH)_4$ are known (Anderson, Shoemaker, Kostiner and Ruszala, 1977; Shoemaker, Anderson and Kostiner, 1981; Shoemaker and Kostiner, 1981). However, the crystal structure of reppiaite is different from those reported for the above referenced minerals.

The new mineral is named reppiaite for Reppia, a village near the Gambatesa Mine. The mineral and the name have been approved by the IMA Commission on New Minerals and Mineral Names. Type material is deposited in the collection of the Dipartimento di Scienze della Terra, sezione di Mineralogia, Università di Genova.

Occurrence and genetic environment

Small amounts of very minute reppiaite crystals are found in few fractures cutting Mn-bearing cherts outcropping in the Gambatesa Mine (Val Graveglia, Eastern Liguria, Italy). These fractures crosscut hausmannite-tephroite-carbonate-bearing mineralizations. Reppiaite occurs associated with a Mn-sheet silicate, showing caryopilite-like chemical composition, and Mn–Ca-carbonates; the values of the Mn/Ca ratio for these carbonates fill two distinct compositional ranges around 60 and 85 mole% $MnCO_3$, respectively. Locally, native copper and rare grains of V-garnet are found.

The crystallization of fracture filling reppiaite is related to hydrothermal deposition from circulating V–As-enriched solutions. Such a fact is also testified by the occurrence in these manganiferous ores of small amounts of many others V- and As-bearing minerals, as sarkinite (Cortesogno, Lucchetti and Penco, 1979), tiragalloite (Gramaccioli, Griffin and Mottana, 1980), saneroite (Lucchetti, Penco and Rinaldi, 1981), medaite (Gramaccioli, Griffin and Mottana, 1982), palenzonaite (Basso, 1987), gamagarite (Basso, Palenzona and Zefiro, 1987), volborthite (Basso, Palenzona and Zefiro, 1988) and Sr-tangeite (Basso, Palenzona and Zefiro, 1989). The hydrothermal event could take place in conditions of decreasing thermality with respect to those of prehnite-pumpellyite facies metamorphism, that affected the ophiolitic sequences of the Northern Apennines (Cortesogno et al., 1979).

Table 1. Optical and physical properties of reppiaite.

Biaxial negative
$\alpha' = 1.803(2)$
$\gamma' = 1.810(5)$
Minimum (α') and maximum (γ') indices measured on (100) face
[at 25°C, for 589 nm]
$2V_{obs}$ = large
Pleochroism [(100) face]:
very weak, yellow-orange to deep orange
Dispersion: medium

Colour: orange-red
Streak: orange-yellow
Lustre: vitreous
Transparent, non-fluorescent

Cleavage: none observed
Hardness [$VHN_{(15)}$ on (100) face]:
mean 100 kg/mm^2
range 90 – 110 kg/mm^2
Density (meas.): 3.92 g/cm^3
(heavy liquids)
Density (calc.): 3.91 g/cm^3
(from structural analysis)

Optical and physical properties

Reppiaite occurs as very minute tabular crystals, {100} flattened, with irregular contour. The crystals, at most 50 μm thick, generally show striation on (100) face, the size of which does not exceed 300 μm in diameter. Under polarizing microscope, the reppiaite crystals commonly appear as fine-grained aggregates, with size of individual grains under 10 μm. Generally the tablets are fairly transparent, but some difficulties were encountered in optical measures owing to morphology, size and amount of the material. Therefore the optical data as pleochroism and refractive indices refer to measures performed only on (100) face. Moreover, the absence of observable cleavage or other crystallographic directions prevents the optical orientation. Micro-hardness was measured by a Leitz Durimet microscope on (100) face only; the VHN values obtained correspond to a Mohs hardness slightly below 3.

The optical and physical properties of reppiaite are summarized in Table 1.

Chemical composition

Ten spot analyses on two different crystals were performed by means of a PHILIPS SEM 515 electron microscope equipped with an EDAX PV9100 spectrometer in energy dispersive mode, with an accelerating voltage of 15 kV and beam current of about 2 nA. Rhodonite (Mn), metallic vanadium (V) and arsenopyrite (As) were used as reference standards for the elements in brackets. Other elements are below their detection limits. The ranges of the measured weight percents and the mean chemical composition are reported in Table 2. The H_2O content was not determined by analytical

Table 2. Chemical data of reppiaite.

	Range (wt%)	Mean (wt%)
MnO	60.55 – 61.21	61.17
V_2O_5	23.27 – 25.90	25.79
As_2O_5	6.50 – 9.80	6.87
Total		93.83

method due to the paucity of material; the water weight percent was evaluated to reach a total amount of 100% and it is in agreement with the value inferred from the structural analysis. The empirical formula, based on 12 oxygen atoms, is $Mn_{5.01}(OH)_{3.98}[(V_{1.65}As_{0.35})O_{8.02}]$.

X-ray powder data

The X-ray powder diffraction pattern was obtained by a Gandolfi camera using a Mn-filtered Fe*Kα* radiation ($\lambda = 1.93728$ Å). Relative intensities were assigned by visual estimate and the reflections were indexed on the basis of the pattern calculated by the Lazy Pulverix program (Yvon, Jeitschko and Parthé, 1977). The input data were the unit cell and the structural model derived from the structure refinement. The scattering factors for neutral atoms were used and the anomalous dispersion correction was applied.

Powder data, reported in Table 3, give the refined cell parameters $a = 9.614(4)$ Å, $b = 9.561(3)$ Å, $c = 5.396(3)$ Å and $\beta = 98.39(1)°$.

Structure solution and refinement

The X-ray data collection was performed on a flat crystal, measuring about $205 \times 51 \times 19$ μm, by means of an ENRAF-NONIUS CAD-4 automatic single-crystal diffractometer. The lattice parameters were determined and refined, using 25 reflections within the angular range $18° < \vartheta < 25°$. Diffraction intensities were measured up to $\vartheta = 30°$, using graphite monochromatized Mo*Kα* radiation ($\lambda = 0.71069$ Å) and operating in the $\omega - \vartheta$ scan mode. Absorption correction was applied, using the ψ scan method (North, Phillips and Scott Mathews, 1968). The Laue symmetry of the reciprocal lattice is $2/m$ and systematic extinctions are present for $hkl{:}\,h + k = 2n + 1$. The existence of a center of symmetry was proved by solution of the crystal structure, and the space group is therefore $C2/m$. The Patterson map was used to solve the structure. Strong vectors gave the cation positions; oxygen atoms were located from short vectors, indicative

Table 3. X-ray powder diffraction data of reppiaite (*d* in Å).

h	*k*	*l*	Calculated[a]		Measured[b]		*h*	*k*	*l*	Calculated		Measured	
			d	*I*	*d*	*I*				*d*	*I*	*d*	*I*
2	0	0	4.750	81	4.76	S	3	3	1	1.997	7	1.996	VW
2	0	$\bar{1}$	3.839	16	3.84	VVW	2	2	2	1.993	8		
2	2	0	3.369	38	3.37	W	3	3	$\bar{2}$	1.814	6	1.812	VVW
2	0	1	3.314	30	3.31	W	4	0	2	1.657	10	1.659	VVW
3	1	0	3.006	34	3.00	M	3	5	0	1.636	6	1.636	VVW
2	2	$\bar{1}$	2.993	26			5	3	$\bar{1}$	1.619	17	1.621	VW
3	1	$\bar{1}$	2.791	30	2.793	VW	0	6	0	1.593	19	1.593	VW
2	2	1	2.723	27	2.726	VW	1	3	$\bar{3}$	1.565	39	1.565	M
1	3	$\bar{1}$	2.683	100	2.680	VS	5	3	1	1.508	33	1.510	M
0	0	2	2.667	50	2.656	M	6	0	$\bar{2}$	1.459	15	1.459	VW
3	1	1	2.475	13	2.483	VW	2	6	1	1.436	4	1.437	VW
3	3	0	2.246	9	2.251	VW	0	6	2	1.368	7	1.369	VW
2	0	2	2.192	28	2.197	W	4	0	4	1.096	8	1.096	W
3	3	$\bar{1}$	2.152	50	2.155	M	8	2	1	1.095	3		
4	2	$\bar{1}$	2.072	9	2.075	VVW	7	3	$\bar{3}$	1.094	5		
							6	6	$\bar{2}$	1.076	15	1.076	W

[a] From single crystal X-ray analysis using the LAZY PULVERIX program (Yvon et al., 1977).

[b] Intensities assigned by visual estimate.

Table 4. Crystal and X-ray data for reppiaite.

Idealized formula	$Mn_5(OH)_4(VO_4)_2$
Formula from structure refinement	$Mn_5(OH)_4[(V_{0.89}As_{0.11})O_4]_2$
Z	2
Space group	$C2/m$
a (Å)	9.604(2)
b (Å)	9.558(2)
c (Å)	5.393(1)
β (°)	98.45(1)
V (Å^3)	489.7
μ (Mo$K\alpha$, mm^{-1})	8.36
Measured reflections:	
$-13 \leq (h,k) \leq 13, 0 \leq l \leq 7$	1575
Independent reflections	760
R (after merging)	0.052
Observed reflections ($I > 3\sigma_I$)	500
Variables	52
R (observed)	0.038
R (all)	0.075

Table 5. Atomic coordinates and equivalent isotropic temperature factors (Hamilton, 1959) for reppiaite.

Atom	Site occupancy	*x*/*a*	*y*/*b*	*z*/*c*	B_H (Å^2)
Mn1	1.0	0.0	0.0	0.0	1.09
Mn2	1.0	0.0	0.3471(2)	0.0	0.76
Mn3	1.0	0.0	0.1818(2)	0.5	0.90
V As	0.89(2) 0.11	0.3111(2)	0.0	0.4464(3)	0.45
O1	1.0	0.3917(5)	0.3247(5)	0.1336(8)	0.88
O2	1.0	0.1281(8)	0.0	0.3855(13)	0.73
O3	1.0	0.3748(8)	0.0	0.1618(12)	0.77
O4	1.0	0.1332(5)	0.3552(5)	0.3817(8)	0.82

of cation-oxygen bonds. Convergence was obtained through eight cycles of least squares refinement, carried out by a largely modified version of the ORFLS program (Busing, Martin and Levi, 1962) and assigning unitary weights to the reflections. The scattering factors for neutral atoms, including anomalous contributions, were taken from the International Tables for X-ray Crystallography. Total occupancy was fixed for manganese in the three octahedral sites. Scale factor, occupancy of V vs. As in tetrahedral site, coordinates and temperature factors were simultaneously derived. The anisotropic temperature factors were introduced after the fourth cycle. Experimental details and structure refinement results are summarized in Tables 4, 5 and 6.[1]

A difference Fourier synthesis revealed a peak of about 1.1 e/Å^3 at 0.297, 0.344, 0.125, which on the basis of geometrical considerations and formula balance turned out to be a hydrogen atom, leading to a bond distance O1 – H = 0.92 Å. The H atom is involved in a weak hydrogen bond, whose geometry is characterized by the distances O1 – O4 = 3.003(7) Å and H ... O4 = 2.25 Å and the angle O1 – H ... O4 = 138.9°. The resulting value of the shortest H – H distance is 2.35 Å.

Structure description

The three average Mn – O distances (Table 6), compared with the mean octahedral bond length reported in literature for Mn^{2+}, virtually exclude

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[1] Additional material to this paper can be ordered referring to the no. CSD 55717, names of the authors and citation of the paper at the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany.

Table 6. Selected interatomic distances (Å) and angles (°) in reppiaite.

4 Mn1–O1	2.151(5)	2 Mn3–O1	2.094(4)
2 –O2	2.255(7)	2 –O2	2.267(5)
Average	2.186	2 –O4	2.243(5)
		Average	2.201
2 O1–O1′	2.699(9)		
2 –O1″	3.351(10)	2 O1–O2	2.984(7)
4 –O2	2.984(7)	2 –O2″	3.117(8)
4 –O2′	3.244(8)	2 –O4	3.035(7)
		2 –O4″	3.167(6)
2 O1–Mn1–O1′	77.68(25)	O2–O2′	2.911(14)
2 –O1″	102.32(25)	2 –O4	3.396(5)
4 –O2	85.20(16)	O4–O4′	3.022(10)
4 –O2′	94.80(16)		
Average	90.0	2 O1–Mn3–O2	86.25(23)
		2 –O2″	91.16(24)
		2 –O4	88.75(18)
2 Mn2–O1	2.125(5)	2 –O4″	93.75(19)
2 –O3	2.157(5)	O2–Mn3–O2′	79.91(28)
2 –O4	2.259(5)	2 –O4	97.69(17)
Average	2.180	O4–Mn3–O4′	84.70(25
		Average	89.98
O1–O1′	2.699(9)		
2 –O3	3.112(5)		
2 –O4	3.035(7)	V–O2	1.740(7)
2 –O4′	3.247(6)	–O3	1.734(6)
O3–O3′	3.173(13)	2 –O4	1.707(5)
2 –O4	2.935(8)	Average	1.722
2 –O4′	3.232(7)		
		O2–O3	2.812(10)
O1–Mn2–O1′	78.83(27)	2 –O4″	2.811(8)
2 –O3	93.24(17)	2 O3–O4″	2.835(7)
2 –O4	87.56(17)	O4–O4″	2.768(9)
2 –O4′	95.50(17)		
O3–Mn2–O3′	94.69(24)	O2–V–O3	108.10(32)
2 –O4	83.26(21)	2 –O4″	109.25(21)
2 –O4′	94.05(21)	2 O3–V–O4″	110.95(19)
Average	90.06	O4–V–O4″	108.30(32)
		Average	109.47

Table 7. Empirical bond valences for reppiaite.

	Mn1	Mn2	Mn3	($V_{0.89}As_{0.11}$)	Σ
O1	0.38	0.40	0.44		1.22
O2	0.28		2×0.28	1.06	1.90
O3		2×0.37		1.19	1.93
O4		0.28	0.29	1.28	1.85

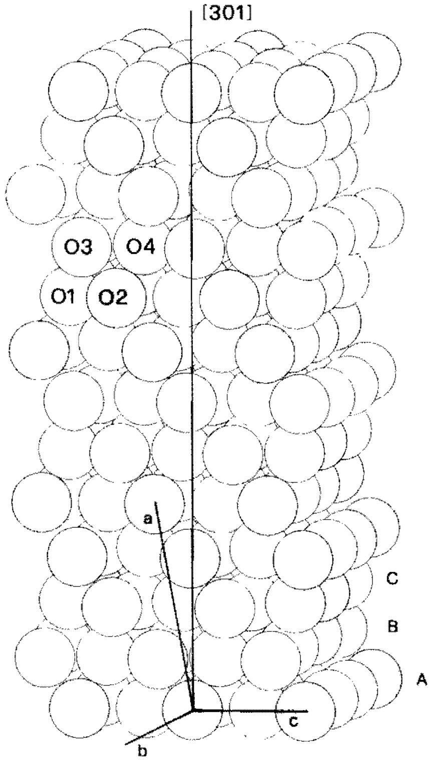

Fig. 1. Orthographic drawing of oxygen close-packing in reppiaite; a value of 1.38 Å is assigned to the oxygen radius (Shannon, 1976).

the presence of Mn in the 3+ oxidation state. The dimensions of the tetrahedron are substantially in agreement with the final V/As occupancy ratio from refinement. Therefore V^{5+} may be retained the dominant ion in the tetrahedral site population for the crystal submitted to structure analysis. Table 7, where the empirical bond valences are estimated from the resulting refined structure according to Brown and Altermatt (1985), also confirms the cationic oxidation state as well as the hydroxyl group involving the O1 oxygen atom.

Using the three different approaches suggested by Brown and Altermatt (1985) for estimating the O1 – H and H...O4 bond valences, the values of about 0.9 and 0.1 are obtained, respectively, and the resulting bond strength sums for O1 and O4 atoms are acceptably near to their ideal values of 2 valence units.

The structure of reppiaite is based on an approximately cubic close-packed array of oxygen atoms whose layers are parallel to (100). The

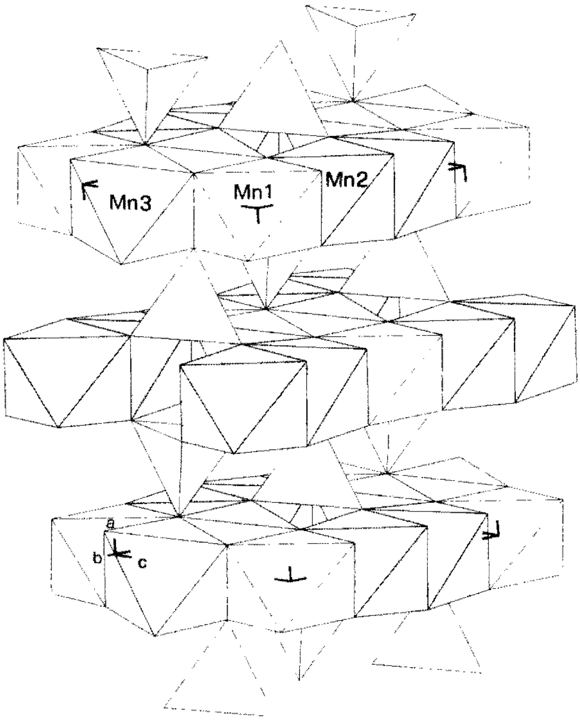

Fig. 2. Orthographic drawing of polyhedra in the reppiaite structure.

stacking sequence of oxygen layers, along the mean direction [301] forming an angle of 87.67° with [001], is related to the lattice parameters geometry as shown in Figure 1.

The polyhedral framework consists of alternate octahedral and tetrahedral layers: in the octahedral layers, with formula $[Mn_5(OH)_4O_8]^{-10}$, five-sixth of the sites are occupied by manganese, whereas (V, As) atoms fill only one-sixth of the cavities in the tetrahedral layers. The structural arrangement can be described in terms of octahedral layers bound together by isolated tetrahedra, located both over and under every empty octahedral cavity. Each tetrahedron shares with an octahedral layer three oxygens surrounding the empty cavity and the fourth oxygen with an adjacent octahedral layer (Fig. 2).

In addition, hydrogen bonds participate to join contiguous octahedral layers. Since vanadium represents the major element occupying the tetrahedral site and accounting for the actual groups of atoms present in the crystal, the ideal structural formula proposed for reppiaite is $Mn_5(OH)_4(VO_4)_2$.

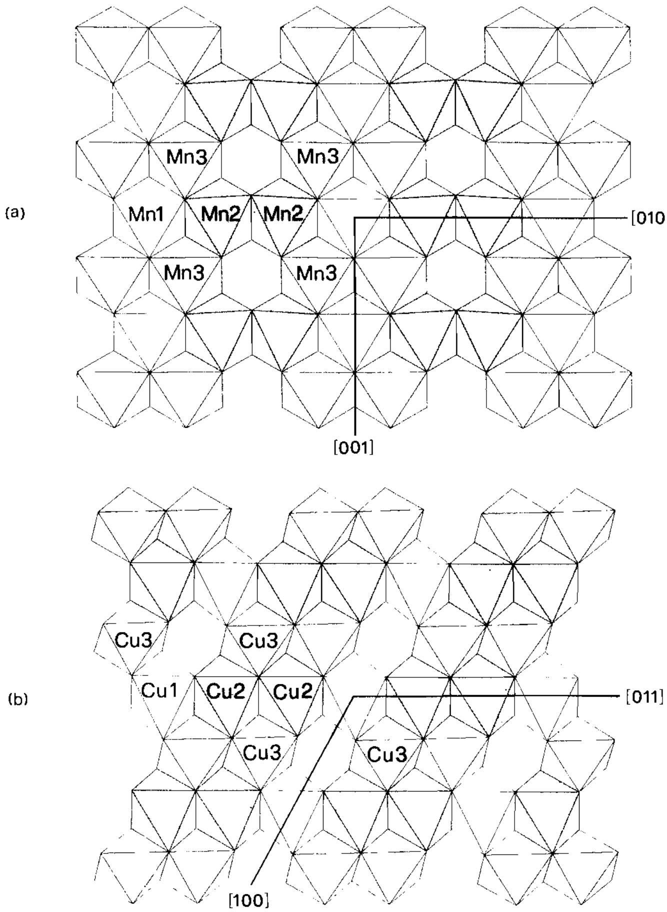

Fig. 3. Orthogonal views of octahedral layers in reppiaite and cornubite: a) (100) layer for reppiaite, b) (0$\bar{1}$1) layer for cornubite.

A comparison from the structural point of view among reppiaite and the other minerals, with identical atomic proportions in chemical formula, leads to some considerations. It can be emphasized that no similarity is observed between the structures of reppiaite and arsenoclasite, $Mn_5(AsO_4)_2(OH)_4$. Also the three polymorphs of $Cu_5(PO_4)_2(OH)_4$ show peculiar structural differences from reppiaite. In fact for example in all these minerals the layers of copper polyhedra are joined by phosphate tetrahedra sharing two vertices in each layer (Shoemaker and Kostiner, 1981). Conversely cornubite is closely related to reppiaite. The common structural feature is represented by the same manner of connecting pairs of octahedral layers via tetrahedral corners and hydrogen bonds. The two structures, both formally based on close-packing of oxygen atoms, substantially show a different arrangement of octahedra within the respective layers. In the octahedral layer of both structures a direction can be found, [010] in reppiaite and [011] in cornubite, along which sequences of all filled octahedral cavities alternate with sequences where only two-third of the octahedral sites are occupied. For reppiaite the previous sequences consist, respectively, in chains of Mn1Mn2Mn2... octahedra and Mn3 empty Mn3 ...octahedra, as shown in Figure 3a. The different arrangement of the analogous chains, made by Cu1Cu2Cu2... and Cu3 empty Cu3 ...octahedra, in the corresponding cornubite layer (Fig. 3b) may be derived from reppiaite starting for example from the upper chain in Figure 3a and applying successively to each chain an incremental shift of one octahedral cavity along [010]. This chain displacement lowers the point symmetry from $2/m$ in reppiaite to $\bar{1}$ in cornubite.

Acknowledgment. This study was supported by the Ministero dell'Università e della Ricerca Scientifica e Tecnologica. Thanks are due to Mr. G. Frenna and Mr. G. Corallo, local mineral collectors who provided a sample of reppiaite.

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