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Short Communication

Structure refinement of Gysinite $La_{0.16}Nd_{1.18}Pb_{0.66}(CO_3)_2(OH)_{1.34} \cdot 0.66\ H_2O$

Bernard Chabot[a] and Halil Sarp[b]

[a] Laboratoire de Cristallographie aux Rayons X, Université de Genève,
24, quai Ernest Ansermet, CH-1211 Genève 4 (Switzerland)
[b] Département de Minéralogie du Muséum d'Histoire Naturelle,
1, route de Malagnou, CH-1211 Genève 6 (Switzerland)

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Hydrous carbonate / Isostructural to Ancylite and to hydroxy-carbonates of R.E. elements

Abstract. The crystal structure of Gysinite has been determined at the composition $La_{0.16}Nd_{1.18}Pb_{0.66}(CO_3)_2(OH)_{1.34} \cdot 0.66\ H_2O$, $M_r = 483.85$. Orthorhombic space group *Pmcn*, $a = 5.0028(8)$, $b = 8.555(1)$ and $c = 7.2392(8)$ Å, $V = 309.83$ Å^3, $Z = 2$, $D_x = 5.18$ g · cm^{-3}. Single crystal X-ray refinement, Mo$K\alpha$, $\lambda = 0.7107$ Å, $\mu = 34.8$ mm^{-1}, $F(000) = 425.4$, room temperature, $R = 0.065$ for 368 independent contributing reflections. The Pb-containing Gysinite is isostructural to the Ca and Sr analog Ancylite and to synthetic hydroxy-carbonates of lanthanides elements.

Introduction

Gysinite is a new hydrous carbonate containing lead and rare earth elements. The mineral has been found in a sample of the Département de Minéralogie du Muséum d'Histoire Naturelle of Geneva coming from Shinkolobwe (Shaba – Zaïre). Mineralogical informations on Gysinite can be found elsewhere (Sarp and Bertrand, 1985). In this paper we report its crystal structure which is shown to be isotypic to Ancylite $(RE)_x(Ca,Sr)_{2-x}(CO_3)_2(OH)_x\ (2-x)H_2O$ (Dal Negro, Rossi and Tazzoli, 1975) and to synthetic compounds RE CO_3 (OH) (Sawyer, Caro and Eyring, 1973).

Experimental and Discussion

Pseudo-octahedrally shaped single crystal with 17 µm mean diameter; Philips PW1100 four circle diffractometer with monochromated Mo – $K\alpha$

radiation; Laue symmetry *mmm*. The lattice parameters (a = 5.0028(8), b = 8.555(1) and c = 7.2392(8) Å), were determined using the diffractometer from 35 reflections with $17° < 2\theta < 28°$, and can be compared with those previously given (a = 5.04, b = 8.50 and c = 7.25 Å) by Sarp and Bertrand, 1985. Data collection with $\sin\theta/\lambda < 0.7024$ Å^{-1}; Lorentz polarization and spherical absorption corrections (2.32 < S.A.C. < 2.39); $\omega - 2\theta$ scans; systematic absences $hk0{:}h + k = 2n + 1$, $h0l{:}l = 2n + 1$, $h00{:}h = 2n + 1$, $0k0{:}k = 2n + 1$ and $00l{:}l = 2n + 1$ lead to two possible space groups $P2_1cn$ and *Pmcn*; 404 independent reflections measured: 368 contributing reflections, 300 with $|F_o| > 3\,\sigma(F_o)$ and 68 less than with $|Fo| < |Fc|$. Structure refined in space group *Pmcn* using point positions of Ancylite, full matrix least-squares using F values; 17 parameters: one scale factor, 16 positional and thermal isotropic parameters. R = 0.065, R_w = 0.071; S = 4.03 and $w = \exp[7.0(\sin\theta/\lambda)^2]/\sigma^2(F_o)$ (Dunitz and Seiler, 1973); maximum ratio of |shift| to error 8.10^{-4}; maximum and minimum residue in the final difference electron density map of 3.6 and −4.6 e/Å^3. Atomic scattering factors for neutral atoms and anomalous dispersion corrections from the International Tables (1974), computer programs from the XRAY '76 system (Stewart et al., 1976) and ORTEP II (Johnson, 1976). The final positional and thermal parameters for Gysinite are listed in Table 1, bond angles and interatomic distances in Table 2[a].

The intensity data set did not allow to refine the cation site occupancy nor to distinguish between (OH) groups and crystalline water. Thus, the chemical formula used for the refinement:

$$[La_{0.16}Nd_{1.18}Pb_{0.66}]_{\Sigma 2}(CO_3)_2(OH)_{1.34} \cdot 0.66\,H_2O$$

was derived from the chemical analysis (Sarp and Bertrand, 1985) and from electroneutrality considerations assuming that the atom occupancy of the cation site is equal to unity. The calculated density, $Dx = 5.18$ g · cm^{-3}, established from the above formula, $Z = 2$ and from the refined cell parameters is notably larger than the one reported previously (Dx = 4.81 g · cm^{-3}) by Sarp and Bertrand, 1985. The discrepancy between these two values comes from the fact that in the latter case the density has been calculated from the empirical formula of Gysinite. It should be noted however that both densities are in the limits of accuracy of the chemical analysis. As mentioned before, it is not possible to differentiate the H_2O and hydroxyl groups present in the structure of Gysinite and no superstructure lines could be identified on overexposed Weissenberg

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[a] Additional material to this paper can be ordered referring to the no. CSD 51215, names of the authors and citation of the paper at the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG

Table 1. Atom position for Gysinite (Space group *Pmcn*). The isotropic temperature factors are expressed as

$T = \exp\{-2\,\pi^2\,U\,(2 \sin \theta/\lambda)^2\}$.

Estimated standard deviations are given in parentheses

		x	y	z	100 U (Å^2)
M[a]	4(c)	1/4	0.3400(3)	0.6491(2)	1.44(4)
C	4(c)	3/4	0.178(6)	0.810(4)	1.5(6)
O(1)	4(c)	3/4	0.318(4)	0.724(4)	2.6(6)
O(2)	8(d)	0.527(3)	0.122(2)	0.852(3)	1.7(3)
O(3)[b]	4(c)	1/4	0.405(5)	0.970(5)	4.1(9)

[a] M = (0.08 La + 0.59 Nd + 0.33 Pb)

[b] O(3) belongs to 0.67(OH) and $0.33H_2O$

Table 2. Bond distances and bond angles in Gysinite

a) Selected interatomic distances (Å) with e.s.d.'s in parentheses

M−O(1)	2.566(6)	(2×)	C−O(1)	1.356(53)	
−O(2)	2.579(17)	(2×)	−O(2)	1.249(24)	(2×)
−O(2)	2.660(16)	(2×)			
−O(2)	2.747(16)	(2×)			
−O(3)	2.385(37)				
−O(3)	2.463(37)		O(3)−O(3)	3.02(3)	(2×)

b) Bond angles (°) with e.s.d.'s in parentheses in the CO_3 group

O(1)−C−O(2)	116.6° (19)	(2×)
O(2)−C−O(2)	126.5° (35)	

photographs. The general chemical formula for isostructural Ancylite (Dal Negro et al., 1975):

$$M_x^{3+}\,M_{2-x}^{2+}(CO_3)_2\,(OH)_x \cdot (2-x)H_2O$$

with $Z = 2$ is thus also valid for Gysinite. It should be noted however that this formulation is valid only for $x \neq 0$. In the particular case where $x = 0$, it has recently been found that the monohydrocalcit, $CaCO_3 \cdot H_2O$, no longer isotypic to Ancylite, can be synthesized (Effenberger, 1981). To stress the analogy of Gysinite with Ancylite we have used here a chemical formula with two CO_3 groups. If there are no particular structural reasons, it is however customary to write any chemical formula in its simplest form. Further, since Gysinite and Ancilyte derive from RE CO_3 OH the general formula in agreement with chemical usage is therefore

$$M_{1-y}^{3+}\,M_y^{2+}\,CO_3(OH)_{1-y} \cdot yH_2O$$

with $y = 1 - x/2 < 1$ and now with 4 formula units in the unit cell. A stereographic drawing for Gysinite is shown in Fig. 1. The cations M (La,

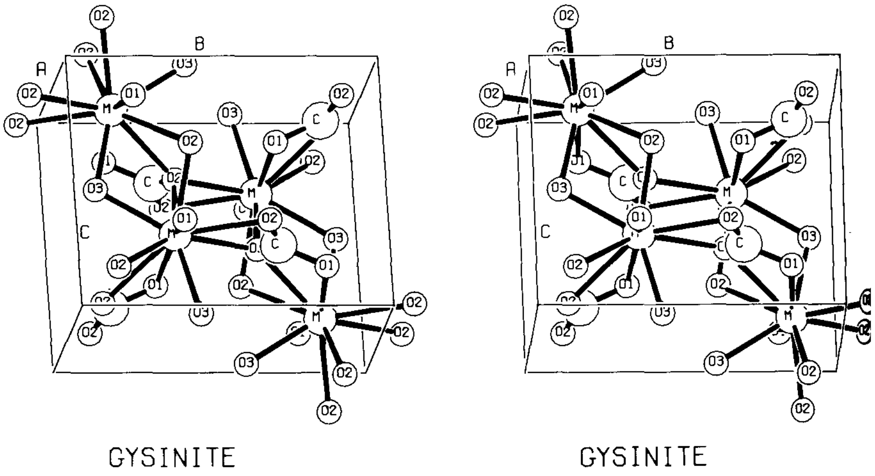

Fig. 1. Stereographic drawings of Gysinite showing the coordinations of the C (carbon) and M (La, Nd, Pb) atoms by oxygens. Sites O(3) correspond to the H_2O and hydroxyl disordered groups. The radii of the circles have been chosen to clarify the drawing and do not correspond to the relative radii of the ions

Nd, Pb) are surrounded by 10 oxygen atoms: 2 O(1) and 6 O(2) belonging to the CO_3 groups and 2 O(3) corresponding to the unresolved H_2O and hydroxyl groups. As can be seen on the drawing, the CO_3 groups are not parallel to the *ab* plane but inclined with respect to it in the *c* direction. This tilting of the CO_3 groups is a characteristic difference between the hydrous carbonates, such as Gysinite, and the orthorhombic carbonates, such as Aragonite, which do not contain water molecules or hydroxyl groups.

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