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Comparison between refinement results of apatites from Celia mine (Murcia, Spain) using X-ray diffraction powder and single-crystal data

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ABSTRACT

The results of crystal structure refinement of apatites, $Ca_5(PO_4)_3(OH,F,Cl)$, found in Celia mine (Murcia, Spain) using X-ray powder diffraction single crystal data are compared. According chemical and X-ray results these apatites are fluorapatites. Finally this study shows that the X-ray powder diffraction technique can be successfully applied in mineralogy to crystal structure studies with a precision probably sufficient for most purposes.

Key words: Apatite. Crystal structure.X-ray powder diffraction.

RESUMEN

En este trabajo se comparan los resultados del afinamiento de la estructura cristalina de apatitos, $Ca_5(PO_3)$ (OH,F,Cl), localizados en la mina Celia (Murcia), a partir de datos de difracción de polvo y de monocristal. Los resultados químicos y de difracción de rayos X muestran que estos apatitos corresponden principalmente a fluorapatitos. La conclusión de este trabajo es mostrar la utilidad que la técnica de difracción de polvo tiene no sólo en la identificación de fases sino en la obtención de información estructural, con una precisión suficiente para la resolución de un gran número de problemas mineralógicos.

Palabras clave: Apatito. Estructura cristalina. Difracción de polvo de rayos X.

INTRODUCTION

Apatites from Celia mine (Murcia, Spain) called locally as "esparraguina" (Navarro and Trigueros, 1961; Rodríguez-Gallego and García-Cervigón, 1970; García-Cervigón, 1973; IGME, 1981) are well known owing to their peculiar colour. This green variety is also called in some texts as "asparagus stone" and it is not common in the jewellery trade because it is both soft and very brittle. It is mainly purchased by gem collectors. The mineral genesis seems related to volcanic processes (Arana et al., 1992).

These apatites are usually light green or yellowish-green and the present study was performed with the aim to compare the structure results obtained by powder and single crystal X-ray diffraction and to test some physical and optical properties that shows the gemmological interest of the stones. Additionally, it was of our interest to find out the structural agent responsible for colour. In order to achieve this powder and single-crystal X-ray refinements, optical absorption and chemical studies have been carried out for apatites from Celia mine.

OCCURRENCE

The Miocene magmatic province of SE Spain includes ultrapotassic plagioclase-free rocks (Group I of Foley et al., 1987), which are widespread in the provinces of Murcia, Almeria and Albacete, ranging in age from about 8.5 to 6 x 10^6 years (Nobel et al., 1981; Bellon et al., 1983). Among the Mediterranean lamproites, the Jumilla ocurrence deserves particular interest since it contains significant amounts of carbonates and an apatite deposit (Venturelli et al., 1991).

The outcrops of Jumilla (province of Murcia) were firstly described by Osann (1906) and more recently by Fuster et al. (1967), Borley (1967), Venturelli et al. (1984, 1988, 1991), Nixon et al. (1984) and in IGME (1981) -Hoja nº 869 (Jumilla) of the Mapa Geológico de España. K-Ar ages of 7.2-7.6 x 10^6 years obtained on sanidine and K-amphibole are reported by Nobel et al. (1981).

PHYSICAL AND OPTICAL PROPERTIES

Specific gravity, refractive indexes and visible spectrum are the most relevant physical and optical properties

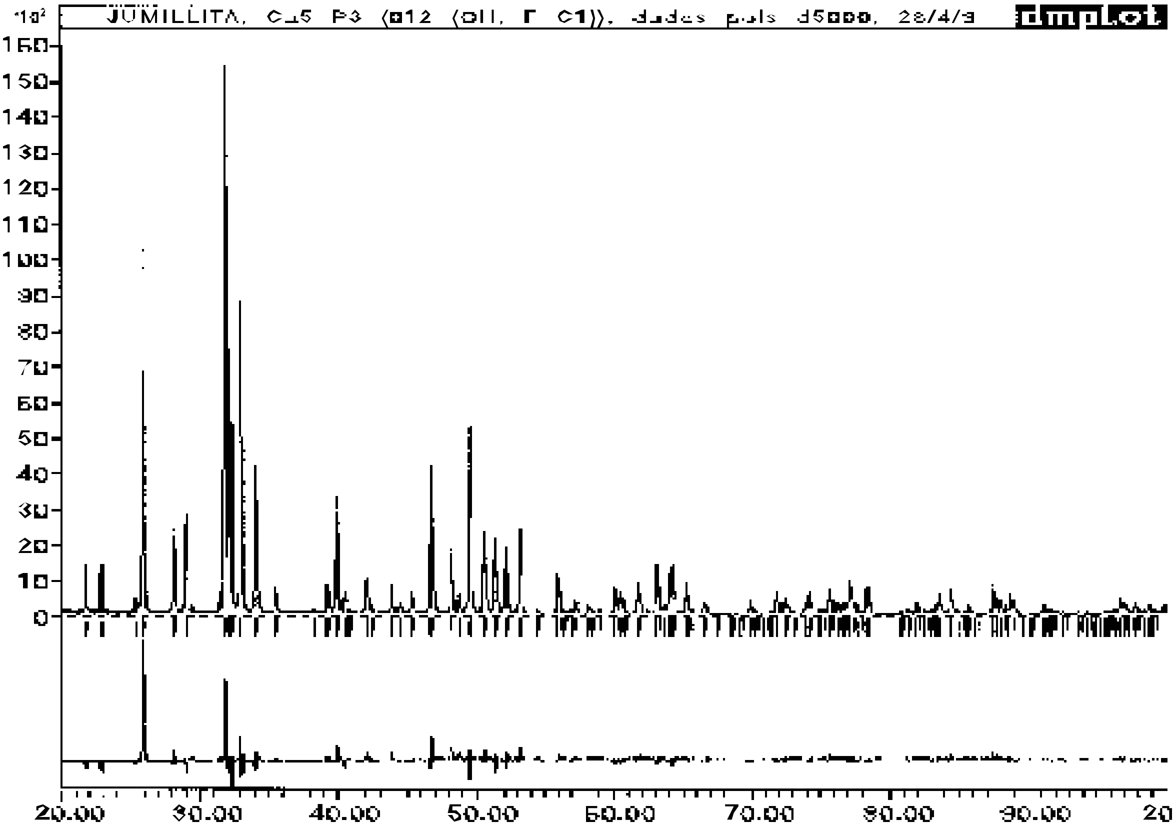

Figure 1. Final Rietveld difference plot of $Ca_5(PO_4)_3F$. Dots= observed pattern, solid line=calculated pattern. Lower portion: difference plot. Vertical markers indicate the positions of Bragg reflections.

Figura 1. Gráfico resultante del análisis de Rietveld de $Ca_5(PO_4)_3F$. Puntos= perfil observado. Línea continua= perfil calculado. Gráfica inferior=perfil diferencia. Marcadores verticales=posición de las reflexiones de Bragg.

Table 1. Comparison of physical and optical properties.

Tabla 1. Comparación de propiedades ópticas y físicas.

	This work	Webster (a)	Baquero Petricorena (b)	Cavenago and Moneta (c)
Specific gravity	2.98-3.25	3.17-3.23	2.90-3.23	3.10-3.23
Refractive indices	1.637-1.647	1.63-1.64	1.63-1.64	1.628-1.649
Double refraction	0.002-0.006	0.002-0.004	0.003	0.003-0.007

(a) Webster and Read,1994
(b) Baquero Petricorena,1989
(c) Cavenago and Moneta,1991

to carry out in order to identify or to verify the identity of a mineral with some gemmological applications. Conventional instruments were used to measure these properties: a Cobos hydrostatic balance, a System Eickhorst Gemled refractometer, and a Shibuya direct-vision prism spectroscope. In this work, five samples were used to test the properties.

The values for the specific gravity are among 2.98 and 3.25, which are in accordance with the average value given in the literature (Webster and Read, 1994; Baquero Petricorena, 1989; Cavenago and Moneta, 1991) (Table 1).

The refractive indexes were measured on a polished facet of rough samples and the values range between 1.637 and 1.647, with a double refraction of about 0.002-0.006 depending on the position of the sample on the refractometer. In all cases, the optical nature is uniaxial negative.

Finally, the very characteristic absorption spectrum is due to the rare earths neodymium and praseodymium (usually named together as "didymium"). It shows two main groups of narrow absorption lines in the yellow and green zones of the visible spectrum. This property is definitive for identification of yellow and yellow-greenish apatites.

With an UV-Vis spectrophotometer for colour evaluation, no relevant absorption lines were observed, so that, it has not been established anything about the possible causes of colour.

These measurements lead us to conclude that Celia mine apatites have no much interest as gemstones because of their low hardness (about 5 - 5.5 in the Mohs scale checked with a Rayner Hardness Pencil Set) and their high fragility which have an important influence in the cutting process.

CHEMICAL DATA

Microprobe analyses (average of the results determined by triplicate in two different samples) of apatite are reported in Table 2 and compared with other analyses given by Venturelli et al. (1991). Experimental conditions were 15 kV and 15 na, the $K\alpha$ line of F was analysed with a TAP crystal in 71315 position and the $K\alpha$ line of P with a PET crystal in 70376 position. As standard sample was used a fluorapatite from Durango (Mexico) established by the Smithsonian Institute.

EXPERIMENTAL AND DATA ANALYSIS

X-ray powder-diffraction data were taken on dried material passing through a 80 μm sieve. The ground powder was placed on a glass slide as a slurry. The powder diffraction pattern was collected on a Siemens 5000 diffractometer with a Bragg-Brentano geometry using Cu$K\alpha$ [40 kV, 20 mA, divergence slit = 1º, detector slit = 0.05º, angular range = 10-116º(2θ), counting time = 30 sec by steps of 0.02º(2θ)], scintillation detector and a secondary crystal graphite monochromator. The X-ray powder pattern was confirmed as corresponding to apatite group [JCPDS (quasi-) identical files nº 15-876, 24-214 and 25-1669].

The reflection positions were estimated by means of the program PROFILE (available in the Socabim PC software package DIFFRAC-AT supplied by Siemens).

Table 2. Microprobe analysis for apatites of Celia mine in weight percent.

Tabla 2. Análisis de microsonda electrónica de apatitos de mina Celia, en tanto por ciento en peso.

	This work	Venturelli *et al.* (1991)
Ce_2O_3	n.d.	0.22 - 0.65
MnO	0.05	—
FeO	0.00	0.32 - 0.67
CaO	53.85	52.8 - 54.0
MgO	0.17	—
SrO	0.83	0.57 - 2.40
P_2O_5	41.28	40.5 - 41.5
H_2O	n.d.	—
F	3.41	2.85 - 3.55
Cl	0.55	—
Total	100.14	99.91 - 100.40
O≡F≡Cl	1.56	
Total	98.58	

n.d.= *not determined*

The intensities diffracted by the single crystal were measured on an Enraf-Nonius CAD-4 diffractometer using MoKα radiation (0.71073 Å). The unit cell derived from least-squares refinements of 25 well centred reflections ($8 \leq \theta \leq 21^\circ$) was similar to that determined by X-ray powder-diffraction data. Intensity data were collected by the ω-scan technique in the 2θ range 5-60.8°(2θ). Examination of three standard reflections monitored throughout the data collection showed no significant decay. Lorentz and polarisation corrections were applied.

Cell parameters and space group

The powder diffraction data were indexed with the computer program DICVOL91 (Louër and Louër, 1972; Boultif and Louër, 1991). The first peak positions, with an ab-

Table 3. Comparative unit cell dimensions of apatites of Celia mine determined by X-ray powder and single-crystal studies (p and c).

Tabla 3. Dimensiones comparativas de la celda de apatitos de mina Celia determinados mediante estudios de polvo de rayos X y de monocristal (p y c).

	This work *(p)*	This work *(c)*	F-apatite[a]	OH-apatite[b]	Cl-apatite[c]
a (Å)	9.4080(5)	9.401(5)	9.367	9.424	9.628
c (Å)	6.8886(7)	6.882(5)	6.884	6.879	6.764
V (Å^3)	528.04(5)	526.8(6)	523.09	529.09	543.01

[a] Sudarsanan et al. (1972)
[b] Sudarsanan and Young (1969)
[c] Mackie et al. (1972)

Table 4. Powder diffraction data of apatite from Celia mine.

Tabla 4. Datos de difracción de polvo de apatito de mina Celia.

h	k	l	$2\theta_{obs}$(°)	$2\theta_{calc}$(°)	d_{obs}(Å)	I_{obs}
1	0	0	10.815	10.858	8.180	<1
1	0	1	16.828	16.853	5.268	3
1	1	0	18.839	18.864	4.710	1
2	0	0	21.790	21.816	4.078	6
1	1	1	22.873	22.892	3.888	5
0	0	2	25.855	25.866	3.446	52
2	1	1	31.820	31.829	2.812	100
1	1	2	32.205	32.210	2.779	41
3	0	0	32.951	32.980	2.718	37
2	0	2	34.085	34.086	2.630	25
3	0	1	35.526	35.530	2.527	5
2	1	2	39.243	39.242	2.295	5
3	1	0	39.859	39.893	2.262	11
2	2	1	40.531	40.527	2.225	3
3	1	1	42.086	42.081	2.147	7
1	1	3	43.889	43.874	2.063	6
4	0	0	44.486	44.477	2.036	2
2	0	3	45.354	45.335	1.999	4
2	2	2	46.779	46.767	1.942	32
3	1	2	48.173	48.160	1.889	16
2	1	3	49.533	49.515	1.840	36
3	2	1	50.608	50.597	1.807	19
4	1	0	51.398	51.390	1.778	16
4	0	2	52.184	52.168	1.753	15
4	1	1	53.217	53.204	1.721	20
3	2	2	55.993	55.970	1.642	9
3	1	3	57.198	57.192	1.610	4
4	2	0	60.097	60.087	1.539	5
3	3	1	60.587	60.558	1.528	4
4	2	1	61.751	61.730	1.502	8
5	0	2	63.139	63.115	1.472	11
3	0	4	64.006	64.016	1.455	4
3	2	3	64.221	64.253	1.450	10
4	2	2	66.525	66.516	1.405	10
5	1	2	69.818	69.832	1.347	3
4	0	4	71.773	71.773	1.315	3
5	2	0	72.425	72.438	1.305	2
5	2	1	73.921	73.938	1.282	1
4	2	3	74.130	74.142	1.279	3
2	1	5	75.617	75.610	1.257	3
4	3	2	76.268	76.270	1.248	<1
4	1	4	77.089	77.099	1.237	4
5	1	3	77.304	77.318	1.234	5
5	2	2	78.360	78.373	1.220	4
5	0	4	81.256	81.277	1.184	<1
4	4	0	81.952	81.918	1.176	3
3	3	4	83.337	83.348	1.159	1
4	3	3	83.563	83.562	1.157	3
4	2	4	84.382	84.380	1.148	3
5	2	3	85.623	85.623	1.134	2
5	1	4	87.465	87.465	1.115	4
3	2	5	88.087	88.071	1.109	2
7	0	2	88.698	88.711	1.103	5

Table 5. Crystallographic and structure refinement data from X-ray powder and single-crystal studies for apatites of Celia mine.

Tabla 5. Datos cristalográficos y de afinamiento de la estructura de los estudios por difracción de polvo y monocristal para los apatitos de la mina Celia.

	Powder		Single-crystal
formula		$Ca_5(PO_4)_3$ (F, Cl)	
M		504.31	
space group		$P6_3/m$	
Z		2	
Dc (g/cm^3)		3.18	
crystal size (mm)			0.32 x 0.32 x 0.44
wavelength (Å)	1.54178		0.71073
Maximum $\sin\theta/\lambda$ ($Å^{-1}$)	0.55		0.71
No. of reflections collected	652		3473
No. of independent reflections	not determined		583*
No. of structural parameters	19		39**
No. of profile parameters	10		—
wRp, the weighted pattern R-factor	0.1763		—
Rp, the pattern R-factor	0.1316		—
R-Bragg, the R-value for Bragg intensities	0.1066		—
R(F), the R-value based on the deduced "observed" and calculated structure factors	0.0630		—
wR2, R-factor based on F^2	—		0.1035
R1, R-factor based on F	—		0.0411

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* Reflections with $I \geq 2\sigma(I)$

** anisotropic thermal parameters are included

solute error of 0.03º(2θ), were used as input data. Only one solution with a hexagonal cell was found [M = 44.5 and F = 47.5 (0.0136, 31)]. After a least-squares reviewing of the data available of the pattern, the refined unit-cell parameters were : $a = 9.4081(5)$, $b = 9.4081(5)$, $c = 6.8886(7)$ Å , V = 528.03(5) $Å^3$. The final figures of merit are $M_{20} = 44.2$ and $F_{30} = 31.8$ (0.0182, 52). Comparison of the cell dimensions from X-ray single-crystal data, F^-, OH^- and Cl^- apatites are also reported in Table 3, and the list of observed and calculated peak positions is given in Table 4.

The extinctions in the diffraction pattern indicate the possible space groups P6, $P\overline{6}$, $P6_3$, P6/m or $P6_3/m$. These results are in accordance with the centro-symmetric $P6_3/m$ space group, confirmed by single-crystal X-ray diffraction data.

5.2. Structure solution and refinement

The structure of $Ca_5(PO_4)_3F$ (Smyth and Bish, 1988) was selected as starting model. The least-squares refinement was performed with the Rietveld method using the program DBWS. The final refinement was carried out using the program DBWS-9411 (Young et al., 1995), and involved the following parameters: one scale factor, 12

Table 6. Comparison of refined final atomic parameters and their standard deviations from single-crystal data (upper value) and powder data (lower vs

Tabla 6. Comparación de parámetros atómicos finales refinados y sus desviaciones estándar a partir de datos de monocristal (valores superiores) y de polvo (valores inferiores).

Atom	site	x	y	z	B_{iso} (Å^2)
F	2a	0	0	0.2500	1.816(4)
		0	0	10.2500	11.11 (22)
Ca1	4f	0.3333	0.6667	0.0011(1)	0.711 (4)
		0.3333	0.6667	0.0020(5)	0.78 (4)
Ca2	6h	0.2417(1)	-0.0074(1)	0.2500	0.553 (4)
		0.2404(3)	-0.0081(3)	0.2500	0.78 (4)
P	6h	0.3985(1)	0.3691(1)	0.2500	0.316 (4)
		0.3982(4)	0.3680(4)	0.2500	0.52 (6)
O1	6h	0.3269(3)	0.4849(3)	0.2500	0.868 (4)
		0.3234(8)	0.4792(7)	0.2500	1.16 (9)
O2	6h	0.5884(3)	0.4670(3)	0.2500	1.026 (4)
		0.5905(8)	0.4720(9)	0.2500	1.16 (9)
O3	12i	0.3423(2)	0.2574(2)	0.0701(3)	1.184 (4)
		0.3313(5)	0.2482(6)	0.0752(7)	1.16 (9)

structural parameters describing the atomic positions and seven isotropic temperature factors, two mixing parameters to define a theta dependent pseudo-Voigt shape function, three peak half-width parameters U,V,W to describe the angular dependence of the peak full-width at half-maximum of the diffraction line, one asymmetry parameter, three coefficients to define the functional angular variation of the background, and two unit cell parameters. The crystallographic and refinement details are summarized in Table 5. Figure 1 displays the accordance between observed and calculated powder patterns. Final atomic parameters are given in Table 6.

The complete dataset obtained from single crystal experiment permits more atomic parameters (*i.e.* anisotropic thermal parameters) to be refined and evidently a greater precision of coordinates (Table 6). All calculations were carried out using SHELXL93 (Sheldrick, 1993). Observed and calculated structure factors can be obtained from the authors. The final Fourier difference maps showed residual maxima and minima of 0.66 and -1.42 e Å^3. The values of the positional parameters obtained from powder data are in reasonable agreement with the results of the single-crystal study.

CONCLUSION

The aim of this study was, firstly, to show the ability of the powder X-ray diffraction to characterize accurately crystal structures and, secondly, to compare the accuracy obtained from powder and single-crystal data. The apatite is an interesting mineral case for this purpose. Actually, *ab-initio* structure determination of minerals from X-ray powder diffraction, with moderate complexity, is possible using Patterson and direct methods (Gies and Rius, 1995; Guirado et al., 1998; Rius et al., 1998).

The present results confirm that apatites of Celia mine are fluorapatites, with minor quantities of chlorine. Optical absorption studies can not explain the green colour of these apatites. Other optical properties are characteristic of apatites.

In this study the solution agreed remarkably well with the results of single crystal analysis. Geometrical calculations (PARST, Nardelli, 1983) of bond-distances and angles can serve as a good statistical test to compare both structures. Table 7 shows a summary of the main

Table 7. Bond distances (Å) and (degrees) in $Ca_5(PO_4)_3F$ apatite from single-crystal and powder data.

Tabla 7. Distancias de enlace (Å) y ángulos (grados) en apatito $Ca_5(PO_4)_3F$ a partir de datos de monocristal y polvo.

Bond	Single-crystal	Powder
F - Ca2	2.3078 (0.0016)	2.3007 (0.0032)
Ca1 - O1	2.3992 (0.0025)	2.4238 (0.0058)
Ca2 - P	3.0795 (0.0021)	3.0775 (0.0043)
Ca2 - O3	2.5040 (0.0023)	2.4359 (0.0057)
P - O1	1.5398 (0.0037)	1.5251 (0.0097)
P - O2	1.5463 (0.0027)	1.5685 (0.0071)
P - O3	1.5362 (0.0021)	1.5514 (0.0052)
Angle		
F - Ca2 - O3	81.85 (0.05)	80.31 (0.13)
F - Ca2 - P	82.99 (0.03)	83.05 (0.11)
P - Ca2 - O3	29.72 (0.07)	29.90 (0.12)
Ca2 - P - O3	53.91 (0.07)	51.50 (0.18)
Ca2 - P - O2	115.52 (0.10)	117.39 (0.32)
Ca2 - P - O1	133.26 (0.11)	131.75 (0.29)
O2 - P - O3	107.88 (0.07)	112.06 (0.19)
O1 - P - O3	111.15 (0.07)	109.85 (0.19)
O1 - P - O2	111.22 (0.17)	110.85 (0.50)
Ca1 - O1 - P	129.76 (0.02)	129.51 (0.00)
Ca2 - O3 - P	96.37 (0.08)	98.60 (0.23)

interatomic distances and angles, calculated with atomic coordinates and cell parameters from single-crystal and powder data, respectively.

The ratio between the estimated standard deviations from powder and single-crystal data is, as an average, 2.37 and 2.89, for bond distances and angles, respectively, which are a reasonable values taking into account the techniques accuracy. In general, the Rietveld refinement of the structure from the X-ray powder diffraction pattern gives atomic coordinates with lower precision than those obtained from the single crystal data, as it was observed by several authors (for example, Bénard et al., 1991).

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