New structural and spectroscopic data for eosphorite

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Abstract

X-ray diffraction refinement of the crystal structure of eosphorite has been carried out with reference to the orthorhombic space group $Cmca$. The structure is similar to that previously described by Hanson (1960), but the standard deviations are improved. Optical absorption and photoluminescence have also been studied for this mineral. Two sharp emission lines, denoted as R_1 and R_2, superimposed to a broad band (630–750 nm) have been related to the presence of Cr^{3+} ions. The excitation spectrum of these emissions confirms that the absorption (excitation) bands centred at 431 nm and 585 are related to with $^4A_2 \rightarrow {}^4T_1$ and $^4A_2 \rightarrow {}^4T_2$ spin allowed transitions of this ion.

KEYWORDS: eosphorite, crystal structure, luminescence optical absorption.

Introduction

EOSPHORITE is the maganese-rich end-member of the childrenite–eosphorite series, $(Fe,Mn)Al-PO_4(OH)_2.2H_2O$, formed by hydrothermal phosphatisation of metasediments and associated with the intrusion of granites (Braithwaite and Cooper, 1982).

Crystals are most commonly of a bipyramidal habit with striated faces elongated parallel to the c crystallographic axis. Members of this diadochic series can exhibit a great variability of colours and hues (e.g. colourless, pale brown, reddish brown, yellowish brown, pale cream, etc.). These colours are probably related to different Fe^{2+}/Mn^{2+} and Fe^{2+}/Fe^{3+} ion ratios.

First studies on the crystal structure of childrenite were carried out by Barnes (1949), Hurlbut, (1950), and Barnes and Shore (1951), respectively. However, their data were not conclusives with respect to the assignment of the space group symmetry ($Bba2$ or $Bbam$; i.e. orthorhombic or pseudo-orthorhombic symmetry). Later, Hanson (1960) proposed an 'approximate' eosphorite structure, belonging to the pseudo-orthorhombic spacial group of symmetry $Bbam$. However the high value calculated by Hanson (1960) for the residual factor $R = 0.16$ $[R = (F_o - F_c)/F_o]$

indicates that, in spite of the correct structure, some refinement has become necessary.

In this paper an X-ray diffraction refinement for the crystal structure of eosphorite is described. In addition, new data regarding the optical properties of this mineral are presented. These data throw light on the nature of some absorption and emission bands of this mineral.

Experimental

The orange prismatic crystals of eosphorite, from Taquaral (Brazil), used in this work were bought from a dealer. In this specimen of eosphorite the Mn:Fe ratio is about 4:1 (Table 1).

The crystal selected for data collection was ground to a sphere of 0,3 mm diameter. Intensity data were collected on an automatic four-circle Enraf-Nonius CAD-4 diffractometer, using graphite-monochromated Mo-$K\alpha$ radiation. Data were corrected for Lorentz and polarisation effects. An absorption correction, incorporated into the XRAY-76 system, was used (Stewart et al., 1976) for all computations.

Piezoelectric tests were carried out in a Hewlett Packard (LF 4260) impedance analyser using the

Table 1

	1	2	3	4
Fe (total)	24.30	-	7.6	5.40
Mn	-	23.99	13.4	19.45
Al	11.73	11.78	10.9	10.18
P	13.48	13.53	13.30	14.15
Ca	-	-	1.74	0.73
Mg	-	-	0.6	0.36
Si	-	-	-	-
Na	-	-	-	-
Cr	-	-	-	5.10^{-4} (*)
Formula	Ch	Eo	$Ch_{36}Eo_{64}$	$Ch_{24}Eo_{76}$

1. Childrenite theoretical.

2. Eosphorite theoretical.

3. Eosphorite, Taquaral, Brazil (Braithwaite, 1982).

4. Sample used in this work.

Analysis of childrenites and eosphorites, wt.%.
Characterization of the chemical composition of our
eosphorite was carried out by means of A.A. (Atomic
Absorption spectrometry, Perkin Elmer 503).
(*) The concentration of chromium was determined by
using induced coupling plasma (ICP)

resonance frequency method. Optical studies were made in a polarising microscope using eosphorite prismatic sections.

Table 1 shows details of the chemical analysis of our eosphorite crystal, compared with other eosphorite–childrenite crystals.

Unpolarised optical absorption measurements were performed in a CARY-2400 spectrophotometer. Samples of 6 × 4 × 2 mm³ were cut perpendicularly to the c crystallographic axis and all faces were polished. Then the electric field of the light was perpendicular to the c-axis in all the spectra.

Photoluminescence (excitation-emission) spectra were measured in a Jobin Ivon, JY-3CS, spectrofluorimeter, with a resolution of 1 nm in emission.

Results and discussion

X-Ray diffraction results. The crystal data, experimental data, solution and refinement of structure, are shown in Table 2.

The structure was solved by the Patterson method, using successive Fourier syntheses, including the H atoms. The structure was refined using first an isotropic thermal parameter, and then an anisotropic parameter, for the non-

hydrogen atoms.* The H atoms were included in a mixed refinement with the isotropic thermal fixed parameter. The Mn/Fe population factor was considered to be the expected from the chemical analysis. Finally, the R values obtained were $R = 0.041$ and $R_w = 0.054$.

The scattering factors were corrected for anomalous dispersion using the values given in the International Tables for X-Ray Crystallography (1974).

The final Fourier synthesis difference was on peaks of 0.5 e/A³. The calculated atomic positions are listed in Table 3. Heavy atoms that do not present standard deviations in Table 3 were considered to be fixed in the refinement, because they present special positions in the structure. No refinement was used for H atoms in the structure. It is considered that the agreement is quite good and then the described structure must be considered as correct.

The crystal structure is described with reference to the orthorhombic space group *Cmca* with $a = 6.928(1)$, $b = 10.445(1)$, $c = 13.501(2)$ Å. The *Cmca* space group is the correct group while the '*Bdam*' one calculated by Hanson (1960) is not recognised in the International Tables (and should be *Bbcm* = *Cmca*). The doubts raised by

* The anisotropic thermal parameters will be made available directly from the authors.

Table 2

Crystal data

Formula	$(Fe,Mn)AlPO_4(OH)_2 \cdot 2H_2O$
Crytal habit	Sphere, 0.3 mm diameter
Symmetry	Orthorombic, Cmca
Unit cell determination:	Least-squares fit from 45 reflexions (0 < 54)
Unit cell dimensions	6.928(1), 10.445(1), 13.501(2) 90. 90. 90.
Packing: V(A), Z	976.97(2), 8
Dc(g.cm), M, F(000)	3.113, 228.921, 904
u(cm)	30.727

Experimental data

Technique	Four circle diffractometer: Nonius CAD4. Graphite oriented monochromator: K- ∝ Mo, w/2θ scans, up θmax. 60. 1 min./reflex.
Number of reflexions :	
Measured	
Independent	5323
Observed	4976 (I > 2σ(I) criterion)
Range of hkl	0 18, 0 28, 0 34, (sin θ/)mx. 1.54
Standard reflexions :	2 reflexiones every 90 minutes Variation : No
Max-min transmission factors :	

Solution and refinement

Solution	Patterson.
Refinement	L.S. on Fobs with 1 block
H atoms	Difference Fourier Synthesis
Final F peaks	0.5 e/A
Final R and Rw	0.041, 0.054
Computer and programs	VAX 750, XRAY76, PARST.
Scattering factors	Int. Tables for X-Ray Crystallography
Anomalous dispersion	Int. Tables for X-Ray Crystallography

Crystal data, experimental data, solution and refinement for the eosphorite crystal

Table 3

ATOM	Number in cell	x	y	z
(Mn,Fe)	8	0.2500	0.1333	0.2500
P	8	0.0000	0.3772	0.3334.
Al	8	0.2500	0.2500	0.0000
$O_1(O)$	8	0.0000	0.2656(1)	0.2584(1)
$O_2(O)$	8	0.0000	0.0067(1)	0.2195(1)
$O_3(H_2O)$	8	0.0000	0.2522(1)	0.0492(1)
$O_4((OH))$	16	0.1801(1)	0.1104(1)	0.4093(0)
$O_5(O^-)$	16	0.3195(1)	0.1324(1)	0.6006(0)
$H_2(H_2O)$	16	0.110	0.285	0.080
$H_4(OH^-)$	16	0.182	0.035	0.421

Atomic positions

Hanson (1960) about the crystal system and space group symmetry for eosphorite were resolved by taking into account the intensities of the hkl and $\overline{hkl}$ reflections and the study of systematic absences. No differences in intensity were detected in this case. Because of this fact it can be suggested that, at least, our crystal does not belong to a monoclinic space group. Moreover, the reflections giving: hkl ($h + k$ = even); $h0l$ (l = even) and $hk0$ (h = even), were observed. This fact indicates that the eosphorite can be unambiguously assigned to the Cmca symmetry group of the orthorhombic system.

To check the presence of a centre of symmetry and thus verifying whether or not the symmetry is lower than orthorhombic, additional experiments

were performed. These included a piezoelectricity test and some crystals-optics studies with a polarising microscope. The piezoelectricity test did not show evidence of activitiy in the frequency range from 100 to 1000 KHz. Thus the presence of a centre of symmetry can be assumed, and the *Cmca* orthorhombic space group of symmetry determined by X-ray diffraction is confirmed.

In relation with the crystal-optics experiments, straight extinction was observed in all cases and thus, again, no evidence of monoclinic symmetry was found.

Consequently it is possible to conclude that the symmetry is not lower than orthorhombic. All data obtained for eosphorite crystals indicate that the *Cmca* space group determined by X-ray diffraction is correct.

The calculated structure is equivalent to that described by Hanson (1960), but the standard deviations are improved. Now the structure can be considered as a system of linked polyhedra assembled in the following way: $(Mn,Fe)O_4(OH)_2$ octahedra share opposite O–O edges to form a set of endless chains parallel to the *a*-axis; $AlO_2(OH)_2(H_2O)$ share opposite H_2O corners to form a parallel set of chains. The two types of chain alternate, sharing OH corners to

form an infinite sheet. Adjacent sheets are held together by phosphorus cations in tetrahedral coordination with oxygen ions, forming a three-dimensional network.

A section of this structure is shown in Fig. 1, and the appropriate atomic positions and interionic distances are given in Tables 3 and 4 respectively. It is evident that the (Mn,Fe) octahedra are somewhat distorted. The shared edge is considerably shorter than the others, suggesting a repulsion between neighbouring (Mn,Fe) cations. The other polyhedra are closer to a regular one (Figs. 2*a* and *b*).

All the cation–anion distances are in good agreement with those found for similar coordination polyedra in other (Al,Fe)-phosphate compounds; King and Sengier-Roberts (1988).

The lengths of the hydrogen bonds, previously suggested by Hanson (1960), have been calculated according to the correct identification of the OH and H_2O groups. Thus the distances obtained for the $O_3–H_2–O_5$ hydrogen bonds show that the $O_3–O_5$ distance is shorter than the oxygen–oxygen distances observed in the aluminium octahedron (Table 4), according to the expected effect of the H atoms on the $O_3–O_5$ oxygen atoms.

Optical properties. As previously mentioned

○ Al　◉ Mn,Fe　◈ P　○ O　● OH　◎ H_2O
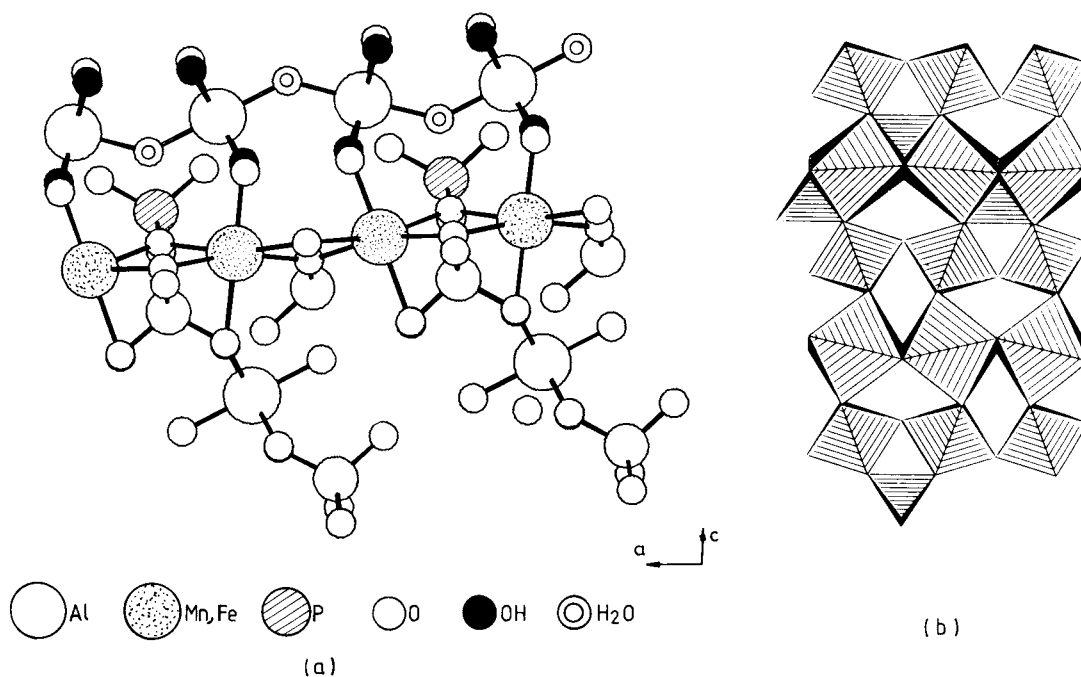
(a)　　　　　　　　　　　　　　　　　　(b)

Fig. 1. (*a*) A section of the eosphorite structure showing the alternate chains of Al and Mn octahedra linked by OH groups. (*b*) Coordination polyhedra of the eosphorite structure.

Table 4

(Mn,Fe)O$_4$(OH)$_2$ octahedron		AlO$_2$(OH)$_2$(H$_2$O)$_2$ octahedron	
O$_1$-O$_1$	3,4714 (5)	O$_3$-O$_4$	2,6803 (2)
			2,7239 (3)
O$_1$-O$_2$	2,7547 (3)	O$_3$-O$_5$	2,6142 (3)
			2,6870(2)
O$_1$-O$_4$	2,8871 (2)	O$_4$-O$_5$	2,7670 (4)
	3,5589 (3)		2,6898 (3)
O$_2$-O$_2$	3,5606 (5)		
O$_2$-O$_4$	3,0181 (3)		
	3,0490 (3)		
(Mn,Fe)-O$_1$	2,2186 (2)	O$_3$-Al	1,8551 (2)
(Mn,Fe)-O$_2$	2,2176 (2)	O$_4$-Al	1,9647 (2)
(Mn,Fe)-O$_4$	2,2175 (3)	O$_5$-Al	1,8935 (2)

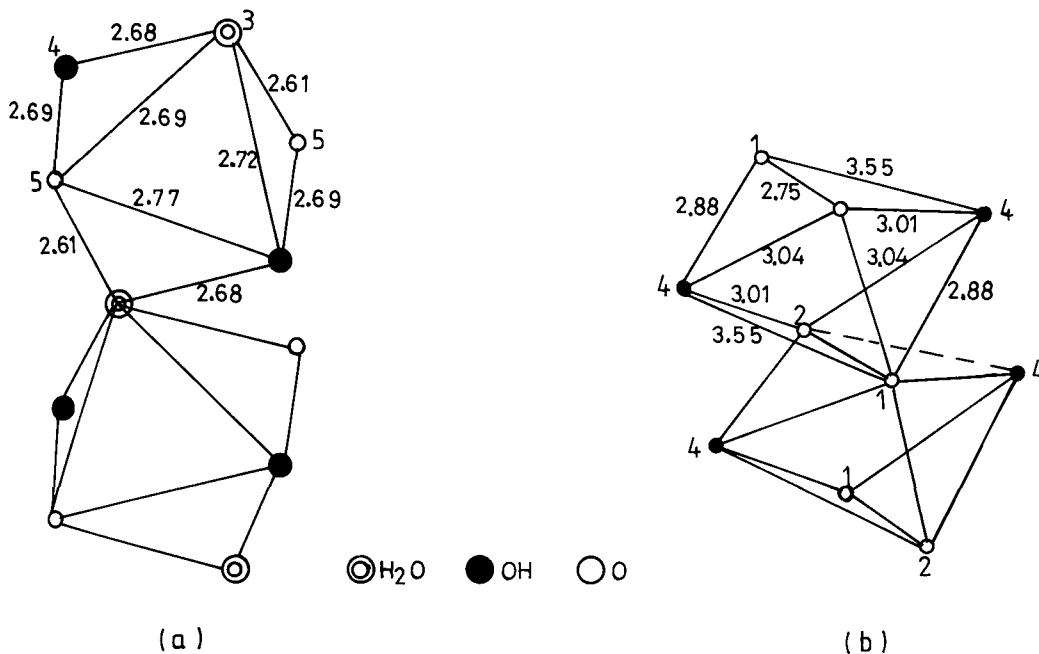| PO$_4$ Tetrahedron		Hydrogen bonds	
O$_1$-O$_2$	2,5359 (2)	O$_3$-O$_5$	2,6142 (3)
O$_1$-O$_5$	2,5145 (2)	O$_3$-H$_2$	0,9333 (1)
O$_2$-O$_5$	2,5003 (2)	O$_5$-H$_2$	1,7112 (2)
O$_5$-O$_5$	2,5010 (4)	O$_3$-H$_2$-O$_5$	161,815 (4).
P-O$_1$	1,5440 (1)		
P-O$_2$	1,5296 (1)		
P-O$_5$	1,5388 (2)		

Interionic distances

(a)   (b)

FIG. 2. (a) Two Al$_2$O$_2$(OH)$_2$H$_2$O octahedra showing the arrangement of anion. (b) The most distorted MnO$_4$(OH)$_2$ octahedra, with the shared opposite O$_1$-O$_2$ edges shorter than the others.

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the eosphorite crystals used in this work showed an orange colour, related to the high content of manganese (see Table 1). In fact, the UV-VIS absorption spectrum of our eosphorite (Fig. 3), measured in the 200–750 nm region at room temperature (RT), consists of bands at 400, 417, 462, 526 and 580 nm (from 350 nm a dramatical rise in the optical density is observed). These bands are due to Mn^{2+} and can be related (Table 5) to the $^6S \rightarrow {}^4G(Eg), {}^4G(A_{1g}), {}^4G(T_{2g}), {}^4G(T_{1g})$ transitions of this ion, in the cubic symmetry approximation (Aguilar and Osendi, 1982; Pappalardo *et al.*, 1983).

Fig. 4*a* shows the emission spectrum of our natural cosphorite crystal. This spectrum is unequivocally associated to Cr^{3+} ions (Vergara *et al.*, 1990). It shows two sharp lines, called R_1 and R_2, associated with the two components of the $^2E-{}^4A_2$ magnetic dipole transition. These two transitions occur as a consequence of a non-cubic crystal field which splits the ^2E level. These bands are superimposed on a broad band which spans from 630 to 750 nm. This broad bands, which is lost at low temperatures, is related to the $^4T_2 \rightarrow {}^4A_2$ transition of the Cr^{3+} ion, (Vergara *et al.*, 1990).

The photoluminescence results show that the typical visible emission spectrum of Mn^{2+} does not appear. This fact is probably due to the high content of manganese, together with the presence of other impurities (such as Fe) that can act as quenchers of the luminescence of the Mn^{2+} ion.

The excitation spectrum (Fig. 4*b*) confirms that the photoluminescence of natural eosphorite crystals is caused by Cr^{3+} ions. It consists of two strong and structured bands centred at 431 nm and 585 nm. These two bands can be related to the $^4A_2 \rightarrow {}^4T_1$ and $^4A_2 \rightarrow {}^4T_2$ spin-allowed transitions (Vergara *et al.*, 1990). It should be pointed out that the resolution of these bands in the absorption spectrum becomes difficult because they are masked by the absorption bands of the Mn^{2+} ion. However the $^4A_2 \rightarrow {}^4T_2$ (585 nm) band of Cr^{3+} can still be resolved in the absorption spectrum shown in Fig. 3.

No signal due to Mn^{2+} was detected in the excitation spectrum of this ion, so that energy transfer from Mn^{2+} to Cr^{3+} ions should be disregarded as a possible excitation mechanism. At the same time it should be pointed out that the emission and excitation spectra in Fig. 3*a* and *b* are very similar to those reported by Powell *et al.*
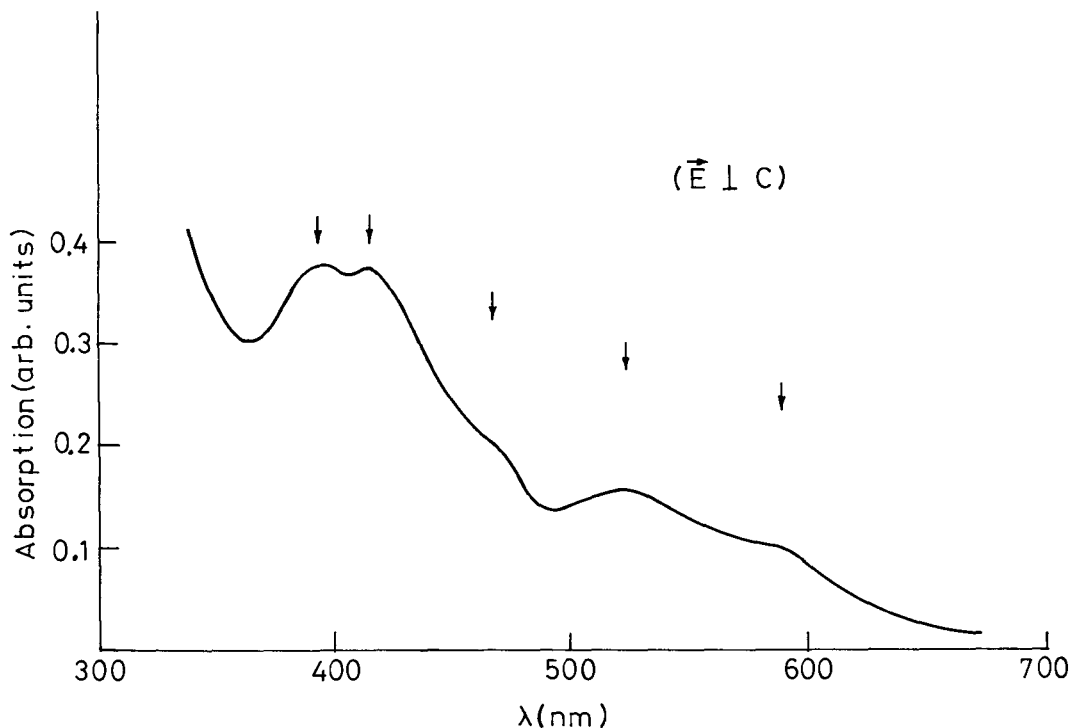

Fig. 3. Absorption spectrum of eosphorite at room temperature (E ⊥ c).

Table 5

Cubic Symmetry	CO₃Ca:Mn Aguilar et al. (1982) (a)	FAP:Sr,Mn Pappalardo et al. (1983) (b)	Eosphorite this work (c)
$^6S \dashrightarrow {}^4T_{1g}$	523	500	526
$^6S \dashrightarrow {}^4T_{2}g$	426	465	462
$^6S \dashrightarrow {}^4A_{1g}$	407	415	417
$^6S \dashrightarrow {}^4E_{g}$	401	406	400
$^6S \dashrightarrow {}^4T_{2}g$	358	350	-

Mn^{2+} ion transition: (a) Mn^{2+}-rich carbonate;
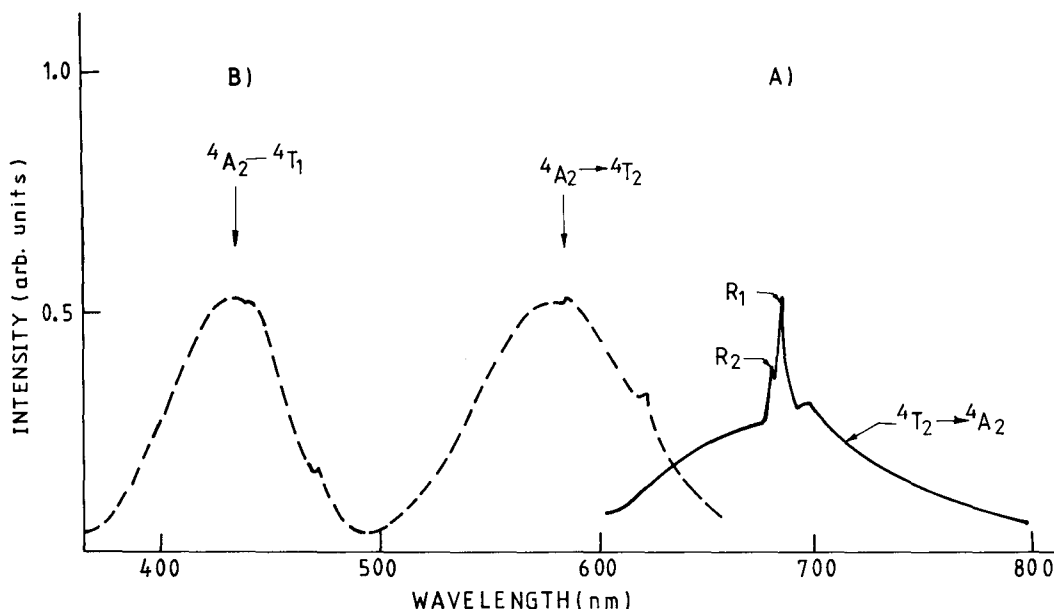(b) Sr, Mn-Flourapatite; (c) Eosphorite. Data in nm.

FIG. 4. (a) Emission spectrum of Cr^{3+} in eosphorite natural crystals at room temperature. (b) Excitation spectrum of Cr^{3+} in eosphorite at room temperature in the $^4A_2 \rightarrow {}^4T_1, {}^4T_2$ absorption range.

(1985) for the alexandrite ($BeAl_2O_4:Cr^{3+}$) laser crystals. This fact makes this mineral a promising solid-state laser.

Photoluminescence results reveal that the fluorescence (emission and excitation) bands are related to the presence of Cr^{3+} ions.

Conclusions

The crystal structure of eosphorite determined by Hanson (1960) has been confirmed but with greatly improved precision, which permitted determination of the hydrogen atom positions and refinement of the anisotropic temperature factors for the other atoms. No evidence of lower symmetry than the orthorhombic space group Cmca has been found.

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