

Mn-rich fluorapatite from Austria: Crystal structure, chemical analysis, and spectroscopic investigations

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ABSTRACT

The crystal structure of a pale blue transparent Mn-rich fluorapatite (MnO: 9.79 wt%) with the optimized formula $\sim(\text{Ca}_{8.56}\text{Mn}_{1.41}\text{Fe}_{0.01}^{2+})\text{P}_6\text{O}_{24}\text{F}_{2.00}$ and space group $P6_3/m$, $a = 9.3429(3)$, $c = 6.8110(2)$ Å, $Z = 2$ has been refined to $R = 2.05\%$ for 609 unique reflections (MoK α). The Mn in the Eibenstein an der Thaya, Austria apatite is strongly ordered at the Ca1 site: Ca1: $\text{Ca}_{0.72(1)}\text{Mn}_{0.28}$, Ca2: $\text{Ca}_{0.96(1)}\text{Mn}_{0.04}$. There is a linear variation in $\langle\text{Ca1-O}\rangle$ as a function of Mn content ($r^2 = 1.00$). The dominant band in the optical absorption spectrum of fluorapatite from Eibenstein is in the 640 nm region with $\mathbf{E} \parallel \mathbf{c} > \mathbf{E} \perp \mathbf{c}$. The 640 nm band is attributed to Mn^{5+} at the P site by analogy with previous studies. This interpretation is consistent with studies of well-characterized synthetic materials of the apatite structure that contain Mn^{5+} . Because Mn^{5+} has intense absorption in the visible region of the spectrum, if a small proportion of the total Mn is Mn^{5+} at the P site, that substituent dominates the spectrum and the color of the mineral. To determine if the pale blue color is due to radiation effects, a fragment of the fluorapatite crystal was heated at 400° C for 1 hour, and the change in color was slight. All of these observations are consistent with the origin of color from Mn^{5+} . Assuming that all the intensity of the 640 nm ($\mathbf{E} \parallel \mathbf{c}$) absorption is from Mn^{5+} , the concentration of Mn^{5+} in this fluorapatite sample was calculated as 2.6% of the total manganese content ($\sim\text{P}_{5.96}\text{Mn}_{0.04}^{5+}$). The calibration was estimated from the spectrum of the related compound $\text{Sr}_5(\text{P}_{0.99}\text{Mn}_{0.01}^{5+})_3\text{Cl}$. The weak band at about 404 nm in the $\mathbf{E} \parallel \mathbf{c}$ spectrum may be the corresponding band for Mn^{2+} in octahedral coordination.

INTRODUCTION AND PREVIOUS WORK

The apatite structure sequesters substituent ions at all of its cation positions, including the Ca1 and Ca2 sites. Cation and anion substituents in the apatite structure are given by Pan and Fleet (2002) and Hughes and Rakovan (2002); both summaries are contained in a volume that summarizes many aspects of apatite and its properties (Kohn et al. 2002).

Mn-bearing apatite, both synthetic and natural, has been the subject of numerous studies because of the high affinity of apatite for Mn in geologic systems and because of the importance of Mn-doped apatite in the fluorescent lighting industry. The phase is particularly important to that industry, as Mn^{2+} in apatite can be a fluorescence activator or coactivator (often sensitized by Sb^{3+}), and is widely used in the manufacture of fluorescent lights (Butler 1980; Blasse and Grabmaier 1994; Waychunas 2002). Numerous experiments (with contradictory results) have addressed ordering of Mn in apatite. Hughes et al. (1991) and references cited therein summarize such studies. In that work, the authors describe crystal structures of natural Mn-rich fluorapatites with MnO contents up to 6.81 wt% (1.00 apfu Mn). In microprobe analyses of Mn-bearing fluorapatite, they found concentrations up to 7.3 wt%, and an unpublished study by Miller and others (Mary K. Roden,

personal communication in Hughes et al. 1991) yielded apatite with up to 7.87 wt% MnO (1.17 apfu Mn). In addition, other published analyses present MnO concentrations of 7.59 wt%, yielding 1.09 apfu Mn (Deer et al. 1962). The structure crystal of Hughes et al. (1991) with the highest Mn concentration, 1.00 apfu Mn by electron microprobe analysis (EMPA), did not contradict the assertion that Mn contents cannot exceed that value, as stated by Suitch et al. (1985). In addition, their crystal contained concentrations of ions at the Ca-sites ($\text{Fe}_{0.10}\text{Na}_{0.07}\text{Ce}_{0.02}$) that obviated unequivocal assignment of Mn between the two Ca sites. More recently, Ercit et al. (1994) abstracted the results of their study on Mn-rich apatite containing 1.37 apfu Mn, the highest Mn-concentrations then found in natural samples; however, their sample also contained substituents other than Mn, as $\text{Fe} + \text{Zn} = 0.11$ apfu. Their conclusions on Mn ordering between the Ca sites were not in accord with the results of the earlier Hughes et al. study (1991).

The partitioning of Mn^{2+} between the two Ca site remains in dispute, although most studies indicate that there is a strong preference for the Ca1 site (Ryan et al. 1970, 1972; Ryan and Vodoklys 1971; Suitch et al. 1985; Hughes et al. 1991; Pan et al. 2002); however, none of these works refuted the putative limit of 1.00 apfu Mn (Suitch et al. 1985). Contrary to this general consensus, several studies suggest little to no preferential

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ordering of Mn²⁺ (Warren 1970; Warren and Mazelsky 1974; Ercit et al. 1994; Gaft et al. 1997). All of these studies draw their conclusions from spectroscopic data except for the X-ray diffraction study of Ercit et al. (1994). Manganese in the most Mn-rich fluorapatite described previously shows only a slight preference for Ca1 (64%) (Ercit et al. 1994), although that sample was not without other substituents. The present work involves apatite essentially devoid of substituents other than Mn (Fe = 0.009 apfu), and thus unequivocal conclusions on Mn-ordering can be drawn from it.

Tourmaline and fluorapatite, both highly enriched in Mn, were recently found in a Variscan topaz- and cassiterite-bearing pegmatite near Eibenstein an der Thaya, Lower Austria, and were described by Ertl et al. (in review). They described pink to yellow-brown Mn-rich tourmaline with up to ca. 9 wt% MnO. The crystal structure and chemical analyses, including the light elements, of Mn-rich tourmaline samples (Li-bearing olenite) with MnO contents in the range 8–9 wt% MnO from this locality were reported in Ertl et al. (2003).

The apatite crystal used in this study was a transparent pale-blue cleavage fragment approximately 300 × 300 × 50 μm. A subfragment of this was separated and used for X-ray diffraction data collection. Another apatite fragment with similar Mn concentration was found within approximately 0.5 m of the sample analyzed for this work. This sample is distinctly different in that it contains abundant secondary fluid inclusions as well as inclusions of other minerals (quartz and mica).

EXPERIMENTAL DETAILS

A preliminary crystal-structure refinement showed high Mn contents in blue apatite for the pegmatite at Eibenstein an der Thaya, Lower Austria. Three apatite crystals were analyzed by EMPA. The crystal with the highest MnO content (9.79 wt%) was used for data collection. The microprobe analyses confirmed the homogeneity of this crystal. The color of the crystals in the Munsel system of color nomenclature is approximately 9B 7/4, corresponding to a pale blue color (Munsell Color 1976; Kelley and Judd 1976).

The crystal was extracted from the epoxy mount used for the electron microprobe analysis and was subsequently mounted on a glass fiber on a Bruker Apex CCD diffractometer equipped with graphite-monochromated MoK α radiation. Refined cell-parameters and other crystal data are listed in Table 1. Redundant data were collected for an approximate sphere of reciprocal space, and were integrated and corrected for Lorentz and polarization factors using the Bruker program SAINTPLUS (Bruker AXS Inc. 2001).

The structure was refined using the Bruker SHELXTL V. 6.10 package of programs, with neutral-atom scattering factors and terms for anomalous dispersion. Refinement included anisotropic-displacement parameters for all atoms. Table 2 lists atom parameters, and Table 3 lists selected interatomic distances.

Chemical analyses (Table 4) were done in wavelength-dispersive spectroscopy mode with a CAMECA SX-50 electron-microprobe at the Ruhr-University-Bochum, Germany, at an acceleration voltage of 15 kV, a sample current of 15 nA, and a beam diameter of approximately 5 μm. Natural and synthetic materials were used as standards: natural andradite (Fe, Ca), natural spessartine (Mn), natural topaz (F), and synthetic AlPO₄ (P). The analytical data were reduced and corrected using the PAP routine. Excellent agreement was obtained between analyzed Mn by EMPA and structure refinement: 1.44 apfu by the former method and 1.36 by the latter. The optimized formula (Wright et al. 2000) resulting from the two methods is given in Table 4. The mean F-value is slightly higher than the theoretical maximum value when OH is not present (Table 4). A likely explanation is the well known effect that the intensity of apatite FK α radiation depends on the crystal orientation relative to the electron beam (Stormer et al. 1993).

A sub-mm crystal fragment of the manganian apatite was prepared as a 0.074 mm thick parallel plate (polished on both sides) that contained the c axis. Polarized optical absorption spectra in the 390–1100 nm range were obtained at about one nm resolution with a home-built microspectrometer system consisting of a 1024-

TABLE 1. Crystal data and results of structure refinement for Mn-rich apatite from Eibenstein an der Thaya, Lower Austria

Space group	<i>P6₃/m</i>
No. of reflections	5221
Unit cell by least squares	<i>a</i> = 9.3429(3), <i>c</i> = 6.8110(2) Å
Frame width, scan time, number of frames	0.20°, 15 s, 4500
Detector distance	5 cm
Effective transmission	0.7052–1.000
<i>R</i> _{int} (before - after SADABS absorption correction)	0.0963–0.0184
Measured reflections, full sphere	11,158
Unique reflections - refined parameters	609–42
<i>R</i> 1	0.0205 for 609 unique data
Largest difference peaks	+0.54(10), -0.44(10) e ⁻ · Å ⁻³
Goodness-of-Fit	1.182

TABLE 2. Atom parameters in Mn-bearing apatite

Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	Occ.
Ca1	1/3	2/3	-0.00256(7)	0.0131(1)	Ca _{0.72(1)} Mn _{0.28}
Ca2	0.75861(5)	0.75194(5)	1/4	0.0124(1)	Ca _{0.96(1)} Mn _{0.04}
P	0.60081(6)	0.97137(6)	1/4	0.0095(2)	P _{1.00}
O1	0.6690(2)	0.15855(18)	1/4	0.0159(3)	O _{1.00}
O2	0.4111(2)	0.8767(2)	1/4	0.0288(5)	O _{1.00}
O3	0.6591(2)	0.91763(16)	0.0701(2)	0.0274(3)	O _{1.00}
F	0	0	1/4	0.0305(7)	F _{1.00}

Site	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
Ca1	0.0137(2)	= <i>U</i> ₁₁	0.0118(2)	0	0	0.00683(8)
Ca2	0.0139(2)	0.0124(2)	0.0115(2)	0	0	0.0069(2)
P	0.0091(2)	0.0079(2)	0.0117(3)	0	0	0.0043(2)
O1	0.0202(7)	0.0086(6)	0.0190(7)	0	0	0.0074(5)
O2	0.0096(7)	0.0138(7)	0.062(1)	0	0	0.0048(6)
O3	0.0537(9)	0.0246(6)	0.0156(5)	0.0066(6)	0.0142(6)	0.0284(6)
F	0.0176(7)	= <i>U</i> ₁₁	0.056(2)	0	0	0.0088(3)

TABLE 3. Selected interatomic distances in Mn-rich apatite

Ca1-	O1 (×3)	2.354(1)	Ca2-	F	2.2871(4)
	O2 (×3)	2.431(1)		O3 (×2)	2.322(1)
	O3 (×3)	2.805(2)		O2	2.376(2)
<Ca1-O>	2.530		O3 (×2)	2.490(1)	
			O1	2.727(2)	
			<Ca2-O>	2.455	
P-	O3 (×2)	1.525(1)			
	O1	1.533(1)			
	O2	1.535(2)			
<P-O>	1.530				

TABLE 4. Composition of Mn-rich fluorapatite from Eibenstein an der Thaya, Lower Austria (wt%)

	Range*	Average*	Fluorapatite†
P ₂ O ₅	40.05–40.96	40.55	41.41
FeO	0.02–0.10	0.06	0.06
MnO	9.71–9.88	9.79	9.73
CaO	46.40–46.93	46.69	46.66
F	3.92–4.05	3.98	3.70
O = F		-1.68	-1.56
Sum		99.40	100.00

Ions on the basis of (O,F) = 26		
P	5.953	6.000
Ca	8.674	8.556
Mn ²⁺	1.438	1.410
Fe ²⁺	0.009	0.009
Sum (Ca+Mn+Fe)	10.121	9.975
F	2.185	2.000

Note: Total Mn and total Fe reported as MnO and FeO.

* Range and average of 14 EMP analyses.

† Weight percent calculated from optimal site occupancies and normalized to 100%.

element Si diode-array detector coupled to a grating spectrometer system and via fiber optics to a highly modified NicPlan infrared microscope containing a calcite polarizer. A pair of conventional 10× objectives was used as an objective and a condenser. Spectra were obtained through the central area of the sample, the clearest region with only minor inclusions. At this thickness, the crystal is pale blue with moderately weak pleochroism: $E \parallel c$ = darker blue; $E \perp c$ = paler blue.

RESULTS AND DISCUSSION

Structure

Virtually all Mn in the Eibenstein an der Thaya sample resides at the Ca1 site, as the sites have the following occupancies: Ca1: $Ca_{0.72(1)}Mn_{0.28}$, Ca2: $Ca_{0.96(1)}Mn_{0.04}$. Hughes et al. (1991) used bond-valence theory to explain the site-preference of Mn for the Ca1 site in apatite. In the Austrian apatite, bond-valence sums for Mn^{2+} clearly illustrate the reason for the ordering of Mn^{2+} at the Ca1 site. Mn^{2+} at the Ca1 site has an incident bond-valence sum of 1.38 v.u., whereas Ca at the Ca2 site has an incident bond-valence sum of 1.12 v.u. (it must be noted that the bond-valence sums were calculated using the average M sites, as different sites for Ca and Mn were not distinguished). Clearly, the incident bond-valence sums are far too low at either site, but closer to the formal valence (2 v.u.) at the Ca1 site; thus it principally resides there.

High-spin Mn^{2+} involves no crystal-field stabilization energy, and only radius and site geometry should control Mn^{2+} substitution in the apatite structure. Indeed, average bond-length at the site that incorporates the smaller Mn^{2+} ion as a substituent for Ca ($<Ca1-O>$) decreases linearly with increasing Mn content (Fig. 1).

Ercit et al. (1994) noted that the incorporation of Mn at Ca1 results in long-range positional disorder of the O2 and O3 sites; such disorder is also evident in our study, as exhibited in the atomic-displacement parameters of those atoms (Table 2; note particularly the values of U_{11} and U_{22} for O3, and U_{33} for O2). Disorder of O2 about the mirror plane implies local symmetry-breaking to accommodate the movement of O2 off the mirror plane. Ercit et al. (1994) suggest such disorder results from the rotation of the phosphate tetrahedra approximately about the P–O1 bond, and the atomic-displacement parameters in the current study support such a contention.

The contradictory results of Ercit et al. (1994) and the present study should be addressed. The samples used in both studies

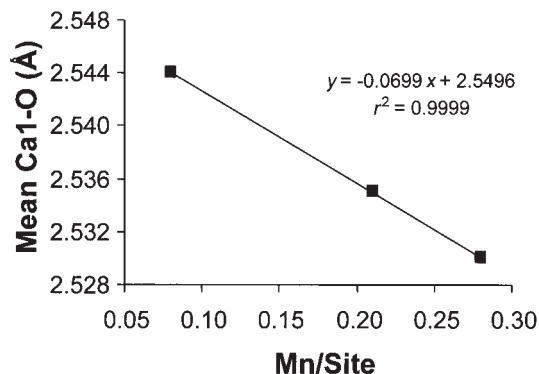


FIGURE 1. Variation of mean Ca1–O distance with Mn-occupancy of site. Lower values of Mn-occupancy from Hughes et al. (1991), largest value from this work.

contain relatively high amounts of Mn, yet the observed cation ordering differs; in the present study 82% of the Mn is ordered at the Ca1 site, whereas in Ercit et al. (1994) 64% of the Mn was so ordered. The essentially pure sample used in this study in contrast to the crystal of Ercit et al. (1994) that contained 0.11 apfu Fe and Zn substituents allows unequivocal assignment of the substituent Mn in the Eibenstein an der Thaya material. The difference between the two results may be the result of the inability to distinguish between Mn and Fe from X-ray diffraction data. However, it may be that ordering of Mn is different in the two samples as a result of different environmental conditions during crystal growth. Analysis of crystals that grew under known P - T - X conditions are required to separate these variables, and is of import in understanding accommodation of substituents in the apatite structure.

Optical spectroscopy

The optical absorption spectrum of Mn^{2+} in octahedral coordination is well-characterized and consists of two broad bands in the 450–600 nm range and a distinctive, sharp band near 408 nm in common minerals (Manning 1968). The weak band at about 404 nm in the $E \parallel c$ spectrum of Mn-rich fluorapatite (Fig. 2) may be the corresponding band. The dominant band in Figure 2 is in the 640 nm region with $E \parallel c > E \perp c$. This band is also seen in spectra of apatite from the Hugo Mine, South Dakota, and Karelia, Russia (Gilinskaya and Mashkovtsev 1995; Rossman 2003). Gilinskaya and Mashkovtsev (1995) attribute the deep blue color of apatite from Karelia to Mn^{5+} at the P site. This interpretation is consistent with studies of well-characterized synthetic materials of the apatite structure that contain Mn^{5+} (Reinen et al. 1986; Dardenne et al. 1999). Because Mn^{5+} has intense absorption in the visible region of the spectrum, a small amount of Mn^{5+} will dominate the spectrum and the color of the mineral.

Blue color may also be associated with radiation damage in apatite (Gilinskaya and Mashkovtsev 1995). To determine if the color is radiation-induced, a fragment of fluorapatite was heated at 400 °C for 1 h along with a crystal of synthetic $Sr_5(P_{0.99}Mn_{0.01})_3Cl$ (Brixner 1973) and a crystal fragment of deep-blue manganese-containing apatite from the Hugo Mine. None of these crystals faded as a result of the heating, indicating that their colors are not due to unstable radiation damage centers. There was an apparent slight change of color of the Eibenstein

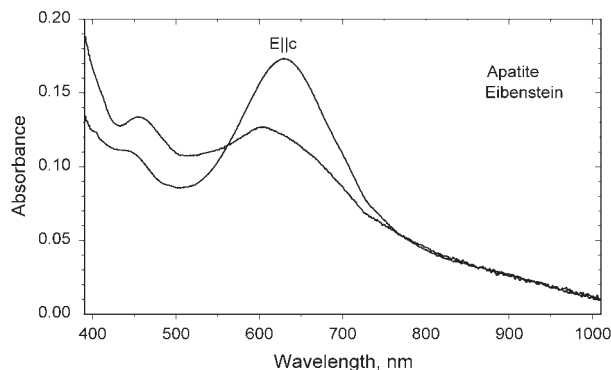


FIGURE 2. The optical absorption spectrum of Mn-rich fluorapatite from Eibenstein an der Thaya

crystal fragment corresponding to the loss of a gray component. The change in color was slight, and the color remained pale blue after heating. All of these observations are consistent with the origin of color from Mn^{5+} .

We can speculate that the 404 nm band (plus the other broad bands near 450 and 600 nm) in the fluorapatite spectrum are from Mn^{2+} . If this is the case, it is surprising that these two bands are not significantly less intense (peak height) than the 404 nm band.

Estimation of the amount of Mn^{5+} at the P site

There is not enough information available to fully quantify the amount of Mn^{5+} in this crystal. However, limits on the Mn^{5+} content can be estimated from two independent methods: (1) The Mn content determined by EMPA is slightly higher (~ 0.08 apfu Mn) than that determined from site-scattering refinement at the Ca sites, and the P content determined from the EMPA is slightly lower (2%; ~ 5.88 apfu P) than for a fully occupied P site (6.00 apfu) (Table 4). Therefore, an upper limit of the Mn^{5+} content at the P site is 5.5% of the total manganese. (2) The amount of Mn^{5+} may be calculated from the intensity of the 640 nm band in the optical spectrum. Although there is no established standard for the intensity of absorption of Mn^{5+} in apatite, it is possible to estimate the intensity from Mn^{5+} in a related compound. In this case, the calibration was derived from the spectrum of $Sr_5(P_{0.99}Mn_{0.01})_3Cl$ obtained from crystals prepared by Brixner (1973). The density of these crystals was calculated from the cell constants of Nötzold et al. (1994) assuming P = 3.0 atoms per formula unit. From these, the molar absorptivity for Mn^{5+} in this synthetic apatite structure was calculated to be 995. Assuming that the molar absorptivity applies to manganian fluorapatite, and assuming that all the intensity of the 640 nm (E || c) absorption is from Mn^{5+} , the concentration of Mn^{5+} in the Eibenstein sample was calculated to be 0.25 wt%, or 2.6% of the total manganese ($\sim P_{5.96}Mn_{0.04}^{5+}$).

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