The location of Mn (MnO: 2.0 wt%) in fluorapatite from Lavra da Golconda, near Governador Valadares, Minas Gerais, Brazil

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The local structural features around Mn in a transparent pale blue Mn-bearing fluorapatite (MnO: 2.0 wt%) from Lavra da Golconda, Minas Gerais, Brazil were investigated by a combined analysis of single crystal X-ray diffraction and XAFS. The crystal structure with the optimized formula (Ca_{4.83}Mn^{2+}_{0.15}Sr_{0.02})P_{3}O_{12}F with space group P\textit{6}_3/\textit{m}, \textit{a} = 9.384(2), \textit{c} = 6.8842 (6) Å, \textit{Z} = 2 has been refined to \textit{R} = 1.92% for the unique 555 reflections (Mo K\textit{\alpha}). The structural refinement suggests that Mn almost exclusively occupies the Ca1 site. The EXAFS analysis indicates that Mn at the Ca1 site is surrounded by nine oxygen atoms with six shorter bonds and three longer bonds. BVS calculated for the local environment around Mn shows good agreement with the expected valence state of Mn. The present EXAFS results suggest that the longer bond distances (Ca1–O3) in fluorapatite structures will not be affected by Mn due to weak bonding interactions.

Keywords: Mn-bearing fluorapatite, XAFS, Single crystal X-ray diffraction

INTRODUCTION

Apatite structure with the two crystallographically distinct Ca sites plays an important role as a reserving host for a variety of the divalent and trivalent cations. Among divalent cations, the most common substituents for the natural apatite are Mn\textsuperscript{2+} and Sr\textsuperscript{2+}. In particular, the distribution of Mn has been an interesting subject for many researchers because of the importance of Mn-doped apatite as a fluorescent activator and coactivator (e.g., Waychunas, 2002; Xia and Liu, 2016).

Most of X-ray diffraction studies on fluorapatite indicate the preference of Mn at the Ca1 site (Suitch et al., 1985; Hughes et al., 1991; Hughes et al., 2004). A similar conclusion was also reported in the measurement of optical properties (Ryan and Vodoklys, 1971; Ryan et al., 1972). However, every sample more or less indicates the distribution of Mn at the Ca2 site, and some reports even indicated no slight ordering of Mn (Warren, 1970; Warren and Mazelsky, 1974).

The optimized formulae for a Mn-bearing fluorapatite from Lavra da Golconda, Minas Gerais, Brazil is (Ca_{4.83}Mn^{2+}_{0.15}Sr_{0.02})P_{3}O_{12}F. The small amount of Mn and coexisting Sr lead to some difficulties in studying manganese preference for two distinct Ca sites when only single crystal X-ray diffraction is used. Additionally, it is difficult to determine the local structure around minor element only using average structure analysis. Hence another experimental approach is strongly required for further understanding of site preferences for minor elements in fluorapatite. This paper demonstrates the combined use of single crystal X-ray diffraction and X-ray absorption fine structure (XAFS) analyses for the characterization of minor Mn in the fluorapatite structure.

EXPERIMENTAL

The present Mn-bearing fluorapatite originates from Lavra da Golconda, near Governador Valadares, Minas Gerais, Brazil. The specimen is transparent and pale blue with purple stains, and indicates a hexagonal prismatic form with flat basal terminations. Quantitative analysis of the chemical composition was carried out using a JEOL JXA–8530F electron probe micro-analyzer (EPMA) in wavelength-dispersion mode with the following operating
conditions: accelerating voltage of 15 kV, beam current of 12 nA and beam diameter of approximately 5 µm. The weight fraction of H2O component was also analyzed by thermogravimetric analysis (Rigaku TG-DTA 8120). Following the report on thermogravimetric analysis (Ton-suadu et al., 2012), weight loss was measured for the present sample between 200 and 800 °C. Almost no weight loss was observed, which suggests that there is no hydroxyl component in the crystal structure. The results of the chemical analysis are listed in Table 1. The structural formula was calculated using O + F = 13.

A single crystal prismatic sample with dimensions of 0.164 × 0.128 × 0.174 mm was selected for single crystal X-ray diffraction. Intensity measurement was carried out by using an X-ray diffractometer equipped with an imaging plate and a conventional X-ray tube (Rigaku R-AXIS RAPID). The Mo Kα radiation was utilized and the ordinary oscillation technique was applied. After Lorentz and polarization corrections, an absorption correction was performed using the integration method based on the specimen’s shape (Higashi, 1995). Data reduction yielded 581 independent reflections, among which 555 reflections met the condition of I_{obs} > 2.0σ(I_{obs}). Scattering factors for neutral atoms and anomalous dispersion coefficients were adopted from Volume C of the International Tables for Crystallography (1992). The structural parameters for fluorapatite reported by Hughes et al. (1989) were used as initial parameters and the least-squares refinement was carried out by using the software program SHELXL (Sheldrick, 2008). Fluorapatite has a generalized structural formula Ca5(PO4)3F, and an initial structural refinement was carried out by using this structural formula. The common procedure with anisotropic displacement parameters with an extinction correction converged to R indices of 2.01% for the observed reflections. Since the optimized chemical composition inferred by EPMA indicated that the heavier Mn and Sr should reside at two Ca sites, Ca1 and Ca2, the site occupation parameters for these Ca sites were further refined. The excess electron observed at Ca1 and Ca2 sites agreed well with the contents of Mn or Sr, respectively. This result indicates a mixed occupation model of Ca/Mn for the Ca1 site and Ca/Sr for the Ca2 site. Further least-square refinements of all variables converged to R indices of 1.92% for 555 observed reflections. Cell parameters and other detailed information on the structural refinement are listed in Table 2. Final positional, displacement and site occupancy parameters are given in Tables 3 and 4. The calculated interatomic distances are listed in Table 5. The chemical composition calculated by the refinement is also given in Table 1. It should be noted that previous results for natural fluorapatite with an appreciated amount of Sr suggested the strong preference of larger Sr at the smaller Ca2 site (Hughes et al., 1991). XAFS spectra at the Mn K-absorption edge were measured at both Photon Factory BL-7C and BL-15A1, Institute of Material Structure Science (IMSS), High Energy Accelerator Research Organization, Tsukuba, Japan. The X-rays were monochromatized with a Si (111) double.
ble–crystal monochromator. The intensities of the incident and transmitted X-ray beam were measured by ionization chambers. XAFS data were collected on the fluorapatite and several standards including reagent grade Mn$_2$O$_3$ and rhodonite MnSiO$_3$ from Chiurucu Mine, Huánuco, Peru, for the X-ray absorption near edge structure (XANES) spectra of Mn$^{3+}$ and Mn$^{2+}$ compounds, respectively. XAFS spectrum of reagent grade MnO was also measured and served as the reference value of the amplitude reduction factor ($S_0$) for the extended X-ray absorption fine structure (EXAFS) simulation. The XANES spectra and EXAFS interference functions were extracted from the measured spectra using the Athena and Artemis software program with an interface to the IFEFFIT library (Ravel and Newville, 2005; Newville, 2001). EXAFS simulation of the local structure around Mn in the fluorapatite was performed based on the structural parameters obtained by single crystal X-ray diffraction. For the simulation models, one Mn atom occupied either the Ca1 or Ca2 site. In order to assess the structural environment of each model, the present calculation included single and multiple scattering paths within the coordination shell up to 6 Å around Mn. Phase shifts and oscillation amplitudes were calculated with FEFF6 code (Rehr and Albers, 2000). The value of the $S_0$ was determined to be 0.85 by EXAFS analysis on standard MnO sample. The EXAFS Debye–Waller factors for each scattering path were estimated from the correlated Debye model (Sevillano et al., 1979), with a Debye temperature of 531 K (Li et al., 2015). The energy shift parameter and local expansion coefficient for each simulation model were determined by curve fitting of the $k^2$-weighted EXAFS oscillation to experimental data.

**RESULTS AND DISCUSSION**

**Crystal structure**

The structure of the present Mn–bearing fluorapatite from Lavra da Golconda is isotypic with that of the ordinary fluorapatite with space group P6$_3$/m (Sudarsanan et al., 1972). The lowering of the symmetry to P6$_3$ or P3 due to the ordering of a small amount of Mn (Suitch et al., 1985) was not observed. The refined structure model, (Ca$_8$Mn$_{0.14}$Sr$_{0.02}$)(PO$_4$)$_3$F, is consistent with the chemical formula (Ca$_8$Mn$_{0.15}$Sr$_{0.02}$)(PO$_4$)$_3$F obtained from the EPMA results using the ideal formula for fluorapatite (recalculation to 13 anions and 5 divalent cations). This
agreement provides a good check on the accuracy of the present refinement. The two Ca sites with nine- and seven-fold coordination environments have the following respective occupancies: $\text{Ca}_{0.928(9)}\text{Mn}_{0.072}$ for Ca1 site and $\text{Ca}_{0.995(3)}\text{Sr}_{0.005}$ for Ca2 site. The present refinement shows that Mn resides at the Ca1 site, and Sr prefers to order the Ca2 site. These results are in good accordance with the previous report (Hughes et al., 1991). Figure 1 shows the structure of fluorapatite and the coordination environments around the Ca1 and Ca2 sites. The Ca1 site is surrounded by nine oxygens and observed Ca1–O bond distances are between 2.391 and 2.811 Å, with an average value of $\langle\text{Ca1–O}\rangle = 2.552$ Å (Table 5). The Ca2 site is coordinated by six oxygens and one monovalent anion (fluorine). Observed Ca2–(O, F) bond distances are between 2.300 and 2.702 Å, and an averaged value of $\langle\text{Ca2–O}\rangle$ is 2.462 Å (Table 5). Although the ionic radius (Shannon, 1976) of Mn$^{2+}$ ($\text{VII Mn}^{2+}$: 0.90 Å) is smaller than those of Ca$^{2+}$ and Sr$^{2+}$ ($\text{VII Ca}^{2+}$, 1.06 Å; $\text{VII Sr}^{2+}$, 1.21 Å), the Mn atoms occupy the larger Ca1 site. Such a tendency is common to the structures of Mn-bearing fluorapatite (Hughes et al., 1991; Hughes et al., 2004).

The size of the Ca1 site in the present study shows a similar trend reported by Hughes et al. (2004), where average distance at the Ca1 site decreases linearly with increasing Mn content and can be attributed to the residence of Mn atom in the Ca1 site. The $\langle\text{Ca1–O}\rangle$ distance, 2.552 Å, is slightly shorter than that observed in Mn-free natural fluorapatite reported by Hughes et al. (1989) (2.554 Å) and longer than those of 2.544 and 2.535 Å measured by Hughes et al. (1991) for natural fluorapatites containing Mn occupancies of 0.08 and 0.21 at the Ca1 site, respectively.

The bond distances of the Ca2 site in this study show no significant deviation from those of the natural fluorapatite studied by Hughes et al. (1989) (2.463 Å), but modestly larger values than those of the synthetic pure fluorapatite reported by Sudarsanan et al. (1972) (2.427 Å). Since the ionic radius of Sr$^{2+}$ is larger than that of Ca$^{2+}$, the present bond distances are likely in accordance with the substitution of Sr for Ca at the Ca2 site. This interpretation is consistent with previous studies, suggesting the preference of Sr at the Ca2 site in apatite structures (Sudarsanan and Young, 1980; Hughes et al., 1991; Rakovan and Hughes, 2000).

Local coordination aspect of Mn

XANES spectra are quite sensitive to the electronic states of X-ray absorbing atoms. Accordingly, they are useful to characterize the valence states of Mn impurities in minerals (e.g., Sugiyama et al., 2016; Sugiyama et al., 2017).
Figure 2 shows the Mn $K$-edge XANES spectra of the fluorapatite sample together with those of $\text{Mn}_2\text{O}_3$ and rhodonite $\text{MnSiO}_3$. Each vertical line on the spectra is the position of the absorption edges, defined as half the normalized edge jump.

For a direct determination of the site preference for minor Mn atoms, we performed a multiple-scattering EXAFS simulation by using the structure parameters obtained by ordinary single crystal X-ray diffraction. Figures 3a and 3b indicate EXAFS spectra in $k$ space and their Fourier transforms in $r$ space for the present fluorapatite, respectively, together with their simulations for two models in which Mn resides at either Ca1 or Ca2 site. The oscillation profiles in Figure 3a indicate that peak positions in the Ca1 model, in which Mn prefers the Ca1 site, correspond reasonably well with the experimental signal. This result is more obvious in Figure 3b, where the Ca1 model shows close agreement with the experimental profile even in the range for $r > 2.2$ Å (approximately 2.8 Å after phase-shift correction), indicating that Mn almost exclusively occupies the Ca1 site in the present fluorapatite.

Figure 4 shows the results of the least-square fitting for the short-range structure around Mn at Ca1 site. The fitting parameters for each path are listed in Table 6. The experimental spectrum can be fitted to a shorter Mn–O path (coordination number, $N = 6$) and a longer one ($N = 3$) together with a second neighbor Mn–P path ($N = 3$). Although the Ca1–O1 and Ca1–O2 coordinations are indistinguishable for the present analysis, the obtained local structure around Mn appears to indicate typical nine-fold coordination of the Ca1 site as shown in Figure 1. It may be interesting to discuss the contribution of longer Mn–O distance in the first-neighbor coordination shell around the Ca1 site. The bond valence sum (BVS), calculated around Mn using the bond distances listed in Table 6 and the BVS parameters reported by Palenik (1997), equals 2.0. This value shows good agreement with the expected valence state of Mn and supports the obtained local structural model. The bond valence for the longer Mn–O distance is roughly one-sixth of that of the shorter Mn–O distance. According to the discussion by Hughes et al. (1991) and Hughes et al. (2004), the shorter bond distances (Ca1–O1 and Ca1–O2) decrease with increasing Mn content, whereas longer bond distances (Ca1–O3) remains constant. The present results imply that Ca1–O3

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**Figure 2.** Mn $K$-edge XANES spectra of fluorapatite from Lavra da Golconda (Mn-bearing FAP), rhodonite $\text{MnSiO}_3$, and $\text{Mn}_2\text{O}_3$. Vertical lines on the spectra are the positions of the absorption edges, defined as half the normalized edge jump.

**Figure 3.** Experimental and simulated profiles of (a) Mn $K$-edge $k^2$-weighted $\chi(k)$ functions and (b) their Fourier transforms in real space.
bond length is not be affected by central atom due to weak bonding interactions.

ACKNOWLEDGMENTS

EXAFS and XANES measurements were carried out at BL7C and BL15A1 beamlines at the Photon Factory, with the approval of the Photon Factory Program Advisory Committee (Proposal No. 2015G575 and 2016G130). This work was supported by JSPS KAKENHI Grant Number JP15K13589.

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