Determination of the locations of Mn and Fe in Mn-bearing andalusite by anomalous X-ray scattering and X-ray absorption fine structure analyses

Hiroshi Arima*, Yuki Tani*, Kazumasa Sugiyama* and Akira Yoshiasa**

*Institute for Materials Research (IMR), Tohoku University, Sendai 980-8577, Japan
**Present address: Neutron Science and Technology Center, CROSS, Ibaraki 319-1106, Japan
***Graduate School of Science and Technology, Kumamoto University, Kumamoto 860-8555, Japan

Local structural features around Mn and Fe in Mn-bearing andalusite from Västanåberget, Sweden were investigated by anomalous X-ray scattering (AXS) and X-ray absorption fine structure (XAFS). The X-ray absorption near edge structure (XANES) spectra indicate that all of the Mn and Fe atoms are in +3 oxidation state. Both the electron density map of Mn obtained by AXS and simulated multiple-scattering extended X-ray absorption fine structure (EXAFS) spectra indicate that the Mn atoms exclusively occupy Al1 sites. Further, the EXAFS analysis indicates that the first neighbor coordinated to Mn at the Al1 site shows a complete structural relaxation and Jahn–Teller distortion owing to Mn3+. In addition, the EXAFS analyses reveal that Fe occupies both Al1 and Al2 sites. The Fe site occupancy ratio (Fe at Al2 to total Fe) in the Mn-bearing andalusite sample is 40–50%. Employing the local structural information around Mn and Fe, a conventional single-crystal structural refinement converged at \( R = 2.34\% \) with a structural formula of \((\text{Al}_{0.82}\text{Mn}_{0.16}\text{Fe}_{0.02})[6](\text{Al}_{0.99}\text{Fe}_{0.01})[5]\text{SiO}_5\) (space group \( \text{Pnnm} \) with \( a = 7.8538(9), b = 7.9463(9), c = 5.5867(6) \) Å).

Keywords: Mn-bearing andalusite, Local structure, Anomalous X-ray scattering, X-ray absorption fine structure

INTRODUCTION

Mn-bearing andalusite, formerly called ‘viridine’, has a structural formula of \((\text{Al}_{2-x-y}\text{Mn}_x\text{Fe}_y)\text{SiO}_5\). The stability and optical properties of andalusite strongly depend on the substitution of transition metals and their coordination environments (Gunter and Bloss, 1982; Abs–Wurmbach et al., 1983; Wang et al., 2017). Therefore, the understanding of local structural features of transition metals in andalusite is important not only in geoscience but also in materials science.

The andalusite structure consists of silicate tetrahedra and two crystallographically distinct Al sites, denoted as Al1 and Al2, which have six- and five-fold coordination environments, respectively (Fig. 1a). Previous X-ray diffraction (XRD) (Abs–Wurmbach et al., 1981) and spectroscopic (Hålenius, 1978; Abs–Wurmbach et al., 1981) studies on Mn-bearing andalusite have indicated the site preferences of Mn and Fe at the Al1 site.

In most cases, a small amount of Mn and coexisting Fe lead to some uncertainties in the modeling of the site preferences for the two distinct Al sites when only conventional single-crystal XRD data are considered, as the scattering factors of Mn and Fe are rather similar. Additionally, it is difficult to determine the individual local environmental structures of minor elements in multiply occupied sites exclusively by an average structural analysis. Therefore, another experimental approach is required for further understanding of structural features of minor elements in andalusite.

In this article, we report direct evidences for the site preferences of Mn and Fe in Mn-bearing andalusite using element-selective analysis methods, anomalous X-ray scattering (AXS), and X-ray absorption fine structure (XAFS) in combination with crystallographic information obtained by ordinary single-crystal XRD and demonstrate the local structural environments of the minor
 constituents, Mn and Fe, in the andalusite structure.

**EXPERIMENTAL METHODS**

The Mn–bearing andalusite sample analyzed in this study originated from Västanåberget, Näsum, Bromölla, Skåne, Sweden and has light green color. Both qualitative and quantitative analyses of its chemical composition was carried out using a scanning electron microscope (SEM, JEOL JSM-7001F) equipped with an energy dispersive X-ray spectroscopy system (EDX, Oxford INCA). The accelerating voltage was 15 kV, while the beam current was 0.5 nA. The following standards were used in the quantitative analysis: SiO₂ for Si, Al₂O₃ for Al, Fe₂O₃ for Fe, and MnO for Mn. The results of the chemical analyses are presented in Table 1. The final chemical formula, (Al₁.₈₁Mn₀.₁₆Fe₀.₀₃)SiO₅, was derived based on the idealized formula for andalusite (recalculated for two trivalent cations at Al sites and one tetravalent Si per formula unit).

A single crystal with dimensions of 0.132 × 0.120 × 0.133 mm³ was selected for single-crystal XRD. The average structure was analyzed using a graphite-monochromatized Mo Kα radiation. The diffraction intensity was measured using an X-ray diffractometer equipped with an imaging plate and conventional X-ray tube (Rigaku R-AXIS RAPID), employing the ordinary oscillation technique. After Lorentz and polarization corrections, an absorption correction was performed using the integration method based on the specimen's shape (Higashi, 1995). Scattering factors for neutral atoms and anomalous dispersion coefficients were obtained from Volume C of the International Tables for Crystallography (1992). A least-squares refinement was carried out using the software program SHELXL (Sheldrick, 2008) implemented in WinGX (Farrugia, 2012). Detailed information on the data collection is provided in Table 2 along with the refinement results.

The AXS-based diffraction experiments for the Mn and Fe K-absorption edges were performed at the Photon Factory (PF) BL–6C, Institute of Material Structure Science, High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. The diffraction intensities were measured using a horizontal-type four-circle diffractometer (Rigaku AFC-5) installed on the beamline. A pair of incident energies, corresponding to 25 and 150 eV below each K-absorption edge, \( E_{\text{abs}} \) (Mn: 6539 eV, Fe: 7112 eV), were used in the measurements. These energies were well tuned by employing a Si (111) monochromator. The monochromatic incident beam was circularly polarized by a transmission-type (001) diamond phase retarder (Hirano et al., 1995) to avoid the loss of intensity due to the polarization effect in the horizontal scattering geometry. The diffraction intensities up to approximately \( \sin \theta \lambda = 0.50 \text{ Å}^{-1} \) were measured for each energy. An absorption correction was performed by the \( \psi \)-scan method reported by North et al. (1968). Detailed procedures of AXS analyses have been described in previous studies (Wulf, 1990; Figure 1. Crystal structure of the Mn-bearing andalusite from Västanåberget, Sweden and coordination environments of the Al₁ and Al₂ sites illustrated by VESTA (Momma and Izumi, 2011).

### Table 1. Chemical composition of the Mn-bearing andalusite from Västanåberget, Sweden

| Oxide wt%* |          |
|------------|----------|
| SiO₂       | 35.5 (0.3) |
| Al₂O₃      | 55.7 (0.6) |
| Fe₂O₃      | 1.4 (0.1)  |
| MnO        | 7.8 (0.8)  |
| **Total**  | 100.4 (0.4) |
| **Atoms** pfu (5 Oxygens) |          |
| Si         | 0.99     |
| Al         | 1.82     |
| Fe⁺        | 0.03     |
| Mn³⁺       | 0.17     |

*Analyses were carried out on 13 points. Standard deviations are in parentheses.
Genba et al., 2002; Sugiyama et al., 2010; Togashi et al., 2011).

Transmission XAFS spectra of the andalusite at the Mn and Fe K-absorption edges were recorded at PF BL-7C and 9C. The X-rays were monochromatized with a Si(111) double-crystal monochromator. We also collected spectra of a reagent-grade Mn$_2$O$_3$ and three natural minerals (rhodonite MnSiO$_3$, aegirine NaFeSi$_2$O$_6$, and ilmenite FeTiO$_3$) as standards for the X-ray absorption near-edge structure (XANES) spectra of Mn$^{3+}$, Mn$^{2+}$, Fe$^{3+}$, and Fe$^{2+}$ compounds, respectively. The XANES spectra and EXAFS interference functions were extracted from the acquired spectra using the Athena and Artemis software program with an interface to the IFEFFIT library (Newville, 2001; Ravel and Newville, 2005). EXAFS simulations of the local structures around Mn and Fe in the andalusite were performed based on the structural parameters obtained by single-crystal XRD. Phase shifts and oscillation amplitudes were calculated with the FEFF6 code (Rehr and Albers, 2000). The value of $S_0$ was fixed at 0.9. The EXAFS Debye-Waller factors for each scattering path were derived from the correlated Debye model (Sevillano et al., 1979), with a Debye temperature of 855 K (Robie and Hemingway, 1984). The energy shift parameter and local expansion coefficient for each simulation model were estimated by fitting the experimental data with the $k^2$-weighted EXAFS oscillation curve.

**STRUCTURAL ANALYSIS**

Andalusite has a generalized structural formula, Al$^{[6]}$Al$^{[5]}$SiO$_5$, and an initial structural refinement was carried out for this formula. The structural parameters of andalusite reported by Winter and Ghose (1979) were used as the initial parameters. The common procedure with anisotropic displacement parameters with an extinction correction converged to $R$ index of 3.79% for 440 symmetry-independent reflections obtained by averaging the symmetry-equivalent intensities. The difference-Fourier map obtained using the initial refinement model shows a significant residual density peak with a height of 0.9 e/Å$^3$ near the Al1 site. In order to revise the structural model, results of the AXS analysis were used. Figure 2 shows the distribution maps of Mn at $z = 0$ and 0.25 obtained by a difference Fourier synthesis of the Mn-AXS data. The electron density of Mn is clearly observed at the Al1 site, whereas no density peak is observed at the Al2 site. These results suggest the strong preference of Mn for the Al1 site. However, the small amount of Fe and influence of the Mn K-absorption edge prevented us from obtaining the Fe-AXS data with sufficient accuracy. However, the obtained distribution map for Fe implies that Fe occupies both Al1 and Al2 sites. Based on these results, the following refinement constraints were applied in the final refinements: (1) all of the atomic sites were fully occupied, (2) the Si site was exclusively occupied by Si, (3) Mn atoms occupied only the Al1 site, and (4) the total occupancies of Al, Mn, and Fe atoms were constrained to correspond with the results of the chemical analysis.

**RESULTS AND DISCUSSION**

**Crystal structure**

The structure of the andalusite sample from Västanåber-
get is isotypic to that of the ordinary andalusite with the space group \( \text{Pnnm} \) (Burnham and Buerger, 1961). Based on the AXS results that Mn in the presented andalusite sample resides at the Al1 site, we obtained the following site occupancies: Al1: \( \text{Al}_{0.82}\text{Mn}_{0.16}\text{Fe}_{0.02} \) and Al2: \( \text{Al}_{0.99}\text{Fe}_{0.01} \). The refinement revealed that Fe occupies both Al1 and Al2 sites and that the fraction of Fe located at the Al2 site is \(~40\%\).

The lattice constants of the analyzed andalusite sample are larger than those of \( \text{Al}_2\text{SiO}_5 \) reported by Winter and Ghose (1979) (\( a = 7.7980(7) \), \( b = 7.9031(10) \), \( c = 5.5566(5) \) Å). In particular, the expansion rate of the \( a \)-axis is 30% larger than those of the other two axes owing to the elongation of the Al1–O4 bond, as discussed below. Using the relationship between the lattice constants and variables \( x \) and \( y \) in the structure formula \( \text{Al}_{2-x-y}\text{Mn}_x\text{Fe}_y\text{SiO}_5 \) (Gunter and Bloss, 1982), the chemical composition of the analyzed andalusite can be estimated to be \( \text{Al}_{1.75}\text{Mn}_{0.18}\text{Fe}_{0.07} \text{SiO}_5 \). Considering the

### Table 3. Atomic positions, site occupancy factors, and equivalent displacement parameters (\( \text{Å}^2 \)) of the Mn-bearing andalusite

| Site | Site occupancy | \( x \) | \( y \) | \( z \) | \( U_{eq} \) |
|------|----------------|------|------|------|--------|
| Al1  | 4e \( \text{Al}_{0.82}\text{Mn}_{0.16}\text{Fe}_{0.02} \) | 0 | 0 | 0.24223(10) | 0.0072(2) |
| Al2  | 4g \( \text{Al}_{0.99}\text{Fe}_{0.01} \) | 0.37154(9) | 0.13856(9) | 1/2 | 0.0061(2) |
| Si   | 4g *           | 0.24679(8) | 0.25278(7) | 0 | 0.0054(2) |
| O1   | 4g *           | 0.4246(2) | 0.3624(2) | 0 | 0.0076(4) |
| O2   | 4g *           | 0.1028(2) | 0.3999(2) | 0 | 0.0085(4) |
| O3   | 4g *           | 0.4239(2) | 0.3628(2) | 0 | 0.0069(3) |
| O4   | 8h *           | 0.23339(15) | 0.13557(15) | 0.2393(2) | 0.0083(3) |

* Assumed to be fully occupied by respective ion.

### Table 4. Anisotropic displacement parameters (\( \text{Å}^2 \)) of the Mn-bearing andalusite

| Site | \( U_{11} \) | \( U_{22} \) | \( U_{33} \) | \( U_{23} \) | \( U_{13} \) | \( U_{12} \) |
|------|------------|------------|------------|------------|------------|------------|
| Al1  | 0.0100(4) | 0.0069(4) | 0.0047(3) | 0 | 0 | 0.0015(2) |
| Al2  | 0.0063(4) | 0.0062(4) | 0.0058(4) | 0 | 0 | 0.0004(3) |
| Si   | 0.0063(4) | 0.0049(3) | 0.0050(4) | 0 | 0 | 0.0004(2) |
| O1   | 0.0067(8) | 0.0085(8) | 0.0076(8) | 0 | 0 | 0.0009(6) |
| O2   | 0.0072(8) | 0.0054(8) | 0.0129(8) | 0 | 0 | 0.0005(6) |
| O3   | 0.0086(8) | 0.0067(8) | 0.0055(8) | 0 | 0 | 0.0004(6) |
| O4   | 0.0100(6) | 0.0085(6) | 0.0062(6) | 0.0010(4) | 0.0014(4) | 0.0000(5) |

### Table 5. Selected interatomic distances (\( \text{Å} \)) in the Mn-bearing andalusite

| Bond | Distance (Å) |
|------|--------------|
| Al1–O1 | 1.902(1) |
| Al1–O3 | 1.838(1) |
| Al1–O4 | 2.126(1) |
| Al2–O1 | 1.955 |
| Al2–O2 | 1.842 |
| Si–O1 | 1.646(2) |
| Si–O2 | 1.627(2) |
| Si–O4 | 1.633(2) |

\( x \)-\( y \)-\( z \)-absorption edge. The contours are drawn at intervals of 0.1 e/Å\(^2\); negative contours are presented as broken lines, while zero contours are omitted.
assumption by Gunter and Bloss (1982) that both Mn$^{3+}$ and Fe$^{3+}$ occupy only the Al$^1$ sites, the $x$ and $y$ values are concordant with our results (Table 1).

Figures 1b and 1c show the coordination environments around the Al$^1$ and Al$^2$ sites, respectively. The Al$^1$ site is surrounded by six O atoms; the observed Al$^1$–O bond distances are in the range of 1.838 to 2.126 Å, with an average value of <Al$^1$–O> = 1.955 Å. The Al$^2$ site is coordinated by five O atoms; the observed Al$^2$–O bond distances are in the range of 1.816 to 1.907 Å. The average <Al$^2$–O> = 1.842 Å and <Si–O> = 1.635 Å determined in this study did not significantly deviate from those of Al$^2$SiO$^5$ andalusite (<Al$^2$–O> = 1.836 Å and <Si–O> = 1.631 Å; Winter and Ghose, 1979), whereas the <Al$^1$–O> bond distance is 1.0% larger than that of andalusite (<Al$^1$–O> = 1.935 Å; Winter and Ghose, 1979). As the minor elements in our sample, Mn$^{3+}$ and Fe$^{3+}$, have larger ionic radii (VIMn$^{3+}$ and VIFe$^{3+}$: 0.65 Å) (Shannon, 1976) than that of Al$^{3+}$ (VIAL$^{3+}$: 0.54 Å), the longer bond distance is responsible for the minor elements occupying the Al$^1$ sites. Furthermore, the variations in the bond distances of the Al$^1$ sites indicate that the Al$^1$O$^6$ octahedra are significantly more distorted in the Mn$^+$–bearing andalusite than in the andalusite. The presented Mn$^+$–bearing andalusite sample exhibited an increase in the longest Al$^1$–O4 bond distance of 1.9% with respect to that of the andalusite, although the bond distances of both Al$^1$–O1 and Al$^1$–O3 increase by only 0.6%. The observed distortions of the Al$^1$O$^6$ octahedra could be attributed to Mn$^{3+}$ with a strong Jahn–Teller effect preferentially distributed at the Al sites.

**Locations of Mn and Fe**

XANES spectra for the Mn and Fe K–absorption edges are shown in Figures 3 and 4, respectively. XANES data are quite sensitive to the electronic states of the X-ray absorbing atoms. Therefore, they are useful to characterize the valence states of minor elements in minerals (Sugiyama et al., 2016; Sugiyama et al., 2017). As shown in Figure 3, the edge position of the XANES of the Mn$^+$–bearing andalusite sample is identical to that of Mn$^2$O$_3$, suggesting that the Mn atoms are in the +3 oxidation state. This result is in reasonable agreement with the Jahn–Teller distortion of the Al$^1$O$^6$ octahedra expected from the structural analysis. In the case of the Fe K–XANES, the edge position of the Mn$^+$–bearing andalusite sample (Fig. 4) coincides with that of aegirine NaFeSi$_2$O$_6$. This result suggests that Fe atoms are also in the +3 oxidation state, and that a small number or none of them are in the +2 oxidation state in the Mn$^+$–bearing andalusite sample, as reported by Meisel et al. (1990).

For further analysis of the local structure of Mn and Fe atoms, we performed a multiple–scattering EXAFS simulation using the structural parameters obtained by the single-crystal XRD analysis. Figure 5 shows the Mn K–edge EXAFS spectra and their Fourier transforms obtained from the experiments and two simulation models, wherein Mn occupies either the Al$^1$ site or Al$^2$ site. The oscillation profiles in Figure 5a indicate that the peak positions in the Al$^1$ model correspond reasonably well to the experimental signals. This result is more obvious in Figure 5b, where the profile in the Al$^1$ model closely agrees with the experimental profile even in the range of second– and third–neighbor distances, indicating that Mn exclusively occupies the Al$^1$ site in the Mn$^+$–bearing andalusite sample.

The dashed curves in Figure 5 represent the least–squares fitting for the short–range structure around Mn assuming the Al$^1$ site model. The fitting parameters for the first–neighbor coordination shell are presented in
A rather distorted octahedron is inferred from the bond distances in the range of 1.87 to 2.26 Å and average value of $<\text{Mn-O}> = 2.03$ Å, which suggest the Jahn-Teller distortion of the Mn$^{3+}$O$_6$ octahedra.

It is worth noting that the $<\text{Mn-O}>$ distance in the Mn-bearing andalusite sample is close to that between the Al$_1$ site and O in kanonaite fully occupied by Mn and Fe ($<\text{Al1-O}> = 2.022$; Schreyer et al., 2004). This result indicates that the local Mn–O bond distances in the andalusite structure are equivalent to those of the end members regardless of the Mn content. This is known as complete structural relaxation (Urusov, 1992), in which the Mn atom retains its atomic size. Such local structures around Mn appear to strongly correlate with the Mn-site preference and maximum possible Mn content in the andalusite structure. The recent first-principle study by Wang et al. (2017) shows that a larger number of Mn atoms can occupy the Al1 sites, owing to the large Jahn-Teller distortion of the Mn$^{3+}$O$_6$ octahedra and low bulk modulus of the andalusite phase, which suggest the structural relaxation discussed above.

In contrast to the case of Mn, for the Fe K-edge EXAFS (Fig. 6), the experimental spectrum is not reproduced by the models derived by substituting the atoms in either the Al1 or Al2 sites with Fe. The discrepancy between the experimental and simulated spectra indicates that the site preference of Fe is more complex than that of Mn. Assuming a mixed model in which the Fe atoms occupy both Al sites, we obtained the ratio of the Fe occupancy in the Al2 site to that in the Al1 site of 1:1, from a least-squares fitting (dashed curve in Fig. 6). This ratio is approximately equal to the value obtained by the structural refinement. According to the previous results of Mössbauer spectroscopy (Abs-Wurmbach et al., 1981), Fe in natural Mn-bearing andalusite samples mainly occupies...
the Al1 site; 10–15% of the total amount of Fe occupy the Al2 sites. Although the Fe site occupancy ratio (Al2 to Al1) in the Mn-bearing andalusite sample is larger than those reported by Abs–Wurmbach et al. (1981), the site occupancy of Fe atoms in the Al2 sites is 0.012(2), well within the range of the reported values of 0.006–0.014. The occupation limit of Fe in the Al2 site is possibly responsible for the relatively small Fe site occupancy ratio (Al2 to Al1) observed in the previous study.

ACKNOWLEDGMENTS

The AXS and XAFS measurements were carried out with the approval of the Photon Factory Program Advisory Committee (Proposal Nos. 2014G546, 2014G665, and 2015G504).

REFERENCES

Abs–Wurmbach, I., Langer, K., Seifert, F. and Tillmanns, E. (1981) The crystal chemistry of (MnV⁵⁺, Fe⁺)V substituted andalusites (viridines and kanonaitc), (Al₁₋ₓMnₓ(Fe⁺)ₓ)(O|SiO₄): crystal structure refinements, Mössbauer, and polarized optical absorption spectra. Zeitschrift für Kristallographie, 155, 81–113.

Abs–Wurmbach, I., Langer, K. and Schreyer, W. (1983) The influence of Mn⁵⁺ on the stability relations of the AlₓSiO₅ polymorphs with special emphasis on manganese andalusites (viridines), [Alₓ₋ₓFe⁺ₓ⁺]: An experimental investigation. Journal of Petrology, 24, 48–75.

Burnham, C.W. and Buerger, M.J. (1961) Refinement of the crystal structure of andalusite. Zeitschrift für Kristallographie, 115, 269–290.

Farrugia, L.J. (2012) WinGX and ORTEP for Windows: an update. Journal of Applied Crystallography, 45, 849–854.

Genba, M., Sugiyama, K., Hiraga, K. and Yokoyama, Y. (2002) Crystalline structure of a Cu-substituted λ-Al₂SiO₅ phase by means of the anomalous X-ray scattering. Journal of Alloys and Compounds, 342, 143–147.

Gunter, M. and Bloss, F.D. (1982) Andalusite-kanonaitc series: lattice and optical parameters. American Mineralogist, 67, 1218–1228.

Hälenius, U. (1978) A spectroscopic investigation of manganese andalusite. Canadian Mineralogist, 16, 567–575.

Higashi, T. (1995) ABSCOR. Rigaku Corporation, Tokyo, Japan.

Hirano, K., Ishikawa, T. and Kikuta, S. (1995) Development and application of χ-ray phase retarders. Reviews of Scientific Instruments, 66, 1604–1609.

International Tables for Crystallography Volume C. (1992) Dordrecht: Kluwer Academic Publishers.

Meisel, W., Schnellfrath, K., Griesbach, P. and Güthlic, P. (1990) The state of iron in andalusite. Hyperfine Interactions, 57, 2261–2268.

Momma, K. and Izumi, F. (2011) VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. Journal of Applied Crystallography, 44, 1272–1276.

Newville, M. (2000) IFEFFIT: interactive EXAFS analysis and FEFF fitting. Journal of Synchrotron Radiation, 8, 322–24.

North, A.C.T., Phillips, D.C. and Mathews, F.S. (1968) A semi-empirical method of absorption correction. Acta Crystallographica, A24, 351–359.

Ravel, B. and Newville, M. (2005) ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. Journal of Synchrotron Radiation, 12, 537–41.

Rehr, J.J. and Albers, R.C. (2000) Theoretical approaches to χ-ray absorption fine structure. Reviews of Modern Physics, 72, 621–654.

Robie, R.A. and Hemingway, B.S. (1984) Entropies of kyanite, andalusite, and sillimanite: additional constraints on the pressure and temperature of the Al₃SiO₅ triple point. American Mineralogist, 69, 298–306.

Schreyer, W., Bernhardt, H.-J., Fransolet, A.-M. and Armbruster, T. (2004) End-member ferrian kanonaitc: an andalusite phase with one Al fully replaced by (Mn, Fe)V in a quartz vein from the Ardennes mountains, Belgium, and its origin. Contributions to Mineralogy and Petrology, 147, 276–287.

Sevillano, E., Meuth, H. and Rehr, J.J. (1979) Extended χ-ray absorption fine structure Debye-Waller factors. I. Monatomic crystals. Physical Review B, 20, 4908–4911.

Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallographica, A32, 751–767.

Sheldrick, G.M. (2008) A short history of SHELX. Acta Crystallographica, A64, 112–122.

Sugiyama, K., Genba, M., Hiraga, K. and Yokoyama, Y. (2010) The structure of Y–Al₁₋ₓCuₓO₄ (x = 0.8) analyzed by single crystal X-ray diffraction with anomalous X-ray scattering. Journal of Alloys and Compounds, 494, 98–101.

Sugiyama, K., Arima, H., Konno, H. and Kawamata, T. (2016) Distribution of Mn in pink eblaitic tourmaline from Mogok, Myanmar. Journal of Mineralogical and Petrological Sciences, 111, 1–8.

Sugiyama, K., Arima, H., Konno, H. and Mikouchi, T. (2017) XAFS study on the location of Cu and Mn in a greenish blue eblaitc from Alto dos Quntos mine, Brazil. Journal of Mineralogical and Petrological Sciences, 112, 139–146.

Togashi, N., Sugiyama, K., Yu, J., Qiu, S. and Terasaki, O. (2011) Single crystal structure analysis of the Se–incorporated mordenite, coupled with the anomalous X-ray scattering. Solid State Sciences, 13, 684–690.

Urusov, V.S. (1992) A geometric model of deviations from Vegard’s rule. Journal of Solid State Chemistry, 98, 223–236.

Wang, Q., Liang, C., Zheng, Y., Ashburn, N., Oh, Y.J., Kong, F., Zhang, C., Nie, Y., Sun, J., He, K., Ye, Y., Chen, R., Shan, B. and Cho, K. (2017) First principles study of the Mn doping effect on the physical and chemical properties of mullite-familly AlₓSiO₅. Physical Chemistry Chemical Physics, 19, 24991–25001.

Winter, J.K. and Ghose, S. (1979) Thermal expansion and high-temperature crystal chemistry of the AlₓSiO₅ polymorphs. American Mineralogist, 64, 573–586.

Wulf, R. (1990) Experimental distinction of elements with similar atomic number using anomalous dispersion (δ synthesis): an application of synchrotron radiation in crystal structure analysis. Acta Crystallographica, A46, 681–688.

Manuscript Received May 20, 2018
Manuscript accepted October 1, 2018
Published online December 11, 2018
Manuscript handled by Atsushi Kyono