Distribution of chromium among the octahedral sites in chromian epidote from Iratsu, central Shikoku, Japan

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The crystal structures of chromian epidotes from the Sambagawa metamorphic rocks, central Shikoku, Japan, were refined using single-crystal data to investigate the distribution of chromium among the three independent octahedral sites. On the basis of the electron probe microanalysis of the chromian epidotes on the polished surface of thin sections, three chromian epidote grains in a thin section were selected for X-ray intensity data collection, and their Cr₂O₃ values were as much as 1.79, 4.99, and 4.74 wt%, respectively, which led to values of 0.113, 0.315, and 0.299 Cr apfu, respectively. Nevertheless, their Fe₂O₃ contents were nearly constant (8.1–8.7 wt%, 0.49–0.52 Fe apfu) and their SrO contents were not significant (1.8–3.2 wt%, 0.08–0.15 Sr apfu). The selected chromian epidote grains were picked out using a binocular optical microscope from the thin sections, and were labeled as CrEp1, CrEp2, and CrEp3, respectively. The oxidation state of chromium was found to be trivalent by the optical spectrum. ⁵⁷Fe Mössbauer doublets with isomer shift of 0.28–0.53 mm/sec and quadrupole splitting of 1.77–2.24 mm/sec indicate an exclusive distribution of Fe³⁺ at the M3 site. The crystal structure of CrEp1 [*a* = 8.8815(6), *b* = 5.5956(5), *c* = 10.1532(5) Å, β = 115.159(2)°], CrEp2 [*a* = 8.9165(4), *b* = 5.6226(2), *c* = 10.1728(5) Å, β = 115.2365(9)°], and CrEp3 [*a* = 8.895(2), *b* = 5.610(1), *c* = 10.146(2) Å, β = 115.177(2)°] were refined using 1145, 1853 and 1438 unique reflections, respectively, and the calculations converged at *R* factors of 5.8%, 6.6%, and 3.2%, respectively. The resulting structural formula were: [Ca]^{Al}[Ca_{0.86}Sr_{0.14}]^{A2}[Al]^{M1}[Al]^{M2}[Al_{0.43}Cr_{0.09}³⁺Fe_{0.48}³⁺]^{M3}Si₃O₁₂(OH) for CrEp1, [Ca]^{Al}[Ca_{0.90}Sr_{0.10}]^{A2}[Al_{0.86}Cr_{0.14}³⁺]^{M1}[Al]^{M2}[Al_{0.34}Cr_{0.17}³⁺Fe_{0.49}³⁺]^{M3}Si₃O₁₂(OH) for CrEp2, and [Ca]^{Al}[Ca_{0.88}Sr_{0.12}]^{A2}[Al_{0.90}Cr_{0.10}³⁺]^{M1}[Al]^{M2}[Al_{0.37}Cr_{0.12}³⁺Fe_{0.51}³⁺]^{M3}Si₃O₁₂(OH) for CrEp3. The selective distribution of Cr³⁺ at the M3 site in CrEp1, and the *K_D* values (*K_D* = (Cr³⁺/Al)^{M1}/(Cr³⁺/Al)^{M3}) of 0.35(3) for CrEp2 and 0.41(3) for CrEp3 show that the preference of Cr³⁺ in the octahedral sites is M3 > M1 ≫ M2. The variations in the M1–O_i and M3–O_i distances indicate an equidimensional expansion of the M1O₆ and M3O₆ octahedra by the substitution of Cr³⁺(+ Fe³⁺) for Al³⁺.

Keywords: Epidote, Chromium, Crystal structure, X-ray, Mössbauer, Optical spectroscopy

INTRODUCTION

Epidote group minerals with the formula Al₁A₂M₁M₂M₃Z₃O₁₂(OH) belong to the sorosilicate class, and their struc-

ture is based on a single chain of M₂ octahedra and multiple chains of central M₁ and peripheral M₃ octahedra parallel to the *b* axis, linked by independent SiO₄ and Si₂O₇ groups (Ito et al., 1954; Dollase, 1968). In calcium epidote, Ca²⁺ cations occupy 9-coordinated A1 and 10-coordinated A2 sites, trivalent cations, such as Al³⁺, Fe³⁺, Mn³⁺, and Cr³⁺, are distributed among the octahedral M₁, M₂ and M₃ sites, and Si cations occur in the tetrahedral Z sites.

The distribution of Fe³⁺ and Mn³⁺ in calcium epidote

doi:10.2465/jmps.060310

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members and the effect on their crystal structures have been investigated by means of structural analysis (Dollase, 1969, 1971; Kvik et al., 1988; Ferraris et al., 1989; Bonazzi et al., 1990, 1992; Bonazzi and Menchetti, 1994, 1995; Langer et al., 2002; Nagashima and Akasaka, 2004; and others) and a variety of spectroscopic methods (Burns and Strens, 1967; Dollase, 1973; Paesano et al., 1983; Fehr and Heuss-Aßbichler, 1997; Langer et al., 2002; and others). On the other hand, the distribution of Cr^{3+} has been studied by means of optical spectroscopy (Burns and Strens, 1967), but the structural refinement of chromian epidote has not been carried out so far, because the occurrence of chromian epidote is not common.

Recently, Nagashima et al. (2006) reported on the occurrence of chromian epidote containing up to 6 wt% Cr_2O_3 in pebbles of omphacite rock from the Sambagawa metamorphic rocks in central Shikoku, Japan. In the present study, we have investigated the structure of chromian epidote obtained using single-crystal X-ray diffraction coupled with ^{57}Fe Mössbauer spectroscopy and optical spectroscopy.

EXPERIMENTAL METHODS

Samples

The chromian epidote studied occurs in omphacite rock pebbles obtained from the Sambagawa metamorphic rocks in central Shikoku, Japan. Nagashima et al. (2006) distinguished three types of chromian epidote: Ca-epidote with < 3 wt% SrO, Sr-rich epidote with 3–11 wt% SrO, and the rare-earth elements (REE)-rich epidote with 2–7 wt% ($\text{Ce}_2\text{O}_3 + \text{La}_2\text{O}_3 + \text{Nd}_2\text{O}_3 + \text{Pr}_2\text{O}_3 + \text{Sm}_2\text{O}_3 + \text{Gd}_2\text{O}_3$), and described the cores of the Sr-rich epidote being overgrown with Ca-epidote, whereas the Ca-epidotes were rimmed by and/or intergrown with REE-rich epidotes. The Cr_2O_3 content in the epidote is variable and attains up to 6 wt% around the chromite grains. The Cr distribution is not related to any zonal structure. The Fe^{3+} content varies within a narrow range: 5–7 or 6–9 wt% of the total Fe_2O_3 (Nagashima et al., 2006).

In order to analyze the oxidation state of the iron and chromium using ^{57}Fe Mössbauer spectroscopy and optical spectroscopy, respectively, the chromian epidote was separated from the omphacite rock pebbles using the following procedure. The pebbles were manually crushed down to grains 0.25–0.5 mm in diameter, and the chromian epidote grains were then separated using a Franz isodynamic separator. They were further purified by handpicking under an optical microscope, and the separated grains were crushed to produce grains with 100–150 μm in diameter. The samples obtained were purified once again using the

isodynamic separation and handpicking procedures. Finally, about 200 mg of the chromian epidote grains were collected and ground using an agate mortar to produce a powdered sample. The purity of the powdered sample was examined using X-ray powder diffraction method.

For the single-crystal structural analysis of the chromian epidote, chemically homogeneous crystals or grains were searched for on the polished surface of thin sections by use of the element concentration and quantitative analysis using a JEOL JXA-8800M electron probe microanalyzer (EPMA). The details of the analytical conditions of the EPMA analysis have been described in Nagashima et al. (2006). Finally, three chromian epidote grains with relatively high Cr_2O_3 content were selected for X-ray data collection. They were picked out under a binocular optical microscope from a thin section of Sample 2, as described in Nagashima et al. (2006). The samples obtained were labeled as CrEp1, CrEp2, and CrEp3 and had dimensions of $0.20 \times 0.40 \times 0.20$, $0.20 \times 0.20 \times 0.20$, and $0.50 \times 0.40 \times 0.10 \text{ mm}^3$, respectively.

X-ray powder diffraction

A part of the powdered sample was spread uniformly over the surface of a silicon non-reflection specimen holder. Step scan powder diffraction data were collected using a Rigaku RINT automated Bragg-Brentano diffractometer system equipped with a curved graphite diffracted-beam monochromator. The Cu X-ray tube generator was operated at 35 kV and 20 mA. The X-ray powder diffraction profile was taken between 5° and 120° in 2θ using a step interval of 0.02° and a step count time of 5 seconds.

To evaluate the purity of the powdered sample, the powder diffraction data was analyzed using the RIETAN-2000 program (Izumi and Ikeda, 2000). The peaks were defined using a modified split pseudo-Voigt function implemented by (Izumi and Ikeda, 2000). The asymmetry parameter was built into this profile function. The preferred orientation was corrected with the March-Dollase function (Dollase, 1986).

^{57}Fe Mössbauer spectroscopy

The ^{57}Fe Mössbauer spectrum of the chromian epidote samples (about 150 mg of powder) was measured at 298 K using 370 MBq ^{57}Co in Pd as the γ -ray source. The Mössbauer data were obtained using a constant acceleration spectrometer fitted with a 1024-channel analyzer. The isomer shift (IS) was referenced to a metallic iron foil. The Doppler velocity was calibrated using the same metallic iron foil. The QBMOSS program of Akasaka and Shinno (1992) was used for the least-squares calcula-

tion of the spectrum. The spectrum was fitted to Lorentzians with the line widths and intensities constrained to be equal at each site. The quality of the fit was judged from the χ^2 value and the standard deviation of the Mössbauer parameters.

Optical spectroscopy

The unpolarized optical spectrum of the chromian epidote was measured in the wavelength range from 280 nm to 840 nm for the powder sample at room temperature using a Hitachi U-3500 optical spectrometer. The powder sample was densely mounted in a glass sample holder with a $20 \times 18 \times 1.5$ mm³ cavity. The diffuse reflectance from 0 to 100% was measured using an integrating sphere.

Single crystal structural analysis

The diffraction data of the chromian epidotes were collected using a Rigaku RAXIS RAPID imaging plate (IP) diffractometer of the University of Tsukuba for CrEp1 and CrEp2, and a Bruker SMART APEX CCD diffractometer of Bruker AXS K.K. for CrEp3.

For CrEp1 and CrEp2, a block crystal was mounted on a glass fiber, and the intensity data were collected at room temperature using graphite monochromatized MoK α radiation ($\lambda = 0.71069$ Å). A total of 88 oscillation images were collected. A sweep of the data was done using ω scans in 5.0° steps from 130.0 to 190.0° for $\chi = 45.0^\circ$ and $\varphi = 0.0^\circ$, and from 0.0 to 160.0° for $\chi = 45.0^\circ$ and $\varphi = 180.0^\circ$. Another sweep was performed using φ scans in 5.0° steps from 130.0 to 190.0° for $\chi = 45.0^\circ$ and $\varphi = 90.0^\circ$ and from 0.0 to 160.0° for $\chi = 45.0^\circ$ and $\varphi = 270.0^\circ$. The exposure rate was 120 seconds per degree. Equivalent reflections were merged using the PROCESS-AUTO program package. The data were corrected for Lorentz and polarization effects. A symmetry-related empirical absorption correction using the ABSCOR program (Higashi, 1995) was applied.

The single crystal of CrEp3 was mounted on a glass fiber and positioned in the CCD diffractometer equipped with a cryo-stream liquid nitrogen cryostat. Preliminary lattice parameters and an orientation matrix were obtained from three sets of frames and refined during the integration process of the intensity data. The intensity data were measured using graphite-monochromatized MoK α radiation. Diffraction data were collected at 90 K using multiple φ scans with different φ settings (i.e., φ and φ scans) (Bruker, 1999). The data were processed using the SAINT (Bruker, 1999). An empirical absorption correction using the SADABS (Sheldrick, 1996) was ap-

plied. The structure was solved using direct methods employing the SHELXS97 program (Sheldrick, 1997) with default parameters, and expanded using Fourier techniques. Structural refinement was performed using the SHELXL97 program (Sheldrick, 1997). The scattering factors of the neutral atoms were employed in our analysis. First, several refinement cycles were carried out using the isotropic thermal displacement parameters for the non-hydrogen atoms, and then, refinement using the anisotropic thermal displacement parameters was made.

RESULTS

Chemical compositions of specimen

Table 1 shows the results of the chemical analyses for the three chromian epidote grains in the thin section from which CrEp1, CrEp2, and CrEp3 were picked out. As described below, the Mössbauer and optical spectroscopy studies revealed all the Fe and Cr to be trivalent in oxidation state. The oxidation state of Mn is regarded as divalent, because the chromian epidote is associated with Fe²⁺-bearing phases such as omphacite, amphibole, and mica (Nagashima et al., 2006) and Mn²⁺ is the most stable manganese cation under the fO_2 conditions where both Fe²⁺ and Fe³⁺ exist. The Cr₂O₃ contents of the chromian epidote grains corresponding to CrEp1, CrEp2, and CrEp3 are 1.79, 4.99, and 4.74 wt%, respectively. The Fe₂O₃ content is nearly constant (8.12–8.67 wt%). The SrO content ranges from 1.79 to 3.15 wt%. A very small amount of REE is also present.

In Table 1, Fe³⁺ and Cr³⁺ are allocated to the octahedral sites based on the spectroscopic studies. The distribution of V³⁺ at the octahedral sites in epidotes has been confirmed in mukhinite (Shepel and Karpenko, 1969), and Ti⁴⁺ has been considered to occupy the octahedral sites (Franz and Liebscher, 2004). Thus, both V and Ti are assigned to the octahedral sites. The deficiency of Ca in the A position is made up for by Sr²⁺, Mn²⁺, and Mg²⁺ (Bonazzi et al., 1990; Akasaka et al., 2000; Armbruster et al., 2002; Miyajima et al., 2003; Bonazzi and Menchetti, 2004).

Purity of the powder sample

The X-ray powder diffraction pattern showed that the powder sample consists of not only epidote but also a very small amount of omphacite. By applying the reported structural parameters of epidote (Dollase, 1971) and omphacite (Mottana et al., 1979) as the initial structural parameters, the mass fractions of epidote and omphacite in the powder sample were readily obtained from ordinary

Table 1. Chemical compositions of the chromian epidotes

Sample No.	CrEp 1	CrEp 2	CrEp 3
SiO ₂	37.08	36.77	37.05
TiO ₂	0.13	0.16	0.09
Al ₂ O ₃	26.74	24.26	23.99
Cr ₂ O ₃ *	1.79	4.99	4.74
Fe ₂ O ₃ *	8.12	8.28	8.67
V ₂ O ₃ **	0.00	0.04	0.00
MnO**	0.09	0.10	0.02
MgO	0.06	0.09	0.06
CaO	20.45	21.87	21.81
SrO	3.15	1.79	1.80
BaO	0.06	0.00	0.00
Na ₂ O	0.01	0.04	0.02
K ₂ O	0.04	0.03	0.00
La ₂ O ₃	0.03	0.06	0.07
Ce ₂ O ₃	0.11	0.04	0.15
Pr ₂ O ₃	0.10	0.00	0.00
Nd ₂ O ₃	0.00	0.00	0.00
Sm ₂ O ₃	0.10	0.08	0.03
Eu ₂ O ₃	0.02	0.01	0.00
Gd ₂ O ₃	0.00	0.02	0.00
Total	98.08	98.63	98.50
Cations per 12.5 oxygens			
Si	2.952	2.932	2.955
Al	0.048	0.068	0.045
Σ	3.000	3.000	3.000
Ti	0.008	0.010	0.005
Al	2.462	2.212	2.210
Cr ³⁺	0.113	0.315	0.299
Fe ³⁺	0.487	0.497	0.521
V ³⁺	0.000	0.003	0.000
Σ	3.070	3.037	3.035
Mn ²⁺	0.006	0.006	0.001
Mg	0.008	0.010	0.007
Ca	1.745	1.869	1.863
Sr	0.145	0.083	0.083
Ba	0.002	0.000	0.000
Na	0.001	0.006	0.002
K	0.004	0.003	0.000
La	0.003	0.002	0.002
Ce	0.000	0.001	0.004
Pr	0.003	0.000	0.000
Nd	0.001	0.000	0.000
Sm	0.000	0.002	0.001
Eu	0.000	0.000	0.000
Gd	0.000	0.001	0.000
Σ	1.918	1.983	1.963

* Oxidation states of Fe and Cr were determined by ⁵⁷Fe Mössbauer and optical spectroscopy, respectively.

** Total V and Mn as V₂O₃ and MnO, respectively.

Figure 1. ⁵⁷Fe Mössbauer spectrum of the chromian epidote at 298 K. The refined Mössbauer parameters are listed in Table 2.

Rietveld analysis where the atomic positions and isotropic atomic displacement parameters were fixed to those of the initial values in the present refinement. The converged mass fractions of epidote and omphacite are 0.99 and 0.01, respectively, and the unit cell parameters were refined as follows: $a = 8.882(7)$, $b = 5.604(3)$, $c = 10.161(8)$ Å, $\beta = 115.32(4)^\circ$, and $V = 457.2(6)$ Å³ for the epidote ($P2_1/m$), and $a = 9.59(2)$, $b = 8.779(7)$, $c = 5.255(6)$ Å, $\beta = 107.1(1)^\circ$, and $V = 423(1)$ Å³ for the omphacite ($P2_1/n$). The values of R_{wp} and R_e were 16.47 and 9.42, respectively, and thus, the goodness-of-fit was 1.748.

Mössbauer spectroscopy

The ⁵⁷Fe Mössbauer spectrum consists of three main doublets (AA', BB', and CC') and one very small doublet (DD') (Fig. 1). The hyperfine parameters are listed in Table 2. In ⁵⁷Fe Mössbauer studies on epidote, the doublets with $IS = 0.22$ to 0.36 mm/sec and quadrupole splitting (QS) = 1.46 to 1.67 mm/sec, and those with $IS = 0.31$ to 0.44 mm/sec and $QS = 1.89$ to 2.32 mm/sec have been assigned to Fe³⁺ at the $M1$ and $M3$ sites, respectively (Bancroft et al., 1967; Dollase, 1973; Bird et al., 1988; Fehr and Heuss-Aßbichler, 1997; Heuss-Aßbichler and Fehr, 2000; Liebscher, 2004). Thus, the doublets AA' and BB' can be assigned to Fe³⁺ at the $M3$ site in epidote. The hyperfine parameters

Table 2. ^{57}Fe Mössbauer hyperfine parameters* and assignments

Doublet	IS (mm/s)	QS (mm/s)	Γ (mm/s)	Area Ratio (%)	Assignment
AA'	0.28(4)	2.24(9)	0.37(4)	25(5)	Fe^{3+} (M3) in epidote
BB'	0.366(8)	2.01(2)	0.28(2)	46(6)	Fe^{3+} (M3) in epidote
CC'	0.53(4)	1.77(9)	0.49(5)	24(4)	Fe^{3+} (M3) in epidote (allanite)
DD'	0.31(1)	0.21(3)	0.26(6)	5(1)	Fe^{3+} in omphacite

* IS , isomer shift referred to metallic iron absorber; QS , quadrupole splitting; Γ , Line width.
 $\chi^2/\text{Freedom} = 1.56$.

Figure 2. Crystal-field spectrum of the chromian epidote. The assignment of the spectrum peaks and crystal-field parameters are listed in Table 3.

of the doublet CC' ($IS = 0.53$ mm/sec, $QS = 1.77$ mm/sec) correspond to Fe^{3+} at the M3 site in allanite with $IS = 0.37$ to 0.55 mm/sec and $QS = 1.61$ to 2.00 mm/sec (Liebscher, 2004). The existence of a couple of doublets of Fe^{3+} at the M3 site with a slightly different QS can be attributed to the heterogeneous chemical composition of the chromian epidotes in the Mössbauer sample, which consists of not only chromian Ca-epidote but also Sr-rich epidote and REE-rich epidote (Nagashima et al., 2006).

The QS of 0.21 mm/sec of the doublet DD' does not agree with that of Fe^{3+} at the M1 and M3 sites in epidote. Nevertheless, the hyperfine parameters of the doublet DD' are similar to those of Fe^{3+} in sodic pyroxene ($QS = 0.29$ to 0.55 mm/sec: Bancroft and Williams, 1969; Aldridge et al., 1978; Dollase and Gustafson, 1982), which was inevitably contaminated during the separation of the chromian epidote.

Optical spectroscopy

Since the measured diffuse reflectance spectrum of the

chromian epidote was very low in intensity, the conversion spectrum to absorption scale by applying the Kubelka-Munk formula was much lower in intensity. Therefore, the reflectance spectrum was directly plotted against wavelength and wave number scales, as shown in Figure 2. The assignment of the peaks in the spectrum and the crystal-field parameters are listed in Table 3.

Five discrete bands were assigned in the spectrum. Four of them centered at 33000 (ν_3), 22170 (ν_2), 15040 (ν_1) and 14410 cm^{-1} are attributed to Cr^{3+} of the quartet state, and the other band centered at 26320 cm^{-1} to Fe^{3+} of the sextet state (Bates, 1962). The band at ν_3 is duplicated with a charge transfer band occurring between the central metal and the ligands. The broadened band of Cr^{3+} centered at the ν_2 position is overlapped with a relatively sharp band of Fe^{3+} . Another spin-forbidden band of ${}^2T_{1g}(\text{G}) \leftarrow {}^4A_{2g}(\text{F})$ for Cr^{3+} is not clearly observed, but it is estimated to be at 15630 cm^{-1} by calculation. The two main ν_1 and ν_2 absorption bands belonging to spin-allowed transitions of Cr^{3+} show $10Dq = 15040$ cm^{-1} and $B = 767$ cm^{-1} , respectively. From the spin-forbidden transi-

Table 3. Assignments of the spectrum peaks to the transitions and crystal field parameters of the chromian epidote

No.	Wavelength (nm)	Wavenumber (cm ⁻¹)	Octahedral ion species	Assignment: Cr ³⁺	Assignment: Fe ³⁺
1	303	33000	Cr ³⁺	$\nu_3: {}^4T_{1g}(P) \leftarrow {}^4A_{2g}(F), CT^*$	CT [*]
2	380	26320	Fe ³⁺		${}^4E_g(D) \leftarrow {}^6A_{1g}(S)$
3 ^{**}	451	22170	Cr ³⁺ , Fe ³⁺ ^{***}	$\nu_2: {}^4T_{1g}(F) \leftarrow {}^4A_{2g}(F)$	${}^4A_{1g}, {}^4E_g(G) \leftarrow {}^6A_{1g}(S)$
4 ^{***}	[640]	[15630]	Cr ³⁺	${}^2T_{1g}(G) \leftarrow {}^4A_{2g}(F)$	
5	665	15040	Cr ³⁺	$\nu_1: {}^4T_{2g}(F) \leftarrow {}^4A_{2g}(F)$	
6	694	14410	Cr ³⁺	${}^2E_g(G) \leftarrow {}^4A_{2g}(F)$	
Crystal field parameters of Cr ³⁺					
10Dq		15040			
B		767			
C		2960			

* CT, charge transfer.

^{**} This Cr³⁺ band is broadened. It is overlapped with the relatively sharp Fe³⁺ band.^{***} Estimated position of a spin-forbidden band of ${}^2T_{1g}(G) \leftarrow {}^4A_{2g}(F)$.

tion, the value of C was determined to be 2960 cm⁻¹. Since the spin-allowed transition of free Cr³⁺ has B = 810 cm⁻¹, the ionic character of the Cr³⁺-O bond in the chromian epidote is 95%. The crystal field of the octahedral site is slightly weaker than that of kosmochlor (NaCrSi₂O₆) having 10Dq = 15600 cm⁻¹, B = 646 cm⁻¹ (White et al., 1971), and a mean M-O bond distance of 1.998 Å (Clark et al., 1969). Subsequently, the mean M-O distance around the octahedral Cr³⁺ ions of the chromian epidote was calculated using the formula, $\Delta/\Delta' = (R/R')^5$ (White et al., 1971), where Δ and R denote 10Dq and the mean M-O distance for a standard specimen and Δ' and R' denote those for an objective unknown specimen. Taking the mean M-O distance (Clark et al., 1969) and 10Dq value (White et al., 1971) of kosmochlor as a standard (Ikeda and Ohashi, 1974; Ikeda, 1984; Ikeda et al., 1992), the mean M-O distance obtained is 2.013 Å, which is consistent with the mean M3-O bond distance of the chromian epidotes (2.005 Å for CrEp1, 2.019 Å for CrEp2, and 2.013 Å for CrEp3) determined by the present X-ray structural refinement.

All the bands of Fe³⁺ are assigned to spin-forbidden transitions, and thus, precise determination of the crystal field parameters of Fe³⁺ is difficult. However, the crystal field parameters of Fe³⁺ were calculated to be 10Dq ≈ 12700 cm⁻¹ and B ≈ 670 cm⁻¹, using a Tanabe-Sugano diagram. Although the other bands of Fe³⁺ are not distinct because of strong overlapping with those of Cr³⁺, the band positions of the ${}^4F_{2g}(G) \leftarrow {}^6A_{1g}(S)$ and ${}^4F_{1g}(G) \leftarrow {}^6A_{1g}(S)$ transitions are calculated to be 16100 cm⁻¹ (620 nm) and

11400 cm⁻¹ (880 nm), respectively.

Structural solution and refinements

The number of measured and unique reflections with R indices in the final least-squares calculations are given in Table 4. The unit cell parameters and crystallographic data are also shown in Table 4. The refined atomic positions are listed in Table 5. The equivalent and anisotropic atomic displacement parameters are represented in Tables 5 and 6, respectively. The interatomic distances calculated from the refined atomic positions are shown in Table 7.

After convergence of the structural refinements for the non-hydrogen atoms, a difference Fourier map was calculated in order to find the hydrogen atoms of the hydroxyl groups. Although the electron density distributions for CrEp1 and CrEp3 were not clear enough to detect hydrogen atoms, the difference Fourier maps of CrEp2 showed peak heights with 0.7 eÅ⁻³ at a position about 1 Å from the O10 atom ($x = 0.059$, $y = 0.25$ and $z = 0.359$), which can be attributed to the hydrogen atom forming an OH group. Upon further refinement including the hydrogen atoms for CrEp2, where isotropic temperature factors were varied and the site occupancy of the hydrogen atom at the H position was fixed to 1.0, the R index and S -value (goodness-of-fit) converged to 0.045 and 1.07, respectively. The bond lengths of the O10-H and O4...H bonds were 0.65 and 2.29 Å, respectively.

The distribution of Ca and Sr at the A1 and A2 sites,

Table 4. Crystallographic data of the chromian epidotes* and experimental details of the single-crystal X-ray diffraction analysis

Sample	CrEp 1**	CrEp 2**	CrEp 3**
Space group	$P2_1/m$	$P2_1/m$	$P2_1/m$
Crystal size (mm)	$0.20 \times 0.40 \times 0.20$	$0.20 \times 0.20 \times 0.20$	$0.50 \times 0.40 \times 0.10$
Cell parameters			
a (Å)	8.8815(6)	8.9165(4)	8.895(2)
b (Å)	5.5956(5)	5.6226(2)	5.610(1)
c (Å)	10.1532(5)	10.1728(5)	10.146(2)
β (°)	115.159(2)	115.2365(9)	115.177(2)
V (Å ³)	456.72(6)	461.33(4)	458.2(2)
D_{calc} (g/cm ³)	3.474	3.459	3.486
Radiation	MoK α	MoK α	MoK α
Monochromator	Graphite	Graphite	Graphite
Diffractometer	Rigaku RAXIS RAPID IP	Rigaku RAXIS RAPID IP	Bruker APEX CCD
Scan type	ω scans	ω scans	ϕ and ω scans
θ_{min} (°)	2.22	2.21	2.22
θ_{max} (°)	27.47	33.14	30.12
μ (mm ⁻¹)	2.02	2.00	2.48
Collected reflections	3930	9590	3405
Unique reflections	1145	1853	1438
R_{int}	0.044	0.071	0.014
Miller index limits	$-11 \leq h \leq 10, -7 \leq k \leq 7, -12 \leq l \leq 13$	$-13 \leq h \leq 13, -8 \leq k \leq 8, -15 \leq l \leq 15$	$-12 \leq h \leq 10, -7 \leq k \leq 5, -13 \leq l \leq 14$
Refinement system used		SHELXL-97 (Sheldrick, 1997)	
Refinement on	F^2	F^2	F^2
R 1 (Unique reflections)	0.0581	0.0661	0.032
wR 2	0.1542	0.0948	0.0912
S	1.275	1.087	1.329
No. of parameters	124	123	124
Weighting scheme	$\omega = 1/[\sigma^2(F_o^2) + (0.0416P)^2 + 8.11P]$	$\omega = 1/[\sigma^2(F_o^2) + (0.0321P)^2 + 1.46P]$	$\omega = 1/[\sigma^2(F_o^2) + (0.0512P)^2 + 0.3144P]$
	where $P = (F_o^2 + 2F_c^2)/3$	where $P = (F_o^2 + 2F_c^2)/3$	where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/s)_{\text{max}}$	0.00	0.00	0.00
Δr_{max} (e Å ⁻³)	1.350	0.903	2.020
Δr_{min} (e Å ⁻³)	-0.899	-0.795	-1.200

* Unit cell parameters were measured at 293 K. Diffraction data were collected at 293 K for CrEp1 and CrEp2 and at 90 K for CrEp3.

** CrEp1: (La_{0.003}Pr_{0.003}Nd_{0.001}K_{0.004}Na_{0.001}Ba_{0.002}Sr_{0.145}Ca_{1.745}Mg_{0.008}Mn_{0.006})_{Σ1.918}(Fe_{0.487}Cr_{0.113}Ti_{0.008}Al_{2.462})_{Σ3.070}(Al_{0.048}Si_{2.952})_{Σ3.000}O₁₃H_{0.992}
 CrEp2: (La_{0.002}Ce_{0.001}Sm_{0.002}Gd_{0.001}K_{0.003}Na_{0.006}Sr_{0.083}Ca_{1.869}Mg_{0.010}Mn_{0.006})_{Σ1.983}(V_{0.003}Fe_{0.497}Cr_{0.315}Ti_{0.010}Al_{2.212})_{Σ3.037}
 (Al_{0.068}Si_{2.932})_{Σ3.000}O₁₃H_{0.984}
 CrEp3: (La_{0.002}Ce_{0.004}Sm_{0.001}Na_{0.002}Sr_{0.083}Ca_{1.863}Mg_{0.007}Mn_{0.001})_{Σ1.963}(Fe_{0.531}Cr_{0.299}Ti_{0.005}Al_{2.210})_{Σ3.035}(Al_{0.045}Si_{2.955})_{Σ3.000}O₁₃H_{0.844}
 where H was calculated based on the charge balance.

and the distribution of Al and Cr³⁺ at the $M1$, $M2$, and $M3$ sites were determined based on the observed site-scattering values (Table 8) (Hawthorne et al., 1995). The site-scattering values were derived from the site occupancy of calcium ions at the $A1$ and $A2$ sites and of aluminum ions at the $M1$, $M2$, and $M3$ sites, refined without any constraint. On the basis of the observed site-scattering values, the site populations (apfu) of the $A1$ and $M2$ sites in CrEp1, CrEp2, and CrEp3, and for the $M1$ site in CrEp1, were fixed to be 1Ca, 1Al, and 1Al, respectively. The site populations of Ca and Sr on the $A2$ site, and of Cr and Al on the $M1$ and $M3$ sites were estimated by use of the following procedure: (1) trace elements not more than 0.01 apfu ($O = 12.5$) were omitted, (2) Fe³⁺ was assigned to the $M3$ site based on the result of the ⁵⁷Fe Mössbauer analy-

sis, and (3) several reasonable constraints were applied as follows; $g(\text{Ca}) + g(\text{Sr}) = 1$ for the $A2$ site, $g(\text{Al}) + g(\text{Cr}) = 1$ for the $M1$ site, and $g(\text{Al}) + g(\text{Cr}) = 1 - g(\text{Fe})$ for the $M3$ site, where g denotes the site population. The final site populations at the A and M sites are listed in Table 8. The values of the Sr apfu at the $A2$ sites (0.14, 0.10, and 0.12 for CrEp1, CrEp2, and CrEp3, respectively) are similar to those given by the EPMA analysis (0.15 for CrEp1, 0.08 for CrEp2, and 0.08 for CrEp3). The Cr contents derived from the site-scattering values for CrEp1 (0.09 apfu) and CrEp2 (0.31 apfu) are consistent with those obtained from the EPMA analysis, whereas that of CrEp3 (0.22 apfu) is less than the EPMA data. The discrepancy of the Cr content in CrEp3 may be attributed to the inhomogeneous composition of CrEp3. Merli et al. (2000) showed that the

Table 5. Atomic positions and equivalent displacement parameters ($\text{\AA}^2$)

Atom	n_{eq}^*	W**	$x, y, z,$ U_{eq}	CrEp 1	CrEp 2	CrEp 3	Atom	n_{eq}^*	W**	$x, y, z,$ U_{eq}	CrEp 1	CrEp 2	CrEp 3
A1	2	<i>e</i>	<i>x</i>	0.7608(2)	0.7600(1)	0.76037(7)	O2	4	<i>f</i>	<i>x</i>	0.3008(6)	0.3017(3)	0.3015(2)
			<i>y</i>	3/4	3/4	3/4				<i>y</i>	0.9834(9)	0.9838(4)	0.9838(3)
			<i>z</i>	0.1547(2)	0.15390(9)	0.15416(6)				<i>z</i>	0.3513(5)	0.3527(2)	0.3524(2)
			U_{eq}	0.0115(7)	0.0131(3)	0.0065(2)				U_{eq}	0.011(1)	0.0122(4)	0.0074(3)
A2	2	<i>e</i>	<i>x</i>	0.6033(2)	0.6040(1)	0.60519(7)	O3	4	<i>f</i>	<i>x</i>	0.7914(6)	0.7926(3)	0.7926(2)
			<i>y</i>	3/4	3/4	3/4				<i>y</i>	0.0135(9)	0.0135(4)	0.0127(3)
			<i>z</i>	0.4231(2)	0.42367(9)	0.42459(5)				<i>z</i>	0.3437(5)	0.3425(2)	0.3430(2)
			U_{eq}	0.0135(6)	0.0149(2)	0.0074(2)				U_{eq}	0.012(1)	0.0129(4)	0.0079(3)
M1	2	<i>a</i>	<i>x</i>	0	0	0	O4	2	<i>e</i>	<i>x</i>	0.0531(8)	0.0533(4)	0.0523(3)
			<i>y</i>	0	0	0				<i>y</i>	1/4	1/4	1/4
			<i>z</i>	0	0	0				<i>z</i>	0.1312(7)	0.1313(3)	0.1315(2)
			U_{eq}	0.0044(9)	0.0085(3)	0.0041(3)				U_{eq}	0.011(1)	0.0110(6)	0.0066(4)
M2	2	<i>c</i>	<i>x</i>	0	0	0	O5	2	<i>e</i>	<i>x</i>	0.0395(8)	0.0403(3)	0.0394(3)
			<i>y</i>	0	0	0				<i>y</i>	3/4	3/4	3/4
			<i>z</i>	1/2	1/2	1/2				<i>z</i>	0.1441(7)	0.1456(3)	0.1445(2)
			U_{eq}	0.0051(9)	0.0082(4)	0.0039(3)				U_{eq}	0.008(1)	0.0090(5)	0.0063(4)
M3	2	<i>e</i>	<i>x</i>	0.2904(2)	0.29148(9)	0.29116(7)	O6	2	<i>e</i>	<i>x</i>	0.0629(8)	0.0647(4)	0.0640(3)
			<i>y</i>	1/4	1/4	1/4				<i>y</i>	3/4	3/4	3/4
			<i>z</i>	0.2225(2)	0.22236(9)	0.22201(6)				<i>z</i>	0.4034(7)	0.4046(3)	0.4043(2)
			U_{eq}	0.0101(7)	0.0095(2)	0.0047(2)				U_{eq}	0.010(1)	0.0109(6)	0.0064(4)
Si1	2	<i>e</i>	<i>x</i>	0.3385(3)	0.3397(1)	0.3399(1)	O7	2	<i>e</i>	<i>x</i>	0.5162(8)	0.5157(4)	0.5165(3)
			<i>y</i>	3/4	3/4	3/4				<i>y</i>	3/4	3/4	3/4
			<i>z</i>	0.0470(3)	0.0477(1)	0.04806(9)				<i>z</i>	0.1773(7)	0.1784(3)	0.1785(2)
			U_{eq}	0.0080(6)	0.0096(2)	0.0049(2)				U_{eq}	0.012(1)	0.0138(6)	0.0081(4)
Si2	2	<i>e</i>	<i>x</i>	0.6820(3)	0.6830(1)	0.6827(1)	O8	2	<i>e</i>	<i>x</i>	0.5177(9)	0.5206(4)	0.5202(3)
			<i>y</i>	1/4	1/4	1/4				<i>y</i>	1/4	1/4	1/4
			<i>z</i>	0.2759(3)	0.2758(1)	0.27594(8)				<i>z</i>	0.3032(8)	0.3051(4)	0.3054(3)
			U_{eq}	0.0098(6)	0.0096(2)	0.0055(2)				U_{eq}	0.017(1)	0.0177(7)	0.0112(4)
Si3	2	<i>e</i>	<i>x</i>	0.1820(3)	0.1828(1)	0.1827(1)	O9	2	<i>e</i>	<i>x</i>	0.6359(9)	0.6340(4)	0.6346(3)
			<i>y</i>	3/4	3/4	3/4				<i>y</i>	1/4	1/4	1/4
			<i>z</i>	0.3161(3)	0.3169(1)	0.31692(9)				<i>z</i>	0.1018(8)	0.1016(4)	0.1018(2)
			U_{eq}	0.0083(6)	0.0091(2)	0.0051(2)				U_{eq}	0.020(2)	0.0214(7)	0.0128(5)
O1	4	<i>f</i>	<i>x</i>	0.2356(5)	0.2354(2)	0.2353(2)	O10	2	<i>e</i>	<i>x</i>	0.0777(8)	0.0798(4)	0.0789(3)
			<i>y</i>	0.9955(9)	0.9954(4)	0.9961(3)				<i>y</i>	1/4	1/4	1/4
			<i>z</i>	0.0444(5)	0.0436(2)	0.0441(2)				<i>z</i>	0.4257(7)	0.4261(3)	0.4255(2)
			U_{eq}	0.012(1)	0.0120(4)	0.0069(3)				U_{eq}	0.009(1)	0.0110(6)	0.0063(4)

* Multiplicity.

** Wyckoff letter.

estimates of the site-scattering values from X-ray diffraction data are often different from those obtained from EPMA analysis on inhomogeneous (zoned) crystals.

To examine the feasibility of the structural models, the bond-valence sums in CrEp1, CrEp2, and CrEp3 were calculated using the function of the electrostatic strength

by Brown and Altermatt (1985) and the bond-valence parameters of Brese and O'Keeffe (1991) (Table 9). The valence sums of the A1, M1, M2, Si1, Si2, O3, O5, O6, O7, O8, and O9 are close to their expected valence sums, whereas those of the A2, O1, O2, O4, O8, and O10 are less than their expected values. Since hydrogen atoms

Table 6. Anisotropic displacement parameters ($\text{\AA}^2$)

Atom	U_{ij}	CrEp 1	CrEp 2	CrEp 3	Atom	U_{ij}	CrEp 1	CrEp 2	CrEp 3
A1	U_{11}	0.014(1)	0.0163(4)	0.0087(3)	O2	U_{11}	0.012(2)	0.0127(9)	0.0082(7)
	U_{22}	0.011(1)	0.0138(5)	0.0072(3)		U_{22}	0.010(2)	0.012(1)	0.0082(7)
	U_{33}	0.012(1)	0.0119(4)	0.0050(3)		U_{33}	0.011(2)	0.0121(9)	0.0061(6)
	U_{23}	0	0	0		U_{23}	-0.001(2)	-0.0007(8)	-0.0011(5)
	U_{13}	0.0085(8)	0.0085(3)	0.0041(2)		U_{13}	0.005(2)	0.0056(8)	0.0034(5)
	U_{12}	0	0	0		U_{12}	-0.003(2)	-0.0024(8)	-0.0019(5)
A2	U_{11}	0.0152(9)	0.0153(4)	0.0090(3)	O3	U_{11}	0.010(2)	0.0123(9)	0.0076(7)
	U_{22}	0.015(1)	0.0194(5)	0.0095(3)		U_{22}	0.010(2)	0.010(1)	0.0056(7)
	U_{33}	0.0102(9)	0.0098(4)	0.0037(3)		U_{33}	0.013(2)	0.0130(9)	0.0075(7)
	U_{23}	0	0	0		U_{23}	-0.001(2)	-0.0001(8)	-0.0003(5)
	U_{13}	0.0054(7)	0.0051(3)	0.0027(2)		U_{13}	0.000(2)	0.0022(8)	0.0003(5)
	U_{12}	0	0	0		U_{12}	0.001(2)	0.0004(8)	0.0002(5)
M1	U_{11}	0.003(1)	0.0089(5)	0.0051(4)	O4	U_{11}	0.011(3)	0.014(1)	0.0074(9)
	U_{22}	0.003(1)	0.0095(6)	0.0045(4)		U_{22}	0.008(3)	0.012(1)	0.0076(9)
	U_{33}	0.006(1)	0.0072(5)	0.0027(4)		U_{33}	0.013(3)	0.010(1)	0.0054(9)
	U_{23}	-0.001(1)	-0.001(4)	-0.0003(3)		U_{23}	0	0	0
	U_{13}	0.001(1)	0.0035(4)	0.0018(3)		U_{13}	0.005(3)	0.007(1)	0.0031(7)
	U_{12}	-0.001(1)	-0.0004(4)	-0.0004(3)		U_{12}	0	0	0
M2	U_{11}	0.004(1)	0.0089(6)	0.0048(4)	O5	U_{11}	0.011(3)	0.009(1)	0.0067(9)
	U_{22}	0.003(1)	0.0070(6)	0.0039(5)		U_{22}	0.005(3)	0.010(1)	0.0070(9)
	U_{33}	0.007(1)	0.0091(6)	0.0030(4)		U_{33}	0.010(3)	0.007(1)	0.0049(9)
	U_{23}	0.001(1)	0.0000(4)	0.0000(3)		U_{23}	0	0	0
	U_{13}	0.001(1)	0.0041(4)	0.0016(3)		U_{13}	0.006(3)	0.003(1)	0.0023(7)
	U_{12}	0.000(1)	0.0005(4)	0.0001(3)		U_{12}	0	0	0
M3	U_{11}	0.010(1)	0.0083(4)	0.0053(3)	O6	U_{11}	0.013(3)	0.013(1)	0.0084(9)
	U_{22}	0.008(1)	0.0108(4)	0.0051(3)		U_{22}	0.008(3)	0.010(1)	0.0058(9)
	U_{33}	0.013(1)	0.0092(4)	0.0038(3)		U_{33}	0.014(3)	0.013(1)	0.0071(9)
	U_{23}	0	0	0		U_{23}	0	0	0
	U_{13}	0.0051(8)	0.0035(3)	0.0020(2)		U_{13}	0.009(3)	0.008(1)	0.0053(7)
	U_{12}	0	0	0		U_{12}	0	0	0
Si1	U_{11}	0.009(1)	0.0095(5)	0.0057(4)	O7	U_{11}	0.008(3)	0.010(1)	0.0072(9)
	U_{22}	0.007(1)	0.0099(5)	0.0054(4)		U_{22}	0.015(3)	0.015(2)	0.009(1)
	U_{33}	0.009(1)	0.0081(5)	0.0035(3)		U_{33}	0.009(3)	0.014(1)	0.0066(9)
	U_{23}	0	0	0		U_{23}	0	0	0
	U_{13}	0.005(1)	0.0043(4)	0.0020(3)		U_{13}	-0.002(3)	0.003(1)	0.0010(8)
	U_{12}	0	0	0		U_{12}	0	0	0
Si2	U_{11}	0.010(1)	0.0106(5)	0.0071(4)	O8	U_{11}	0.016(3)	0.018(2)	0.012(1)
	U_{22}	0.007(1)	0.0098(5)	0.0053(4)		U_{22}	0.017(4)	0.017(2)	0.011(1)
	U_{33}	0.011(1)	0.0085(5)	0.0043(4)		U_{33}	0.020(4)	0.024(2)	0.015(1)
	U_{23}	0	0	0		U_{23}	0	0	0
	U_{13}	0.004(1)	0.0043(4)	0.0027(3)		U_{13}	0.010(3)	0.015(1)	0.0105(9)
	U_{12}	0	0	0		U_{12}	0	0	0
Si3	U_{11}	0.009(1)	0.0097(5)	0.0061(4)	O9	U_{11}	0.023(4)	0.027(2)	0.018(1)
	U_{22}	0.008(1)	0.0101(6)	0.0061(4)		U_{22}	0.025(4)	0.030(2)	0.016(1)
	U_{33}	0.008(1)	0.0081(5)	0.0034(3)		U_{33}	0.013(3)	0.011(1)	0.007(1)
	U_{23}	0	0	0		U_{23}	0	0	0
	U_{13}	0.004(1)	0.0043(4)	0.0023(3)		U_{13}	0.009(3)	0.011(1)	0.0070(9)
	U_{12}	0	0	0		U_{12}	0	0	0
O1	U_{11}	0.010(2)	0.0120(9)	0.0074(6)	O10	U_{11}	0.014(3)	0.013(1)	0.0079(9)
	U_{22}	0.008(2)	0.011(1)	0.0060(7)		U_{22}	0.007(3)	0.008(1)	0.0068(9)
	U_{33}	0.017(2)	0.014(1)	0.0070(6)		U_{33}	0.009(3)	0.015(1)	0.0052(9)
	U_{23}	0.001(2)	0.0013(8)	0.0007(5)		U_{23}	0	0	0
	U_{13}	0.004(2)	0.0063(8)	0.0029(5)		U_{13}	0.009(3)	0.008(1)	0.0038(8)
	U_{12}	0.001(2)	0.0004(8)	0.0008(5)		U_{12}	0	0	0

Table 7. Interatomic distances (Å)

		CrEp 1	CrEp 2	CrEp 3
A1	-O1 ×2	2.484(5)	2.482(2)	2.479(2)
	-O3 ×2	2.342(5)	2.342(2)	2.336(2)
	-O5	2.524(7)	2.537(3)	2.525(2)
	-O6	2.796(7)	2.825(3)	2.811(2)
	-O7	2.278(7)	2.295(3)	2.285(2)
	Average	2.464	2.472	2.464
	-O9 ×2	2.973(3)	2.990(1)	2.983(1)
	Average	2.577	2.587	2.580
A2	-O2 ×2	2.791(5)	2.803(2)	2.806(2)
	-O2' ×2	2.557(5)	2.548(2)	2.538(2)
	-O3 ×2	2.600(5)	2.624(2)	2.610(2)
	-O7	2.277(7)	2.274(3)	2.276(2)
	-O10	2.586(7)	2.571(3)	2.564(2)
	Average	2.595	2.599	2.594
	-O8 ×2	3.017(3)	3.024(1)	3.021(1)
	Average	2.679	2.684	2.679
Si1	-O1 ×2	1.644(5)	1.654(2)	1.656(2)
	-O7	1.571(7)	1.566(3)	1.566(2)
	-O9	1.621(8)	1.633(3)	1.631(2)
	Average	1.620	1.627	1.627
Si2	-O3 ×2	1.612(5)	1.618(2)	1.621(2)
	-O8	1.598(7)	1.598(3)	1.596(2)
	-O9	1.635(8)	1.634(3)	1.631(2)
	Average	1.614	1.617	1.617
Si3	-O2 ×2	1.621(5)	1.630(2)	1.626(2)
	-O5	1.665(7)	1.662(3)	1.670(2)
	-O6	1.643(7)	1.646(3)	1.642(2)
	Average	1.638	1.642	1.641
M1	-O1 ×2	1.944(4)	1.952(2)	1.945(2)
	-O4 ×2	1.849(4)	1.856(2)	1.853(1)
	-O5 ×2	1.945(4)	1.961(2)	1.950(1)
	Average	1.913	1.923	1.916
M2	-O3 ×2	1.860(4)	1.862(2)	1.856(2)
	-O6 ×2	1.923(5)	1.931(2)	1.925(2)
	-O10 ×2	1.856(4)	1.872(2)	1.866(1)
	Average	1.880	1.888	1.882
M3	-O1 ×2	2.188(5)	2.198(2)	2.184(2)
	-O2 ×2	1.960(5)	1.975(2)	1.971(2)
	-O4	1.908(7)	1.921(3)	1.923(2)
	-O8	1.828(7)	1.848(3)	1.844(2)
	Average	2.005	2.019	2.013

forming the H-O10 and H···O4 bonds were observed in CrEp2, the low bond-valence sums for the O4 (1.73 v.u.) and O10 (1.30 v.u.) in this study may be compensated by the bond valences between the hydrogen and oxygen atoms. Similar results have also been reported for allanite (Hoshino et al., 2005) and dissakisite-(La) (Lavina et al., 2006). On the other hand, the reason for smaller valence sums of the O1, O2, and O8 is not obvious. Hoshino et al. (2005) interpreted the reason of the low O2 and O8 bond

valences in terms of the effect of defect at the A2 site. However, there is no strong evidence suggesting defects at the A2 site in the present chromian epidotes. On the basis of the fact that the O1, O2, and O8 oxygen atoms belong to the strongly distorted *M3* site, and the effect of the distortion of coordination polyhedra on the bond-strength to bond-length relationship (Brown and Shannon, 1973), the relatively low bond valences of the O1, O2, and O8 oxygen atoms are suggested to be caused by the distortion of the *M3* octahedra.

DISCUSSION

Cr distribution in the octahedral sites

In epidote group minerals, the *M3* site is essentially larger and more distorted than the *M1* and *M2* sites (Ito et al., 1954; Dollase, 1968). This feature controls the distribution of transition elements in the three independent octahedral sites. Thus, the stronger preferences of Fe³⁺ and Mn³⁺ than Al³⁺ for the *M3* site are reasonable in both natural and synthetic epidotes (Dollase, 1971; Giuli et al., 1999; others) and piemontites (Dollase, 1969; Langer et al., 2002; Nagashima and Akasaka, 2004; others), although it is also noted that Fe³⁺ and Mn³⁺ ions tend to occupy the *M1* site, even when the *M3* site is not fully occupied by Fe³⁺ and Mn³⁺ (Giuli et al., 1999; Langer et al., 2002; Nagashima and Akasaka, 2004). In addition to the geometric properties of the *M* sites, REE cations in the A2 site also affect the distribution of cations among the *M* sites. In allanite, larger divalent cations, such as Fe²⁺ occupy the *M3* site, and smaller Fe³⁺ ions distribute in the *M1* sites, which can be explained in terms of the substitution of [Ca²⁺]^{A2} + [Al³⁺]^{M3} ↔ [REE³⁺]^{A2} + [M²⁺]^{M3} (Dollase, 1971). On the basis of similar considerations, Mg²⁺ and Cr³⁺ in chromian dissakisite-(Ce) were assigned to the *M3* and *M1* sites, respectively (Yang and Enami, 2003). For the Outokumpu chromian epidote, in which 33% of the octahedral sites were filled with Cr³⁺ ions, Treloar (1987) predicted that Cr³⁺ might be preferentially partitioned into one of the three octahedral sites, probably the *M1* site. This interpretation was partly based on the results of a polarized absorption spectroscopic study by Burns and Strens (1967) which showed that Cr³⁺ had a strong preference for the *M1* site. In terms of the assignment of the crystal field spectra, Liebscher (2004) expressed doubts about the distribution of Cr³⁺ at the *M1* site. If the amounts of Fe³⁺ and/or Mn³⁺ are sufficient to fill the *M3* site in chromian epidotes, then Cr³⁺ ions would be partitioned on the *M1* site, because the ionic radius of Cr³⁺ (0.62 Å after Shannon (1976)) is smaller than those of both Mn³⁺ (0.65 Å) and Fe³⁺ (0.645 Å). However, Cr³⁺

Table 8. Refined site-scattering values* and assigned site-populations** for the A1, A2, M1, M2 and M3 sites

Sample	Site	Site scattering	Site populations (apfu)	Number of electrons***
CrEp1	M1	12.94(20)	1Al	13
	M2	12.44(20)	1Al	13
	M3	20.14(23)	0.43Al + 0.09Cr ³⁺ + 0.48Fe ³⁺	20.23
	A2	22.72(24)	0.86Ca + 0.14Sr	22.52
	A1	19.66(24)	1Ca	20
CrEp2	M1	14.50(9)	0.86Al + 0.14Cr ³⁺	14.54
	M2	13.12(9)	1Al	13
	M3	21.28(9)	0.34Al + 0.17Cr ³⁺ + 0.49Fe ³⁺	21.24
	A2	21.86(10)	0.90Ca + 0.10Sr	21.80
	A1	19.78(10)	1Ca	20
CrEp3	M1	14.09(7)	0.90Al + 0.10Cr ³⁺	14.10
	M2	12.75(7)	1Al	13
	M3	20.93(7)	0.37Al + 0.12Cr ³⁺ + 0.51Fe ³⁺	20.95
	A2	22.16(6)	0.88Ca + 0.12Sr	22.16
	A1	19.86(8)	1Ca	20

* The site-scattering values were derived from the site occupancies of calcium at the A1 and A2 sites and aluminum at the M1, M2 and M3 sites refined without any constraint.

** Cations not more than 0.01 apfu were neglected. Fe³⁺ was assigned to the M3 site by the Mössbauer analysis. The amounts of Fe³⁺ were recalculated from the EPMA data by normalizing total cations at the octahedral sites to the ideal value, 3 apfu.

*** Calculated from the site populations.

is considered to occupy the M3 site in epidote in which the amounts of Fe³⁺ and/or Mn³⁺ ions on the M3 site and of REE ions on the A2 site are insignificant.

The result in this study gives a solution to the questions on the distribution of Cr³⁺ among the octahedral sites in the epidote structure. As shown in Table 8, the Cr³⁺ + Fe³⁺ population at the M3 site and the Cr³⁺ population at the M1 site are related to the Cr³⁺ + Fe³⁺ content in the epidote, i.e., a certain amount of Cr³⁺ is distributed at the M1 site in the samples with the Cr³⁺ + Fe³⁺ exceeding 0.6 apfu. It is also evident that Cr³⁺ ions are distributed at the M1 site even if the M3 site is not fully occupied by Cr³⁺ + Fe³⁺. In addition, the behavior of Cr³⁺ and Fe³⁺ is different from each other: Fe³⁺ ions exclusively distribute at the M3 site, whereas Cr³⁺ ions distribute at both the M3 and M1 sites with Cr³⁺(M1):Cr³⁺(M3) ratios of 0:0.07, 0.136:0.153, and 0.100:0.101 for CrEp1, CrEp2, and CrEp3, respectively. The exclusive distribution of Fe³⁺ at the M3 site in the chromian epidotes is reasonable, because if the total Fe³⁺ content is less than 0.5 apfu, Fe³⁺ cations occupy the M3 site (Dollase, 1971; Guili et al., 1999). Although the site populations of Cr³⁺ at the M1 and M3 sites are nearly even in CrEp2 and CrEp3, the distribution coefficient ($K_D = (\text{Cr}^{3+}/\text{Al})^{M1}/(\text{Cr}^{3+}/\text{Al})^{M3}$) representing the relationship between Cr³⁺ and Al populations at the M1 and M3 sites are 0.35(3) for CrEp2 and 0.41(3) for CrEp3. The selective distribution of Cr³⁺ at the M3 site in CrEp1 and the K_D values of CrEp2 and CrEp3 indicate a stronger preference of Cr³⁺ for the M3 site than that of

Al³⁺. Thus, in the case of the distributions of Cr³⁺ and Al³⁺ in epidote, the preference of Cr³⁺ at the M sites is M3 > M1 > M2. On the other hand, the preferences of Fe³⁺, Cr³⁺, and Al³⁺ for the M1 and M3 sites are Al³⁺ > Cr³⁺ > Fe³⁺ for the M1 site and Fe³⁺ > Cr³⁺ > Al³⁺ for the M3 site.

Relationship between Cr distribution in the octahedral sites and structural changes

In the chromian epidotes, the unit-cell parameters of *a*, *b*, and *c* and the cell volume increase with increasing Cr³⁺ content in epidote, which would be caused by the expansion of the M3O₆ and M1O₆ octahedra due to the ionic substitutions of the larger Cr³⁺ and Fe³⁺ for the smaller Al³⁺.

The expansion of the M1 and M3 octahedra by the substitutions of Cr³⁺ for Al³⁺ at the M1 site and of Cr³⁺ + Fe³⁺ for Al at the M3 site, respectively, is confirmed by the relationship between the mean M–O distance, <M–O>, and the mean ionic radius, *r* (Å), (Figs. 3 and 4) represented as follows;

$$\langle \text{M1-O} \rangle = 1.343r + 1.186 \quad (R^2 = 0.75) \quad (1)$$

and

$$\langle \text{M3-O} \rangle = 0.586r + 1.659 \quad (R^2 = 0.93) \quad (2).$$

The gradients of Equations (1) and (2) are close to those of the synthetic Ca₂(Al,Fe³⁺)₃Si₃O₁₂(OH) epidote

Table 9. Estimated bond valence (v.u.)

Sample	Anions	<i>A</i> 1	<i>A</i> 2	<i>M</i> 1	<i>M</i> 2	<i>M</i> 3	Si1	Si2	Si3	ΣC^v	Anion chemistry
CrEp1	O1	0.25*		0.45*		0.28*	0.95*			1.93	O ²⁻
	O2		0.11* 0.21*			0.51*			1.01*	1.84	O ²⁻
	O3	0.36*	0.19*		0.57*			1.03*		2.15	O ²⁻
	O4			0.59* [†]		0.59				1.77	O ²⁻
	O5	0.22		0.45* [†]					0.90	2.02	O ²⁻
	O6	0.11			0.48* [†]				0.95	2.02	O ²⁻
	O7	0.43	0.46				1.15			2.04	O ²⁻
	O8		0.06* [†]			0.73		1.07		1.92	O ²⁻
	O9	0.07* [†]					1.01	0.97		2.12	O ²⁻
	O10		0.20		0.57* [†]					1.34	OH ⁻
	ΣA^v	2.12	1.80	2.98	3.24	2.90	4.06	4.10	3.87		
CrEp2	O1	0.25*		0.46*		0.27*	0.92*			1.90	O ²⁻
	O2		0.11* 0.22*			0.50*			0.98*	1.81	O ²⁻
	O3	0.36*	0.18*		0.57*			1.02*		2.13	O ²⁻
	O4			0.59* [†]		0.58				1.76	O ²⁻
	O5	0.21		0.44* [†]					0.90	1.99	O ²⁻
	O6	0.10			0.47* [†]				0.94	1.98	O ²⁻
	O7	0.41	0.45				1.17			2.03	O ²⁻
	O8		0.06* [†]			0.71		1.07		1.90	O ²⁻
	O9	0.06* [†]					0.98	0.97		2.07	O ²⁻
	O10		0.20		0.55* [†]					1.30	OH ⁻
	ΣA^v	2.06	1.79	2.98	3.18	2.83	3.99	4.08	3.80		
CrEp3	O1	0.25*		0.46*		0.28*	0.92*			1.91	O ²⁻
	O2		0.11* 0.22*			0.50*			0.99*	1.82	O ²⁻
	O3	0.37*	0.18*		0.57*			1.01*		2.13	O ²⁻
	O4			0.59* [†]		0.57				1.75	O ²⁻
	O5	0.22		0.45* [†]					0.88	2.00	O ²⁻
	O6	0.10			0.48* [†]				0.95	2.01	O ²⁻
	O7	0.42	0.46				1.17			2.05	O ²⁻
	O8		0.06* [†]			0.71		1.08		1.91	O ²⁻
	O9	0.06* [†]					0.98	0.98		2.08	O ²⁻
	O10		0.21		0.56* [†]					1.33	OH ⁻
	ΣA^v	2.10	1.81	3.00	3.22	2.84	3.99	4.08	3.81		

Note: ΣA^v is the valence of bonds emanating from cation summed over the bonded anions.

ΣC^v is the valence of bonds reaching anions.

* Two bonds per cation.

† Two bonds per anion.

(Giuli et al., 1999) and the synthetic $\text{Ca}_2(\text{Al,Mn}^{3+})_3\text{Si}_3\text{O}_{12}(\text{OH})$ piemontite (Langer et al., 2002; Nagashima and Akasaka, 2004).

As shown in Figure 3, the *M*1-O1, *M*1-O4 and *M*1-O5 distances increase with the increase of Cr^{3+} content in the *M*1 site, and their gradients are similar to each other,

indicating an equidimensional expansion of the *M*1O₆ octahedra. Although the *M*3O₆ octahedra are essentially more distorted than the *M*1O₆ octahedra (Figs. 3 and 4), an almost equidimensional expansion of the *M*3O₆ octahedra with the substitution of $\text{Cr}^{3+} + \text{Fe}^{3+}$ for Al^{3+} is also shown by the similar trends of the variations in *M*3-O1,

Figure 3. The $M1-O$ distances as a function of mean ionic radius. The mean ionic radii were calculated using the ionic radius values of Shannon (1976). Open symbols, clinozoisite (Dollase, 1968); Filled symbols, chromian epidote (this study); Diamond, $M1-O1$ distance; Square, $M1-O4$ distance; Triangle, $M1-O5$ distance; $\times$, mean $M1-O$ distance of chromian epidote (this study); $+$, mean $M1-O$ distance of clinozoisite (Dollase, 1968); Broken line, the regression line between the mean $M1-O$ distance and the mean ionic radius in chromian epidote (this study) and clinozoisite (Dollase, 1968).

$M3-O2$, $M3-O4$ and $M3-O8$ lengths as a function of the mean ionic radius (Fig. 4).

Such variations in the $M1-Oi$ and $M3-Oi$ distances are also observed in synthetic $\text{Ca}_2(\text{Al}, \text{Fe}^{3+})_3\text{Si}_3\text{O}_{12}(\text{OH})$ -epidote (Giuli et al., 1999). In the synthetic $\text{Ca}_2(\text{Al}, \text{Mn}^{3+})_3\text{Si}_3\text{O}_{12}(\text{OH})$ -piemontite (Nagashima and Akasaka, 2004), the $M1O_6$ and $M3O_6$ octahedra expand nonequidimensionally with the substitution of Mn^{3+} for Al ions in the $M1$ and $M3$ sites due to the Jahn-Teller effect: the $M1-O1$ and $M3-O1$ distances increase more rapidly than other $M1-Oi$ ($i = 4$ and 5) and $M3-Oi$ ($i = 2, 4$, and 8) distances, respectively, with the substitution of Mn^{3+} for Al^{3+} . The nearly equidimensional expansion of the $M1$ and $M3$ octahedra caused by the substitution of Cr^{3+} and/or Fe^{3+} for Al is consistent with the fact that Cr^{3+} and Fe^{3+} in the octahedral sites do not give rise to a Jahn-Teller distortion.

ACKNOWLEDGMENTS

The authors thank Prof. Mitsuyoshi Kimata, Mr. Norimasa Nishida, and Ms. Mihoko Hoshino for their guidance and assistance in the X-ray single-crystal analyses at Tsukuba University, Drs. Kazuyoshi Kitajima and Kenji Yoza of Bruker AXS KK for their kind permission

Figure 4. The $M3-O$ distances as a function of mean ionic radius. Mean ionic radii were calculated using the ionic radius values of Shannon (1976). Open symbols, clinozoisite (Dollase, 1968); Filled symbols, chromian epidote (this study); Diamond, $M3-O1$ distance; Square, $M3-O2$ distance; Triangle, $M3-O4$ distance; Circle, $M3-O8$ distance; $\times$, mean $M3-O$ distance of chromian epidote (this study); $+$, mean $M3-O$ bond distance of clinozoisite (Dollase, 1968); Broken line, the regression line between the mean $M3-O$ bond distance and the mean ionic radius in chromian epidote (this study) and clinozoisite (Dollase, 1968).

to use and help in the X-ray single-crystal analyses using a Bruker SMART APEX CCD diffractometer, Mr. Tsuyoshi Sakurai of Shimane University for providing the samples, Dr. Fujio Izumi of the National Institute for Materials Science for his permission and help in using the RIETAN-2000 program, and to Dr. Barry P. Roser of Shimane University for his critical reading of the manuscript.

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Manuscript received March 10, 2006

Manuscript accepted February 11, 2007

Manuscript handled by Kazumasa Sugiyama