

Vanadoallanite-(La): a new epidote-super group mineral from Ise, Mie Prefecture, Japan

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[Received 13 May 013; Accepted 28 June 2013; Associate Editor: D. Gatta]

ABSTRACT

The new mineral, vanadoallanite-(La), found in the stratiform ferromanganese deposit from the Shobu area, Ise City, Mie Prefecture, Japan, was studied using electron microprobe analysis and single-crystal X-ray diffraction methods. Vanadoallanite-(La) is a rare-earth element-rich monoclinic epidote-super group mineral with simplified formula $\text{CaLaV}^{3+}\text{AlFe}^{2+}(\text{SiO}_4)(\text{Si}_2\text{O}_7)\text{O}(\text{OH})$ ($Z = 2$, space group $P2_1/m$) characterized by predominantly V^{3+} at one of three octahedral sites, $M1$. The crystal studied shows large V ($\sim 8.4 \text{ V}_2\text{O}_3$ wt.%), Fe ($\sim 13.8 \text{ Fe}_2\text{O}_3$ wt.%; $\text{Fe}^{2+}/\text{total Fe} = 0.58$) and Mn ($\sim 8.8 \text{ MnO}$ wt.%) contents. A small amount of Ti is also present ($\sim 1.3 \text{ TiO}_2$ wt.%). Structural refinement converged to $R_1 = 2.96\%$. The unit-cell parameters are $a = 8.8985(2)$, $b = 5.7650(1)$, $c = 10.1185(2) \text{ \AA}$, $\beta = 114.120(1)^\circ$ and $V = 473.76(2) \text{ \AA}^3$. The cation distributions determined at $A1$, $A2$ and $M3$ are $\text{Ca}_{0.61}\text{Mn}_{0.39}$, $(\text{La}_{0.46}\text{Ce}_{0.14}\text{Pr}_{0.07}\text{Nd}_{0.18})_{\Sigma 0.85}\text{Ca}_{0.15}$ and $\text{Fe}_{0.56}^{2+}\text{Mn}_{0.30}^{2+}\text{Mg}_{0.06}\text{V}_{0.05}^{3+}\text{Fe}_{0.03}^{3+}$, respectively. On the other hand, depending on Ti assignment, two different schemes of the cation distribution at $M1$ and $M2$ can be considered: (1) $^{M1}(\text{V}_{0.58}^{3+}\text{Fe}_{0.34}^{3+}\text{Ti}_{0.08}^{4+})^{M2}(\text{Al}_{0.92}\text{Fe}_{0.08}^{3+})$, and (2) $^{M1}(\text{V}_{0.58}^{3+}\text{Fe}_{0.42}^{3+})^{M2}(\text{Al}_{0.92}\text{Ti}_{0.08}^{4+})$. In both cases, the dominant cations at $A1$, $A2$, $M1$, $M2$ and $M3$ are Ca, La, V^{3+} , Al and Fe^{2+} , respectively. According to ionic radius, Ti^{4+} possibly prefers $M2$ rather than Fe^{3+} . A large Mn^{2+} content at $A1$ also characterizes our vanadoallanite-(La). The structural change of Mn^{2+} -rich allanite-group minerals is considered to be controlled by two main factors. One is the large Mn^{2+} content at $A1$ in vanadoallanite-(La), which modifies the topology of the AlO_6 polyhedron. The other is the expansion of M_3O_6 and M_1O_6 octahedra caused by large octahedral cations, such as Fe^{2+} and Mn^{2+} , at $M3$ and the trivalent transition elements, V^{3+} and Fe^{3+} , at $M1$.

KEYWORDS: vanadoallanite-(La), lanthanum, vanadium, epidote super group, new mineral.

Introduction

EPIDOTE-SUPER GROUP minerals occur in various types of rock in many geological settings. Among them, the allanite-group minerals contribute an important class of the rock-forming minerals as the reservoir of rare-earth elements (*REE*) (e.g. Gieré and Sorensen, 2004). Recent studies have

revealed that the stratiform ferromanganese deposits in Japan are rich in *REE* (e.g. Kato *et al.*, 2005; Moriyama *et al.*, 2010; Fujinaga *et al.*, 2011), while the *REE*-bearing minerals are scarcely known from these deposits. In the study of *REE*-bearing minerals in a stratiform ferromanganese deposit, we found an allanite-group mineral from the Shobu area, Ise City, Mie Prefecture, Japan. The mineral corresponded to a La- and V-rich endmember which has not been found previously. This discovery should provide a new insight into the epidote-super group minerals.

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DOI: 10.1180/minmag.2013.077.6.04

Monoclinic epidote-supergroup minerals with the structural formula $A1A2M1M2M3(\text{SiO}_4)(\text{Si}_2\text{O}_7)\text{O}(\text{OH})$ belong to sorosilicates with mixed SiO_4 and Si_2O_7 groups. Their structure is based on a chain of edge-sharing $M2$ octahedra and a central chain of $M1$ octahedra with $M3$ octahedra attached on alternate sides along its length. Chains of octahedra run parallel to the b axis, linked by SiO_4 and Si_2O_7 groups (Ito *et al.*, 1954; Dollase, 1968). This structural arrangement gives rise to two types of highly coordinated sites: 9-coordinated $A1$ and 10-coordinated $A2$. In natural epidote-group minerals (Mills *et al.*, 2009) corresponding to the clinozoisite subgroup defined by Armbruster *et al.* (2006), $A1$ and $A2$ are filled with Ca, and the octahedral $M1$, $M2$ and $M3$ sites are occupied by trivalent cations. The cations having large ionic radius such as REE, Sr and Ba occupy $A2$, and cations smaller than Ca, such as Mn^{2+} , may substitute at $A1$. The allanite group is defined by the heterovalent substitution of the type $\text{Ca}^{2+}(\text{A}2) + \text{M}^{3+}(\text{M}3) \leftrightarrow \text{REE}^{3+}(\text{A}2) + \text{M}^{2+}(\text{M}3)$ (Armbruster *et al.*, 2006). The predominant cation at $A2$ is REE^{3+} , such as Ce^{3+} , La^{3+} and Y^{3+} . For members of the allanite-group minerals, the Levinson-type suffix designation is used to characterize the dominant REE. The $M3$ site is predominantly occupied by divalent cations, such as Mg, Fe^{2+} and Mn^{2+} . Moreover, the prefix is added if the predominant cation at $M1$ is not Al. Although the smallest $M2\text{O}_6$ octahedron is generally occupied by Al only in natural epidote-supergroup minerals, a small amount of octahedral cations, such as Fe^{3+} may substitute at $M2$ in allanite-group minerals (e.g. Holstam *et al.*, 2003). Moreover, it was suggested that a small amount of Ti^{4+} also possibly substitutes at $M2$ (Nagashima *et al.*, 2011a). The key cation-sites $M3$ and $A1$ determine the root name.

The occurrence of V^{3+} -rich epidote-supergroup minerals is uncommon. The V^{3+} -analogue of clinozoisite, mukhinite, simplified formula $\text{Ca}_2\text{Al}_2\text{V}^{3+}(\text{SiO}_4)(\text{Si}_2\text{O}_7)\text{O}(\text{OH})$, and the V^{3+} -analogue of androsite, vanadoandrosite-(Ce), $\text{Mn}^{2+}\text{Ce}^{3+}\text{V}^{3+}\text{AlMn}^{2+}(\text{SiO}_4)(\text{Si}_2\text{O}_7)\text{O}(\text{OH})$, are known (Shepel and Karpenko, 1969; Cenki-Tok *et al.* 2006). Although the occurrence of mukhinite had been known from the Tashelginsk iron deposit, Gornaya Shoriya, western Siberia (type loc.), several recent studies have reported new finds (Uher *et al.*, 2008; Bačík and Uher, 2010; Gobla, 2012). The Cr- and V-rich clinozoisite from the Outokumpu copper mine, Finland, contains 7.93 V_2O_3 wt.% at maximum

with up to 12.68 wt.% Cr_2O_3 (Nagashima *et al.*, 2011a). Vanadoandrosite-(Ce) occurs at the Vielle Aure mining district, central Pyrénées, France, in and around quartz-rhodochrosite-sulfide veinlets cross-cutting the rhodochrosite ore (Cenki-Tok *et al.*, 2006). This vanadoandrosite-(Ce) contained 14.36 wt.% V_2O_3 . In the case of other allanite-group minerals, the strongly zoned allanite-(Ce) and allanite-(La) from the Hemlo deposit have 9.07 and 8.89 wt.% V_2O_3 , respectively (Pan and Fleet, 1991), and “vanadian allanite” in the manganese-iron ore from the Kyurazawa mine contains 9.58 wt.% V_2O_3 (Kato *et al.*, 1994).

The La- and V-rich allanite-group mineral from Ise was approved as a new mineral, vanadoallanite-(La), by the Commission on New Minerals, Nomenclature and Classification (CNMNC) (IMA2012-095). The ideal formula is represented as $^{A1}\text{Ca}^{A2}\text{La}^{M1}\text{V}^{3+M2}\text{Al}^{M3}\text{Fe}^{2+}(\text{SiO}_4)(\text{Si}_2\text{O}_7)\text{O}(\text{OH})$ ($Z = 2$). The type specimen of vanadoallanite-(La) is deposited in the National Museum of Nature and Science, Tokyo, Japan (NSM M-43737). In this study, we describe the new mineral, vanadoallanite-(La) and examine its chemico-crystallographic features.

Experimental

Samples

Vanadoallanite-(La) was found in the ferro-manganese deposit from the Shobu area, Ise City, Mie Prefecture, Japan. The ore from this deposit consists mainly of magnetite, hematite and caryopillite as the matrix. Monazite-(La), chalcopyrite, and Ni-Fe sulfides such as pentlandite and heazlewoodite, are also observed as ore minerals. Three types of mineral veinlets characterized by rhodochrosite, bementite and tephroite cut the ore body at random. The uncommon Mo-Mn mineral, iselite, $\text{Mn}_2\text{Mo}_3\text{O}_8$ (IMA2012-020), was also found in the rhodochrosite veinlets (Nishio-Hamane *et al.*, 2013). The La-rich allanite-group minerals characterized by large V_2O_3 content are formed in bementite and tephroite veinlets. The vanadoallanite-(La) crystal studied occurs in the tephroite vein closely associated with tephroite and rhodochrosite (Fig. 1).

Aggregates formed by euhedral to subhedral prismatic crystals elongated parallel to [010] represent the most common occurrence of vanadoallanite-(La) (Fig. 1). The crystals are dark brown with vitreous lustre. The length of

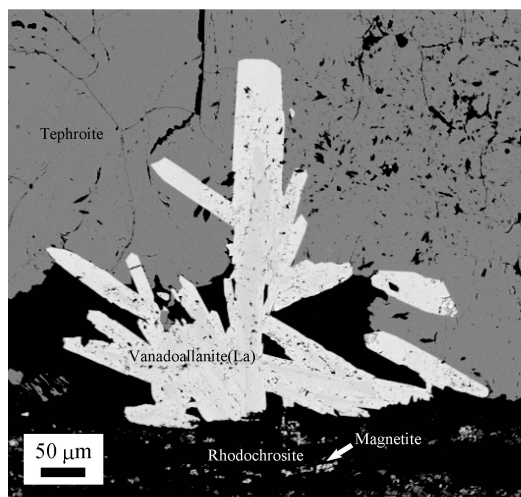


FIG. 1. Back-scattered image of vanadoallanite-(La) associated with tephroite, rhodochrosite and magnetite.

the crystals varies from several micrometres up to 300 μm . The mineral is brittle with imperfect cleavage on $\{001\}$. The calculated density is 4.15 g/cm^3 .

Chemical analysis (EMPA)

The chemical composition of our sample was determined using a JEOL JXA-8230 electron microprobe analyser at Yamaguchi University. Operating conditions were: accelerating voltage of 15 kV, a beam current of 20 nA and an a beam diameter of 1–5 μm . Wavelength-dispersion spectra were collected with LiF, PET and TAP monochromator crystals to identify interfering elements and locate the best wavelengths for background measurements. The abundances of Si, Ti, Al, Cr, V, Fe, Mn, Ni, Mg, Ca, Sr, Ba, Na, K, Y, F, Cl and REE (La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er) were measured. Several elements, which are not shown in Table 1, are below the detection limit. The probe standards for the measured elements excluding rare-earth elements (REE) are as follows; wollastonite (Si, Ca), rutile (Ti), corundum (Al), eskolaite (Cr), $\text{Ca}_3(\text{VO}_4)_2$ (V), hematite (Fe), manganosite (Mn), NiO (Ni), periclase (Mg), $\text{SrBaNb}_4\text{O}_{12}$ (Sr, Ba), albite (Na), K-feldspar (K), fluorite (F) and halite (Cl). The following standards and spectral lines for REE were used: synthetic REE-bearing hexaborides, REEB_6 , for LaLa_1 , CeLa_1 , PrLa_1 and NdLa_1 ;

synthetic REE-bearing phosphate standards for SmLa_1 , EuLa_1 , GdLa_1 , DyLa_1 , HoLa_1 and ErLa_1 ; $(\text{Zr,Y})\text{O}_2$ for YLa_1 . The measured intensities of EuLa_1 and GdLa_1 were corrected for peak-overlap interference of PrLa_2 for Eu and LaLa_2 and CeLa_1 for Gd using JEOL software. The ZAF correction-method was used for all elements. Table 1 gives the average composition and the composition of the crystal used for the structural analysis, respectively.

Single-crystal structure analysis

The X-ray diffraction (XRD) data for a single crystal were collected using a Bruker SMART APEX II CCD diffractometer (Bruker AXS K.K.) installed at the University of Bern, Switzerland. A crystal (0.08 mm $\times$ 0.06 mm $\times$ 0.02 mm) picked from thin section (Fig. 1), was mounted on a glass fibre and intensity data were measured at room temperature using graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). Preliminary lattice parameters and an orientation matrix were obtained from 12 sets of frames and refined during the integration process of the intensity data. Diffraction data were collected with ω scans at different ϕ settings (ϕ - ω scan) (Bruker, 1999). Data were processed using SAINT (Bruker, 1999). An empirical absorption correction using SADABS (Sheldrick, 1996) was applied. The reflection statistics and systematic absences were consistent with space groups $P2_1$ and $P2_1/m$. Subsequent attempts to solve the structure indicated that the observed structure is centrosymmetric and for this reason $P2_1/m$ is the correct space group. Structural refinement was performed using SHELXL-97 (Sheldrick, 2008). Scattering factors for neutral atoms were employed. The position of the hydrogen atom of the hydroxyl group was derived from difference-Fourier syntheses. Subsequently, hydrogen positions were refined at a fixed value of $U_{\text{iso}} = 0.05 \text{ \AA}^2$. The site occupancy of A1 and A2 was refined with Ca and La, respectively, without restraints. Site assignments were made using the chemical composition of measured crystals. The site occupancies of three octahedral sites were refined with V for M1, Al and Fe for M2 and Fe for M3. The site occupancies at Si1, Si2 and Si3 were fixed as 1.0 Si atoms per formula unit (a.p.f.u.), because their occupancies at the preliminary stage indicated that these three sites are fully occupied with Si within standard deviation. The hydrogen position was refined

TABLE 1. Chemical composition of a vanadoallanite-(La) crystal used for single-crystal XRD analysis.

	Analytical point			Ave.	Std.
	1	2	3		
SiO ₂	30.02	29.84	30.05	29.97	0.12
TiO ₂	1.32	0.83	0.89	1.01	0.27
Al ₂ O ₃	7.64	7.21	8.06	7.64	0.42
Cr ₂ O ₃	0.21	0.10	0.16	0.16	0.05
V ₂ O ₃ * ¹	7.79	8.38	6.75	7.64	0.83
FeO* ²	7.29	7.38	6.41	6.94	0.54
Fe ₂ O ₃ * ²	5.66	4.73	5.73	5.47	0.56
MnO* ¹	7.73	7.59	8.77	8.03	0.65
NiO	0.00	0.07	0.07	0.05	0.04
MgO	0.18	0.32	0.67	0.39	0.25
CaO	7.55	6.94	6.42	6.97	0.57
SrO	0.10	0.12	0.25	0.16	0.08
Y ₂ O ₃	0.03	0.01	0.01	0.02	0.01
La ₂ O ₃	11.04	13.16	12.22	12.14	1.06
Ce ₂ O ₃	3.78	3.86	3.62	3.75	0.12
Pr ₂ O ₃	1.68	2.11	1.78	1.86	0.23
Nd ₂ O ₃	5.14	4.93	4.75	4.94	0.19
Er ₂ O ₃	0.11	0.09	0.06	0.09	0.02
F	0.05	0.07	0.08	0.07	0.01
−O = F	−0.02	−0.03	−0.04	−0.03	
Total	97.30	97.70	96.72	97.25	
H ₂ O (calc)* ³	2.70	2.30	3.28	2.75	
Cations	8	8	8	8	
Si	3.01	3.03	3.04	3.03	0.01
Ti	0.10	0.06	0.07	0.08	0.02
Al	0.90	0.86	0.96	0.91	0.05
Cr	0.02	0.01	0.01	0.01	0.00
V ³⁺	0.63	0.68	0.55	0.62	0.07
Fe ²⁺	0.61	0.63	0.54	0.59	0.05
Fe ³⁺	0.43	0.36	0.44	0.42	0.04
Mn ²⁺	0.66	0.65	0.75	0.69	0.06
Ni	0.00	0.01	0.01	0.00	0.00
Mg	0.03	0.05	0.10	0.06	0.04
Ca	0.81	0.75	0.70	0.75	0.06
Sr	0.01	0.01	0.01	0.01	0.00
Y	0.00	0.00	0.00	0.00	0.00
La	0.41	0.49	0.46	0.45	0.04
Ce	0.14	0.14	0.13	0.14	0.00
Pr	0.06	0.08	0.07	0.07	0.01
Nd	0.18	0.18	0.17	0.18	0.01
Er	0.00	0.00	0.00	0.00	0.00
Total	8.00	8.00	8.00	8.00	
F [−]	0.02	0.02	0.03	0.02	0.00
OH [−]	0.90	0.78	1.11	0.93	0.17

*¹ V, Fe and Mn as V₂O₃, Fe₂O₃ and MnO*² FeO and Fe₂O₃ are calculated based on charge-balance calculation, number of total positive charge = 25.*³ The difference between analytical total and 100 wt.% was assumed to be the H₂O content.

with a bond-distance constraint of $O-H = 0.980(1) \text{ \AA}$ (Franks, 1973).

A simulated powder diffraction pattern with $CuK\alpha$ radiation was obtained using *RIETAN-FP* (Izumi and Momma, 2007) on the basis of the unit-cell dimensions and atomic parameters from the single-crystal analysis, as the amount of sample was insufficient for powder XRD measurement.

Results

Chemical composition of vanadoallanite-(La)

The chemical composition of vanadoallanite-(La) in this study is characterized by large V^{3+} ($\sim 8.4 \text{ V}_2\text{O}_3 \text{ wt.}\%$) and Mn^{2+} ($\sim 8.8 \text{ MnO wt.}\%$) contents. The chemical composition of the vanadoallanite-(La) crystal used for single-crystal XRD analysis is given in Table 1, where the total number of cations, except H ions, was normalized

to 8. The corresponding chemical formula based on average chemical data ($n = 3$) is $(Ca_{0.75}Sr_{0.01}La_{0.45}Ce_{0.14}Pr_{0.07}Nd_{0.18}Mn_{0.38})_{\Sigma 1.98}(Mn_{0.31}^{2+}Mg_{0.06}Fe_{1.00}V_{0.63}^{3+}Cr_{0.01}Al_{0.91}Ti_{0.08})_{\Sigma 3.00}Si_{3.02}O_{12}(OH)_{0.98}F_{0.02}$. The Fe^{2+}/Fe^{3+} value was calculated based on a total positive charge of 25 to maintain charge balance. As a result, $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ is 0.58. Because of the limited amount of sample, a Mössbauer spectrum could not be measured. The crystal used for single-crystal analysis was originally an aggregate (Fig. 1). The slight heterogeneity of allanite in this aggregate is related to $Mn^{2+} \leftrightarrow Ca$ zonation.

Crystal-structure refinements

Crystallographic data and refinement parameters are summarized in Table 2. The refined atomic positions and anisotropic displacement parameters are listed in Tables 3 and 4. Interatomic distances,

TABLE 2. Data collection and details of structure refinement.

Space group	$P2_1/m$
Crystal size (mm)	$0.08 \times 0.06 \times 0.02$
Cell parameters	$a \text{ (\AA)}$ $b \text{ (\AA)}$ $c \text{ (\AA)}$ $\beta \text{ (}^\circ\text{)}$ $V \text{ (\AA}^3\text{)}$
Dcalc (g/cm ³)	4.15
Absorption coefficient μ (mm ⁻¹)	10.29
Corrected reflections	6605
Unique reflections	1920
Criteria for observed reflections	
R_{int} (%)	3.35
R_{σ} (%)	4.74
θ_{max} (°)	33.2
Miller index limit	$-11 \leq h \leq 13, -8 \leq k \leq 6, -15 \leq l \leq 13$
R_1 (%)	2.96
wR_2 (%)	5.19
S	1.02
No. of parameters	125
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0190P)^2 + 0.23P]$
$\Delta\rho_{\text{max}}$ (e $\text{\AA}^{-3}$)	1.07 (1.51 $\text{\AA}$ from O8)
$\Delta\rho_{\text{min}}$ (e $\text{\AA}^{-3}$)	-1.23 (0.68 $\text{\AA}$ from A2)

XRD data were collected using a Bruker SMART APEX II CCD diffractometer. Intensity data were measured at room temperature using graphite-monochromatized $MoK\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). Diffraction data were collected with φ - ω scan (Bruker, 1999). Data were processed using *SAINT* (Bruker, 1999). An empirical absorption correction using *SADABS* (Sheldrick, 1996) was applied. Structural refinement was performed using *SHELXL-97* (Sheldrick, 2008). The function of the weighting scheme is $w = 1/[\sigma^2(F_o^2) + (a \cdot P)^2 + b \cdot P]$, where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$, and the parameters a and b are chosen to minimize the differences in the variances for reflections in different ranges of intensity and diffraction angle.

TABLE 3. Refined atomic positions and isotropic displacement parameters ($\text{\AA}^2$).

Site	W^*	x	y	z	U_{eq}
A1	$2e$	0.7602(1)	$\frac{3}{4}$	0.15207(8)	0.0126(2)
A2	$2e$	0.59344(3)	$\frac{3}{4}$	0.42812(3)	0.01005(8)
M1	$2a$	0	0	0	0.0083(2)
M2	$2c$	0	0	$\frac{1}{2}$	0.0069(3)
M3	$2e$	0.30910(8)	$\frac{1}{4}$	0.21191(7)	0.0110(2)
Si1	$2e$	0.3446(1)	$\frac{3}{4}$	0.0356(1)	0.0089(3)
Si2	$2e$	0.6905(1)	$\frac{1}{4}$	0.2806(1)	0.0090(3)
Si3	$2e$	0.1913(1)	$\frac{3}{4}$	0.3257(1)	0.0081(2)
O1	$4f$	0.2401(2)	0.9884(3)	0.0242(2)	0.0127(5)
O2	$4f$	0.3159(2)	0.9702(3)	0.3652(2)	0.0107(4)
O3	$4f$	0.8002(2)	0.0140(3)	0.3330(2)	0.0120(4)
O4	$2e$	0.0590(4)	$\frac{1}{4}$	0.1373(3)	0.0127(6)
O5	$2e$	0.0510(3)	$\frac{3}{4}$	0.1572(3)	0.0113(6)
O6	$2e$	0.0755(3)	$\frac{3}{4}$	0.4168(3)	0.0110(6)
O7	$2e$	0.5126(4)	$\frac{3}{4}$	0.1761(3)	0.0144(6)
O8	$2e$	0.5498(4)	$\frac{1}{4}$	0.3406(3)	0.0189(7)
O9	$2e$	0.6057(4)	$\frac{1}{4}$	0.1037(3)	0.0152(7)
O10	$2e$	0.0895(4)	$\frac{1}{4}$	0.4307(3)	0.0112(6)
H10	$2e$	0.072(7)	$\frac{1}{4}$	0.328(2)	$0.05U_{\text{iso}}$

* W = Wyckoff notation of point position with multiplicity.

selected angles and distortions of octahedral sites are listed in Table 5. The crystal structure of vanadoallanite-(La) is shown in Fig. 2. The simulated powder diffraction is listed in Table 6.

The observed and estimated electron numbers and the determined site occupancy are given in Table 7. The A1 site, for which the number of electrons is obviously >20 , was occupied by Ca

TABLE 4. Anisotropic displacement parameters ($\text{\AA}^2$).

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
A1	0.0167(5)	0.0111(4)	0.0121(4)	0	0.0080(3)	0
A2	0.00762(13)	0.01290(13)	0.00883(11)	0	0.00253(9)	0
M1	0.0062(4)	0.0094(4)	0.0085(3)	-0.0002(3)	0.0022(3)	-0.0005(3)
M2	0.0049(6)	0.0076(6)	0.0076(6)	-0.0007(4)	0.0020(4)	0.0000(4)
M3	0.0079(3)	0.0120(3)	0.0101(3)	0	0.0008(3)	0
Si1	0.0087(6)	0.0090(5)	0.0083(5)	0	0.0027(4)	0
Si2	0.0075(6)	0.0088(5)	0.0110(5)	0	0.0041(4)	0
Si3	0.0067(6)	0.0089(5)	0.0087(5)	0	0.0032(4)	0
O1	0.0090(10)	0.0111(10)	0.0169(11)	-0.0025(8)	0.0042(9)	0.0010(8)
O2	0.0093(10)	0.0113(10)	0.0115(10)	-0.0006(8)	0.0042(8)	-0.0022(8)
O3	0.0085(10)	0.0105(10)	0.0138(10)	0.0001(8)	0.0014(8)	-0.0006(8)
O4	0.0108(15)	0.0122(14)	0.0141(15)	0	0.0041(12)	0
O5	0.0104(15)	0.0107(14)	0.0105(13)	0	0.0020(12)	0
O6	0.0122(15)	0.0104(13)	0.0122(14)	0	0.0068(12)	0
O7	0.0114(15)	0.0153(15)	0.0134(14)	0	0.0019(12)	0
O8	0.0111(16)	0.0334(19)	0.0117(15)	0	0.0042(13)	0
O9	0.0153(16)	0.0201(16)	0.0110(14)	0	0.0061(13)	0
O10	0.0124(15)	0.0097(13)	0.0113(13)	0	0.0046(12)	0

VANADOALLANITE-(La): A NEW EPIDOTE-SUPERGROUP MINERAL

TABLE 5. Selected interatomic distances (Å), angles (°), volume of polyhedra (Å³), and distortion parameters for the octahedral sites*.

A1– O1 × 2	2.335(2)	M1– O1 × 2	2.050(2)	O1–M1–O4	88.6(1)
O3 × 2	2.294(2)	O4 × 2	1.920(2)	O1–M1–O5	90.3(1)
O5	2.567(3)	O5 × 2	2.055(2)	O4–M1–O5	93.31(8)
O7	2.313(3)	Ave.	2.008		
Ave.	2.356	$V^{M1(VI)}$ (Å ³)	10.76	O3–M2–O6	89.4(1)
O6	2.984(3)	DI (oct)	0.029	O3–M2–O10	91.2(1)
O9 × 2	3.145(1)	<λ oct>	1.003	O6–M2–O10	97.59(9)
Ave.	2.601	σ _θ (oct) ²	4.76		
$V^{A1(VI)}$ (Å ³)	16.03			O1–M3–O1'	81.8(1)
$V^{A1(IX)}$ (Å ³)	26.88	M2– O3 × 2	1.889(2)	O1–M3–O2	91.28(7)
		O6 × 2	1.923(2)	O1–M3–O4	79.15(8)
A2– O2 × 2	2.614(2)	O10 × 2	1.913(2)	O1–M3–O8	112.97(8)
O2' × 2	2.500(2)	Ave.	1.908	O2–M3–O2'	93.1(1)
O3 × 2	2.842(2)	$V^{M2(VI)}$ (Å ³)	9.18	O2–M3–O4	88.42(8)
O7	2.350(3)	DI (oct)	0.007	O2–M3–O8	80.17(8)
O10	2.590(3)	<λ oct>	1.006		
Ave.	2.607	σ _θ (oct) ²	21.51	O1–Si1–O1'	114.2(2)
O8 × 2	2.9939(8)			O1–Si1–O7	111.29(9)
Ave.	2.684	M3– O1 × 2	2.304(2)	O1–Si1–O9	106.5(1)
$V^{A2(VIII)}$ (Å ³)	28.92	O2 × 2	2.221(2)	O7–Si1–O9	106.5(2)
$V^{A2(X)}$ (Å ³)	38.40	O4	2.038(3)		
		O8	2.001(3)	O3–Si2–O3'	113.0(2)
Si1– O1 × 2	1.637(2)	Ave.	2.182	O3–Si2–O8	109.5(1)
O7	1.587(3)	$V^{M3(VI)}$ (Å ³)	12.99	O3–Si2–O9	107.6(1)
O9	1.640(3)	DI (oct)	0.050	O8–Si2–O9	109.5(2)
Ave.	1.625	<λ oct>	1.046		
$V^{Si1(IV)}$ (Å ³)	2.19	σ _θ (oct) ²	142.73	O2–Si3–O2'	102.8(2)
				O2–Si3–O5	114.0(1)
Si2– O3 × 2	1.632(2)	Si3– O2 × 2	1.624(2)	O2–Si3–O6	112.6(1)
O8	1.599(3)	O5	1.651(3)	O5–Si3–O6	101.3(2)
O9	1.634(3)	O6	1.640(3)		
Ave.	1.624	Ave.	1.635	Si1–O9–Si2	140.9(2)
$V^{Si2(IV)}$ (Å ³)	2.20	$V^{Si3(IV)}$ (Å ³)	2.21		
O10...O4	2.868(4)				

* DI (oct) = $1/6 \sum |R_i - R_{av.}|/R_{av.}$ (R_i : each bond length, $R_{av.}$: average distance for an octahedron) (Baur, 1974), $\langle \lambda_{oct} \rangle = \sum_{i=1}^6 (l_i - l_0)^2/6$ (l_i : each bond length, l_0 : centre-to-vertex distance for an octahedron with O_h symmetry, whose volume is equal to that of a distorted octahedron with bond lengths l_i) (Robinson *et al.*, 1971), and σ_{θ} (oct)² = $\sum_{i=1}^{12} (\theta_i - 90^\circ)^2/11$ (θ_i : O–M–O angle) (Robinson *et al.*, 1971).

and Mn²⁺. Although some compositions obtained from allanite-group minerals occurring in the same veinlet imply Mn dominance at A1, the predominant cation of the crystal used for structural analysis is Ca. The A2 site is occupied mainly by REE, and the dominant cation at A2 is La. The cation assignment at A1 based on the observed number of electrons is very close to that obtained by chemical analysis. On the other hand, the observed number of electrons of A2 is larger than the calculated value, and the deepest hole locates

around the cation at A2. It implies that the REE content varies slightly. The site occupancies at M1, M2 and M3 were calculated using the following procedure: (1) elements with <0.05 a.p.f.u. based on the result of chemical analysis were omitted; (2) Fe, V and Ti were treated as Fe during the refinement; (3) based on the results of chemical analysis, the total amounts of Fe, V and Ti were restricted to 1.01, 0.63 and 0.08 a.p.f.u., respectively, after the total number of cations at the A and M sites was re-normalized as

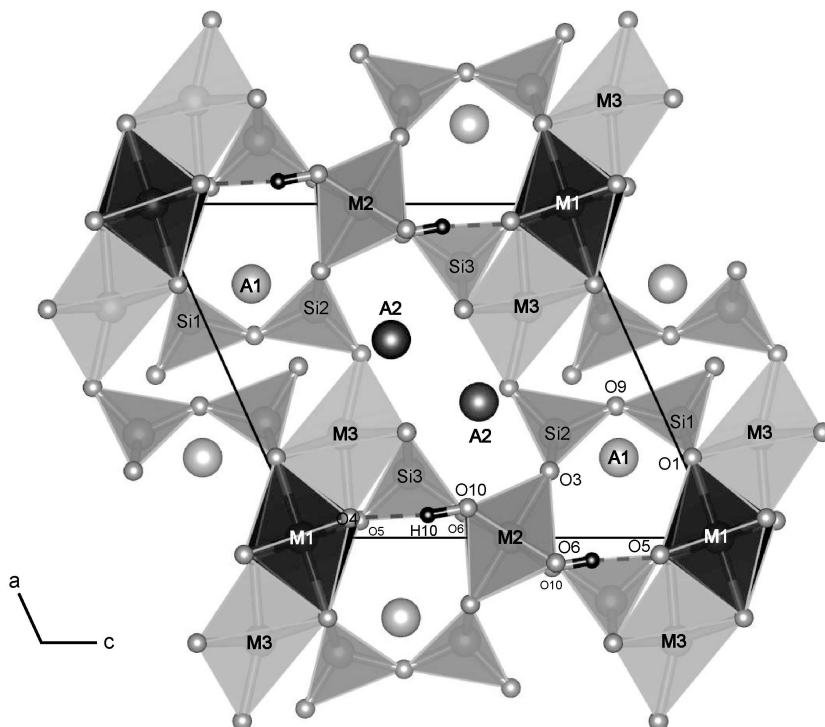


FIG. 2. Crystal structure of vanadoallanite-(La) projected onto (010) drawn with the program *VESTA* (Momma and Izumi, 2011). Dashed lines indicate H...O bonds.

5, and Fe^{2+} content, 0.56 a.p.f.u., was calculated based on charge-balance calculation; (4) Ti ions were assigned to *M1* and/or *M2* (Nagashima *et al.*, 2011b); (5) because the site distribution of V^{3+} ions was unknown, their behaviour was treated as Fe^{3+} . As a result, the determined cation distributions at *A1*, *A2* and *M3* are $\text{Ca}_{0.61}\text{Mn}_{0.39}$, $(\text{La}_{0.46}\text{Ce}_{0.14}\text{Pr}_{0.07}\text{Nd}_{0.18})_{\Sigma 0.85}\text{Ca}_{0.15}$ and $\text{Fe}_{0.56}\text{Mn}_{0.30}\text{Mg}_{0.06}\text{V}_{0.05}\text{Fe}_{0.03}^{3+}$, respectively. However, there are two possible cation assignments for *M1* and *M2* because of different models for the distribution of Ti.

On the basis of chemical data and occupancy refinement, the two possible cation assignments at three crystallographically independent octahedra are as follows; (1) $^{M1}(\text{V}_{0.58}^{3+}\text{Fe}_{0.34}^{3+}\text{Ti}_{0.08}^{4+})$ $^{M2}(\text{Al}_{0.92}\text{Fe}_{0.08}^{3+})$, or (2) $^{M1}(\text{V}_{0.58}^{3+}\text{Fe}_{0.42}^{3+})$ $^{M2}(\text{Al}_{0.92}\text{Ti}_{0.08}^{4+})$. The cation assignments at *M1* and *M2* are different in each case. However, in both cases, the predominant cations at *A1*, *A2*, *M1* and *M3* are Ca, La^{3+} , V^{3+} and Fe^{2+} , respectively. Thus, this mineral can be named vanadoallanite-(La) based on the assignment model after the

recommended nomenclature of epidotes (Armbruster *et al.*, 2006). The difference between the observed and calculated number of electrons however, is striking and may be related to zonation.

Discussion

The site assignment of V, Ti and Fe was not determined directly by X-ray structure analysis because of their similar X-ray scattering factors. The V, Ti and Fe ions can be distributed among the three crystallographically independent octahedral sites, *M1*, *M2* and *M3*. Their volumes decrease in the sequence $\text{M3O}_6 > \text{M1O}_6 > \text{M2O}_6$. Corresponding cation distributions are controlled mainly by the volumes of MO_6 -octahedra, ionic radii of cations and the Jahn-Teller effect based on the studies of synthetic Me^{3+} -bearing clinozoisite ($\text{Me} = \text{Fe}$, Mn, Cr, Fe+Mn; Langer *et al.* 2002; Nagashima and Akasaka, 2004, 2010; Nagashima *et al.*, 2009). The behaviour of V^{3+} ions among the octahedra,

TABLE 6. Calculated powder diffraction pattern based on the result of single-crystal XRD analysis*.

<i>h</i>	<i>k</i>	<i>l</i>	2θ (°)	<i>d</i> (Å)	<i>I</i> _{cal}	<i>h</i>	<i>k</i>	<i>l</i>	2θ (°)	<i>d</i> (Å)	<i>I</i> _{cal}
0	0	1	9.57	9.235	24	2	1	$\bar{4}$	39.36	2.287	4
1	0	0	10.89	8.122	15	3	0	$\bar{4}$	39.59	2.275	8
1	0	$\bar{1}$	11.18	7.908	27	1	2	2	40.74	2.213	9
1	0	1	17.22	5.145	20	1	2	$\bar{3}$	41.17	2.191	7
1	0	$\bar{2}$	17.78	4.983	9	4	0	$\bar{1}$	41.41	2.179	22
0	1	1	18.13	4.890	7	2	2	1	41.80	2.159	20
1	1	0	18.86	4.701	16	4	0	$\bar{3}$	42.09	2.145	6
1	1	$\bar{1}$	19.04	4.659	5	0	1	4	42.13	2.143	7
0	0	2	19.21	4.618	12	2	2	$\bar{3}$	42.48	2.126	19
1	1	$\bar{2}$	23.58	3.770	10	0	2	3	42.95	2.104	13
0	1	2	24.68	3.604	11	2	0	3	43.51	2.078	9
2	1	$\bar{1}$	25.27	3.521	49	2	2	2	47.33	1.919	15
2	1	0	26.83	3.320	14	1	1	4	47.78	1.902	7
2	1	$\bar{2}$	27.33	3.261	5	3	1	2	48.00	1.894	6
2	0	1	27.35	3.259	12	2	2	$\bar{4}$	48.24	1.885	13
2	0	$\bar{3}$	28.31	3.150	4	0	2	4	50.61	1.802	4
1	1	2	30.14	2.962	4	5	0	$\bar{2}$	51.40	1.776	5
3	0	$\bar{2}$	30.68	2.912	23	2	3	$\bar{1}$	51.78	1.764	7
1	1	$\bar{3}$	30.70	2.910	100	4	2	$\bar{2}$	51.90	1.760	6
0	2	0	31.00	2.883	38	4	1	$\bar{5}$	54.04	1.696	7
2	1	1	31.51	2.837	14	2	0	$\bar{6}$	54.39	1.686	5
0	2	1	32.51	2.752	6	1	3	$\bar{3}$	54.96	1.669	13
1	2	0	32.95	2.716	37	4	2	0	55.30	1.660	6
0	1	3	32.96	2.715	36	5	1	$\bar{1}$	55.58	1.652	6
3	0	0	33.06	2.707	13	1	2	4	55.61	1.651	5
3	0	$\bar{3}$	33.98	2.636	5	3	2	2	55.81	1.646	10
3	1	$\bar{1}$	34.18	2.621	53	1	0	$\bar{6}$	56.04	1.640	12
2	0	2	34.85	2.572	26	4	2	$\bar{4}$	56.39	1.630	20
1	0	4	35.80	2.506	5	0	3	3	56.40	1.630	6
1	2	$\bar{2}$	35.96	2.495	7	5	1	$\bar{4}$	56.60	1.625	5
0	2	2	36.73	2.445	6	3	3	$\bar{1}$	57.21	1.609	12
3	1	$\bar{3}$	37.48	2.397	13	1	1	5	57.74	1.595	9
2	2	$\bar{2}$	38.62	2.329	14	4	0	$\bar{6}$	58.56	1.575	8
1	1	4	39.16	2.299	4	4	1	2	58.85	1.568	9

* Only reflections with relative intensity >4% are listed.

and its effect on the crystal structure has not been examined. After Shannon (1976), the ionic radius of V^{3+} (0.64 Å 6-coordinated) is slightly smaller than that of Fe^{3+} (0.645 Å in 6-coordinated high-spin configuration). On the basis of their ionic radii, the behaviour of V^{3+} is assumed to be very similar to that of Fe^{3+} .

Vanadium may be present in silicates as V^{3+} , V^{4+} and V^{5+} (Evans, 1969; Schindler *et al.*, 2000). However, the oxidation state of vanadium in our vanadoallanite-(La) is assumed to be trivalent based on the chemical neutralization and mineral assemblages as well as the reported V-bearing epidote-supergroup minerals such as vanado-

androsite-(Ce) (Cenki-Tok *et al.*, 2006) and Cr^{3+} - and V^{3+} -rich clinozoisite (Nagashima *et al.*, 2011a). Although piemontite is occasionally associated with ardennite, $Mn_4^{2+}MgAl_5[Si_5(As^{5+}, V^{5+})O_{22}](OH)_6$ ($Z = 2$) (e.g. Barresi *et al.*, 2007), the V^{3+} -bearing piemontite has not been confirmed until now.

The Al content of three analytical points in the vanadoallanite-(La) crystal is <1 a.p.f.u. and 0.92 a.p.f.u. on average (Table 1). Moreover, the observed number of electrons of $M2$ is 13.67 (Table 7). In epidote-supergroup minerals, the smallest $M2$ site is filled with Al^{3+} , the deficit ($1 - Al$) is compensated by Fe^{3+} (Armbruster *et*

TABLE 7. Number of electrons and cation assignments*.

Site	Observed no. e^-	Cation assignment based on EMPA	Estimated no. e^-
A1	21.92	$\text{Ca}_{0.61}\text{Mn}_{0.39}$	21.94
A2	56.08	$(\text{La}_{0.46}\text{Ce}_{0.14}\text{Pr}_{0.07}\text{Nd}_{0.18})_{\Sigma 0.85}\text{Ca}_{0.15}$	52.27
Si1	14	$\text{Si}_{1.00}(\text{fix})$	14
Si2	14	$\text{Si}_{1.00}(\text{fix})$	14
Si3	14	$\text{Si}_{1.00}(\text{fix})$	14
Case 1 (Fe^{3+} in M2)			
M1	22.09	$\text{V}_{0.58}^{3+}\text{Fe}_{0.34}^{3+}\text{Ti}_{0.08}^{4+}$	24.52
M2	13.67	$\text{Al}_{0.92}\text{Fe}_{0.08}^{3+}$	14.04
M3	24.71	$\text{Fe}_{0.56}^{2+}\text{Mn}_{0.30}^{2+}\text{Mg}_{0.06}\text{V}_{0.05}^{3+}\text{Fe}_{0.03}^{3+}$	24.76
Case 2 (Ti^{4+} in M2)			
M1	22.09	$\text{V}_{0.58}^{3+}\text{Fe}_{0.42}^{3+}$	24.84
M2	13.67	$\text{Al}_{0.92}\text{Ti}_{0.08}^{4+}$	13.72
M3	24.71	$\text{Fe}_{0.56}^{2+}\text{Mn}_{0.30}^{2+}\text{Mg}_{0.06}\text{V}_{0.05}^{3+}\text{Fe}_{0.03}^{3+}$	24.76

* The cation contents are fixed by EMPA data. The $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio was estimated based on charge-balance calculation.

al., 2006; Nagashima and Akasaka, 2010). Therefore, it is reasonable to assign some Fe^{3+} to the M2 site if the observed number of electrons at the M2 site is >13 . However, Nagashima *et al.* (2011b) pointed out that Ti^{4+} , with an octahedral ionic radius of 0.605 Å (Shannon, 1976), might be preferred in the M2 site over Fe^{3+} . There is no unique solution for this problem at present.

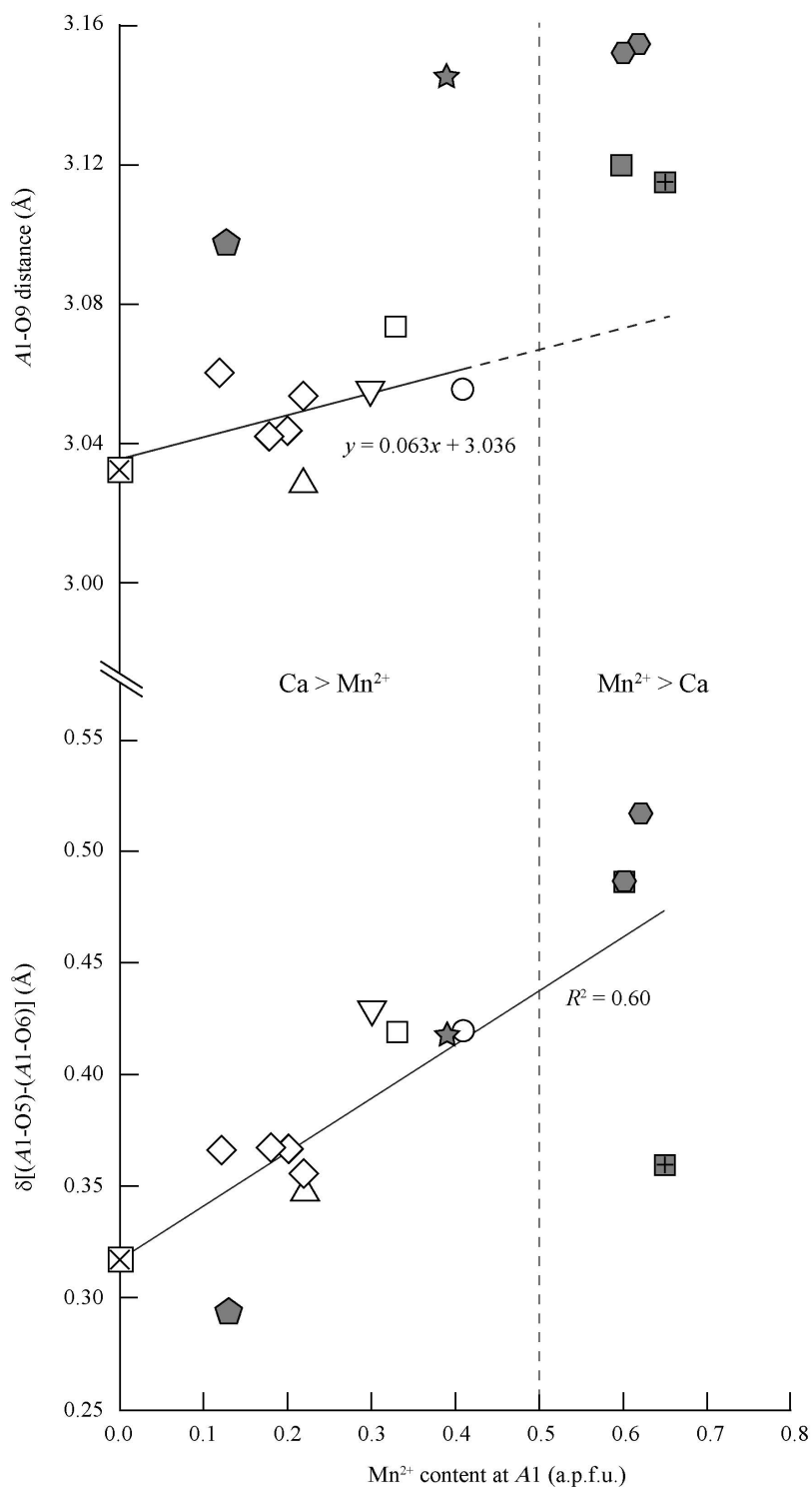
The relationship between Mn^{2+} content at the A1 site and the A1–O_i distance was addressed by Bonazzi *et al.* (1996). The increase of Mn^{2+} content at A1 changes the topology of the AlO_6 polyhedron, and the Mn substituted polyhedron is described approximately as a distorted 6-coordinated site. The increase of Mn^{2+} content at A1

leads the shortened A1–O1 ($\times 2$) and A1–O3 ($\times 2$) distances and the lengthened A1–O6 ($\times 1$) and A1–O9 ($\times 2$) distances (Bonazzi *et al.* 1996; Nagashima *et al.* 2010). This behaviour is very similar to other Mn^{2+} -rich epidote-supergroup minerals. However, the A1–O9 distance (3.145(8) Å) is relatively longer than the expected value (3.061 Å) applying a regression equation between the A1–O9 distance (y) and the Mn^{2+} content at A1 (x) on Mn^{2+} -rich epidote supergroup minerals (except for manganiandrosite-(La)), $y = 0.063x + 3.036$ (Fig. 3). In allanite-group minerals, the observed A1–O9 distances tend to be longer than the estimated ones: the difference between observed value and estimated one is ~ 0.08 Å for

FIG. 3 (*facing page*). Variation of A1–O9 distance and $\delta[(\text{A1}–\text{O5})–(\text{A1}–\text{O6})]$ (Å) as a function of Mn^{2+} content at the A1 site. The grey symbols represent the allanite-group minerals and the open symbols, clinozoisite-group minerals. ★: vanadoallanite-(La) (this study), ●: vanadoandrosite-(Ce) and manganiandrosite-(Ce) (Cenki-Tok *et al.*, 2006), ■: uedaite-(Ce) (Miyawaki *et al.*, 2008), ○: Mn^{2+} -, Sr-rich and REE-bearing piemontite (Nagashima *et al.*, 2010), ☒: piemontite (Dollase, 1969), △: piemontite-(Sr) (SRPM from Bonazzi *et al.*, 1990), ◇: REE-bearing piemontite (Bonazzi *et al.*, 1992), □, ■: piemontite and androsite-(La) (Bonazzi *et al.*, 1996), ▽: Pb- and REE-rich piemontite (Bermanec *et al.*, 1994), and ●: allanite-(Nd) (Škoda *et al.*, 2012). The break line running parallel to the y axis shows the boundary Ca- and Mn^{2+} -dominant series. Standard deviations (esd) of all distances are smaller than the symbol size.

Note: The site occupancy at A1 in allanite-(Nd) studied by Škoda *et al.* (2012) was inconsistent between the result of structural refinement and its final occupant. In this figure, the value derived from structural refinement at A1 was applied, $\text{Ca}_{0.872}\text{Mn}_{0.128}$.

VANADOALLANITE-(La): A NEW EPIDOTE-SUPERGROUP MINERAL



manganiandrosite-(Ce) and vanadoandrosite-(Ce) (Cenki-Tok *et al.*, 2006), and for uedaite-(Ce) (Miyawaki *et al.*, 2008). It is suggested that the Me^{2+} distribution at octahedral sites is responsible for the longer observed A1–O9 distance compared to the estimated one, because the cation distributions at *M1* and *M3* influence the topology of the A1 coordination polyhedron (Nagashima *et al.*, 2011b). The relationship between cation distributions at the *M1* and *M3* sites and the topology of the A1 coordination polyhedron is characterized by the variation of the Si1–O9–Si2 bridging angle. The Si1–O9–Si2 bridging-angles of epidote-supergroup minerals vary significantly from $\sim 137^\circ$ (manganiandrosite-(Ce) and vanadoandrosite-(Ce); Cenki-Tok *et al.* 2006; uedaite-(Ce): Miyawaki *et al.*, 2008) to 164° (clinozoisite: Dollase, 1968) because the Si_2O_7 group is compressed along the Si1–O9–Si2 direction due to the expansions of the $M1O_6$ and $M3O_6$ octahedra as a consequence of substitution of large octahedral cations, such as $Fe^{2+/3+}$ and $Mn^{2+/3+}$, and Mg for Al. The reduced Si1–O9–Si2 angle causes deviation of the O9 atom position to shift away from the cation at the A1 site, and the A1–O distance becomes longer.

The difference between A1–O5 and A1–O6 distances (6th and 7th neighbour oxygens from the atom at A1 site with $Ca_{0.61}Mn_{2+0.39}$, respectively) is 0.417 Å in this study. This value is nearly the same as that, 0.42 Å, of the Mn^{2+} -rich piemontite with Mn^{2+} population of 0.41 Mn^{2+} at the A1 site (Nagashima *et al.*, 2010). The specimens where Mn^{2+} cations occupy >60% of the A1 site show the larger $\delta[(A1-O5)-(A1-O6)]$, ~ 0.50 Å (Cenki-Tok *et al.*, 2006). The positive correlation between Mn^{2+} at the A1 site (a.p.f.u.) and $\delta[(A1-O5)-(A1-O6)]$ (Å) suggested by Bonazzi *et al.* (1996) is also confirmed in this study ($R^2 = 0.60$ in Fig. 3). However, it noted that the values derived from the structural data of allanite-(Nd) (0.294 Å; Škoda *et al.*, 2012) and uedaite-(Ce) (0.360 Å; Miyawaki *et al.*, 2008) deviate significantly from the regression line. The Mn^{2+} contents of those crystals may be less than those of the chemical compositions shown in their original papers.

Thus, the structural change of Mn^{2+} -rich allanite-group minerals is controlled mainly by two factors. One is the Mn^{2+} distribution at A1. The other is the expansion of $M3O_6$ and $M1O_6$ octahedra caused by large octahedral cations, such as Fe^{2+} and Mn^{2+} , at *M3* and the trivalent transition elements, V^{3+} and Fe^{3+} , at *M1*.

Acknowledgements

We thank the Principal Editor Prof. Peter Williams, Prof. Peter Leverett, and anonymous reviewers for their constructive comments on this manuscript. We also thank Prof. T. Armbruster for his permission to use Bruker *SMART APEXII* at the University of Bern and his constructive comments, Mr V. Malogajski for his help in preparing the single-crystal analysis, and Prof. M. Akasaka for his constructive comments on this manuscript. The chemical analysis using the JEOL JXA-8230 was performed at the Centre for Instrumental Analysis, Yamaguchi University. One of the authors, M.N., is supported by Grant-in-Aid for Research Activity Start-up (No. 22840029) from the Japan Society for the Promotion of Science (JSPS).

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