

Allanite-(Nd), $\text{CaNdAl}_2\text{Fe}^{2+}(\text{SiO}_4)(\text{Si}_2\text{O}_7)\text{O}(\text{OH})$, a new mineral from Åskagen, Sweden

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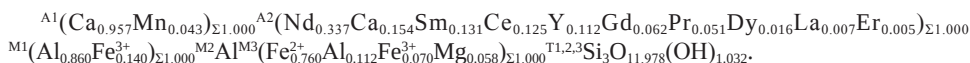
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ABSTRACT

Allanite-(Nd), ideally $\text{CaNdAl}_2\text{Fe}^{2+}(\text{SiO}_4)(\text{Si}_2\text{O}_7)\text{O}(\text{OH})$, the Nd-analog of allanite-(Ce), occurs in the Åskagen pegmatite, central Sweden. It forms fine-grained aggregates within altered thalénite-(Y). The other associated minerals include: iimoriite-(Y), keiviite-(Y), allanite-(Y), and tenerite-(Y). Allanite-(Nd) is biaxial (–); with refractive indices $\alpha = 1.723(5)$, $\beta = 1.754(7)$, $\gamma = 1.772(5)$, and measured $2V = 82^\circ(\pm 3^\circ)$. Larger fragments of allanite-(Nd) are moderately pleochroic (α = pale grayish-brown, γ = grayish-brown); small fragments are colorless. Allanite-(Nd) is monoclinic, space group $P2_1/m$, with the following unit-cell parameters: $a = 8.8897(5)$, $b = 5.7308(2)$, $c = 10.1010(6)$ Å, $\beta = 115.166(7)^\circ$, $V = 465.75(4)$ Å³, $Z = 2$. The strongest five peaks from the X-ray powder diffraction patterns [d (Å)(I)(hkl)] are: 3.51(46)($\bar{2}11$), 2.89(100)($\bar{1}13$), 2.87(45)(020), 2.70(60)(120), 2.61(60)($\bar{3}11$). Allanite-(Nd) has a density of 3.98 g/cm³, vitreous luster, grayish-brown streak, and the Mohs hardness is ca. 6. It is brittle, with imperfect cleavage, and conchoidal fracture. The Mössbauer spectroscopy revealed $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio of 0.27 in the type sample. The refined empirical formula of the crystal used for the structure determination is:



The allanite-(Nd) was approved by CNMNC (IMA 2010-060).

Keywords: Epidote supergroup, allanite, neodymium, pegmatite, Åskagen

INTRODUCTION

Minerals belonging to the allanite group (with monoclinic symmetry; space group $P2_1/m$) are part of the epidote supergroup, with a general formula $\text{A}^1(\text{A}^{2+})\text{A}^2(\text{REE}, \text{Y}^{3+})\text{M}(\text{M}_2^{3+}\text{M}^{2+})\text{T}[\text{Si}_2\text{O}_7]^{+}[\text{SiO}_4]\text{O}(\text{OH})$ (Armbruster et al. 2006; Mills et al. 2009). The A1 site is preferentially occupied by Ca and Mn, along with minor Pb, Sr, MREE, and HREE (Cressey and Steel 1988). The octahedral positions are represented by three independent sites M1, M2, and M3 occupied mainly by Al^{3+} , Fe^{3+} , Mn^{3+} , V^{3+} , Cr^{3+} , Fe^{2+} , Mn^{2+} , and Mg^{2+} (Armbruster et al. 2006).

Allanite, ideally $\text{Ca}(\text{REE}, \text{Y})\text{Al}_2\text{Fe}^{2+}[\text{Si}_2\text{O}_7][\text{SiO}_4]\text{O}(\text{OH})$, has three known end-members: allanite-(Ce), allanite-(La), and allanite-(Y) (Armbruster et al. 2006). In this paper we report data on allanite-(Nd), a new allanite end-member with Nd as dominant REE+Y. The allanite-(Nd) was approved as new mineral by CNMNC (IMA 2010-060; Škoda et al. 2011). Analyses of allanite with Nd as dominant REE were also reported from La Cabrera, Spain (González del Tánago 1997), Ryoke, Japan (Minakawa et al. 2001), and Mojave district, U.S.A. (Hanson et al. 2011).

The holotype crystal is deposited in the collection of Depart-

ment of Mineralogy and Petrology, Moravian Museum, Brno, Czech Republic (catalog number B10589). The type specimen is deposited in the collections of the Department of Mineralogy and Petrology, National Museum, Prague, Czech Republic (catalog number P1P 1/2010).

OCCURRENCE AND SAMPLE

Allanite-(Nd) occurs as an accessory phase in the blocky zone of the NYF-family granitic pegmatite near Åskagen (GPS N59° 42' 34", E14° 21' 23"), Värmland, Sweden. The pegmatite forms an approximately 20 m thick and 200 m long lenticular body, crosscutting leptyte. It was mined for K-feldspar and quartz at the beginning of twentieth century; other minerals include albite, biotite, muscovite, gadolinite-(Y), allanite-group minerals, native Bi, topaz, yttracrasite-(Y), thalénite-(Y), keiviite-(Y), and secondary REE-carbonates (Wilke 1997; Chukanov et al. 2010). So far, three allanite-group minerals were found in the pegmatite: allanite-(Ce), allanite-(Y), and the newly described allanite-(Nd). Moreover, the Åskagen pegmatite is the type locality for allanite-(Y) (Armbruster et al. 2006) and another mineral of epidote supergroup, åskagenite-(Nd) (Chukanov et al. 2010).

Fresh, crystalline allanite-(Nd) fills thin cracks and forms fine-grained aggregates (up to a few cubic millimeters) in crystals

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of thalénite-(Y). Other associated minerals are iimoriite-(Y), keiviite-(Y), tengerite-(Y), quartz, and allanite-(Y) that usually forms rims of the thalénite-(Y) crystals. Allanite-(Nd) replaced the primary thalénite-(Y), probably during an episode of late hydrothermal activity. Small inclusions of metamict allanite-(Nd) to allanite-(Y) were found in crystals of gadolinite-(Y), as well. Due to the metamict state and small size of allanite-(Nd) inclusions in gadolinite-(Y), the further investigation was exclusively focused on the well-crystalline allanite-(Nd) associated with thalénite-(Y). Thalénite-(Y) aggregates of macroscopically different degree of alteration, with common allanite-(Nd), were mounted in epoxy, polished, and labeled as: Ask1 = the less altered thalénite-(Y), Ask2 = the medium altered thalénite-(Y), and Ask3 = the highly altered thalénite-(Y). Grains of allanite-(Nd), which were used for powder X-ray data and subsequently for Mössbauer spectroscopy (Ask2a) and for single-crystal structure refinement (Ask2b), were extracted from the same sample from which Ask2 was extracted.

APPEARANCE AND PHYSICAL PROPERTIES

Allanite-(Nd) associated with thalénite-(Y) forms aggregates of prismatic crystals. The size of the individual grains does not exceed 0.5 mm. No twinning was observed. The color of the hand specimen is black but translucent fragments show dark brown tint. The luster is vitreous and its streak is grayish-brown. The Mohs hardness is ca. 6. Moreover, the indentation hardness and reduced elastic modulus were measured using nanoindentation technique with a NanoTest instrument equipped with a calibrated Berkovich indenter. The measured microhardness at an indentation load of 25 mN is 11.9 ± 0.5 GPa and the modulus of elasticity is equal to 158.1 ± 3.7 (GPa). Allanite-(Nd) is brittle with imperfect cleavage along {001} and conchoidal fracture. It is non-fluorescent. Locally, it is metamict.

The density of allanite-(Nd) was measured in heavy liquids as $D_{\text{meas}} = 3.98$ g/cm³; the density calculated from the crystal-structure data using the empirical formula of the measured crystal is $D_{\text{calc}} = 4.04$ g/cm³. The small fragments of allanite-(Nd) are commonly not useful for measuring of some optical properties (e.g., 2V) due to the high amount of small dark inclusions/domains and alteration. It is biaxial (–); at the wavelength of 589 nm, the refractive indices are $\alpha = 1.723(5)$, $\beta = 1.754(7)$, and $\gamma = 1.772(5)$. The angle 2V measured using spindle stage is $82^\circ(\pm 3^\circ)$. Dispersion is strong ($r > v$). Larger fragments of allanite-(Nd) are moderately pleochroic (α = pale grayish-brown, γ = grayish-brown); small fragments are colorless. The compatibility index based on the empirical formula and refractive indices, $1 - (K_p/K_c) = 0.035$, is “excellent.”

CHEMICAL COMPOSITION

Electron microprobe

The chemical composition of allanite was determined using a CAMECA SX100 electron microprobe (EMP) at an accelerating voltage of 15 kV, a beam current of 20 nA, and a beam size 2–5 μm . Concentrations of P, Si, Ti, Zr, Th, U, Al, Sc, Y, La-Sm, Gd-Er, Yb, Mg, Ca, Fe, Mn, Sr, Pb, Na, K, F, and Cl were measured. The standards, lines, and monochromators are listed in Table 1. The raw data were normalized using the PAP routine

(Pouchou and Pichoir 1985). Based on the counting statistics, the measurement error expressed as 2σ is approximately 2 rel% for concentrations around 20 wt% and 15 rel% for concentrations around 1 wt%. The mineral formula was calculated on the basis of 8 cations and 13 anions, but very similar results were obtained by normalization on 3 atoms per formula unit (apfu) of Si. The amount of H₂O was not measured, due to the small volume of crystalline material available; the content of H₂O was calculated from the ideal stoichiometry.

Four samples containing allanite-(Nd), labeled as Ask1, Ask2, Ask3, and Ask2b, were investigated by electron microprobe. Thalénite-(Y) dominates over iimoriite-(Y) in the sample Ask1; the amount of thalénite-(Y) equals to iimoriite-(Y) in the Ask2 sample; and iimoriite-(Y) prevails over thalénite-(Y) in the sample Ask3. The 32 point analyses from these four samples reveal a slight chemical heterogeneity within the individual allanite-(Nd) crystals. The backscattered-electron image shows a weak patchy zoning of the larger crystals mainly caused by variation of the REE and Ca. Small crystals are homogeneous. Inclusions observed in the optical microscope were not recorded in the BSE. The crystal of allanite-(Nd) used for the structure refinement (sample Ask2b), which was subsequently mounted into the epoxy resin, polished, and analyzed, showed homogeneous composition free of zoning.

On the A sites, the contents of Ca vary from 0.741 to 1.230 apfu, with the most frequent value ~ 1.1 apfu; contents of Mn are also variable in the range 0.04–0.172 apfu. The sum of REE+Y ranges from 0.768 to 0.933 apfu. In all analyses, Nd (0.209–0.430 apfu) predominates over Ce (0.080–0.241 apfu), Sm (0.070–0.222 apfu), and other REE (Gd ≤ 0.115 apfu; Pr ≤ 0.066 apfu; Dy ≤ 0.027 apfu; La, Tb, and Er, each ≤ 0.020 apfu). The contents of Y vary in the range of 0.053 to 0.174 apfu.

Generally, M sites of allanite-(Nd) are dominated by Al (1.693–2.081 apfu) and Fe²⁺ (0.645–0.987 apfu); the amount of calculated Fe³⁺ is low (up to 0.058–0.496 apfu) as well as the Mg content (≤ 0.1 apfu), see Table 1. The $\text{Fe}_{\text{calc}}^{3+}/\text{Fe}_{\text{tot}}$ ratio ranges from 0.07 to 0.40 with a median of 0.23 ($n = 32$).

The contents of P, U, Zr, Sc, Ho, Yb, Sr, Pb, K, Na, and Cl were below the detection limits of the EMP. Concentrations of Th and Ti were usually below detection limit of the EMP, but they sporadically grow up to 0.22 wt% ThO₂ and 0.21 wt% TiO₂, respectively. Analyses with elevated Th content show a lowered sum of the oxides and incoherent stoichiometry probably due to a metamictization-induced alteration.

Although Nd is the dominant rare earth, the chondrite-normalized REE pattern of allanite-(Nd) exhibits conspicuous maxima at Sm, and it is distinct from åskagenite-(Nd) (Chukanov et al. 2010), which shows a weak maximum at Nd (Fig. 1). The weak maximum at Nd is also seen in allanite-(Nd) from La Cabrera, Spain (González del Tánago 1997), whereas allanite-(Nd) from Ryoke (Japan; Minakawa et al. 2001) is more enriched in the heavier REE and its REE pattern exhibits a maximum at Gd (see Fig. 1).

Mössbauer spectroscopy

The transmission ⁵⁷Fe Mössbauer spectrum of powdered allanite-(Nd) sample Ask2a (ground under acetone in an agate mortar) was recorded in a constant acceleration mode at room

TABLE 1. Chemical composition of allanite-(Nd) expressed in wt% and supplemented by the detection limits and the standards, lines, and monochromators used for EMPA

	Ask1	Ask1	Ask2	Ask2	Ask3	Ask3	*Ask2b n=7	Ask2b St.dev.	Det. limit (wt% ox)	Standard/line, monochromator
SiO ₂	31.06	31.91	31.00	31.03	31.10	31.03	31.70	0.15	0.10	sanidine/Kα,TAP
Al ₂ O ₃	15.42	17.91	15.95	17.16	16.86	15.46	16.92	0.31	0.21	sanidine/Kα,TAP
Y ₂ O ₃	1.03	2.55	2.35	1.16	1.84	1.71	2.21	0.39	0.13	YAG/Lα,TAP
La ₂ O ₃	0.22	0.50	0.08	0.27	0.19	0.24	0.20	0.05	0.19	LaPO ₄ /Lα, PET
Ce ₂ O ₃	4.45	6.23	2.26	3.28	2.28	3.87	3.59	0.60	0.20	CePO ₄ /Lα, PET
Pr ₂ O ₃	1.62	1.61	1.06	1.19	0.95	1.80	1.47	0.14	0.20	PrPO ₄ /Lβ,LIF
Nd ₂ O ₃	11.90	7.22	9.02	10.47	9.64	12.45	9.91	0.86	0.20	NdPO ₄ /Lβ,LIF
Sm ₂ O ₃	4.59	2.36	5.38	5.87	6.68	4.30	3.99	0.36	0.19	SmPO ₄ /Lα,LIF
Gd ₂ O ₃	1.80	1.39	3.38	2.91	3.52	1.54	1.96	0.19	0.22	GdPO ₄ /Lβ,LIF
Tb ₂ O ₃	0.16	0.12	0.37	0.21	0.27	0.14	n.a.	–	0.14	TbPO ₄ /Lα,LIF
Dy ₂ O ₃	0.34	0.50	0.85	0.28	0.44	0.30	0.52	0.09	0.22	DyPO ₄ /Lβ,LIF
Er ₂ O ₃	0.13	0.15	0.20	0.09	0.13	0.10	0.17	0.01	0.10	ErPO ₄ /Lα,LIF
MgO	0.26	0.14	0.18	0.05	0.05	0.16	0.41	0.11	0.05	Mg ₂ SiO ₄ /Kα,TAP
CaO	9.92	11.31	9.52	9.85	10.06	8.82	10.85	0.24	0.09	andradite/Kα,PET
MnO	0.65	0.69	1.33	0.89	0.67	1.65	0.54	0.04	0.08	Mn ₂ SiO ₄ /Kα,TAP
FeO†	10.94	9.95	10.86	11.12	11.04	11.49	10.15	0.41	0.12	andradite/Kα,LIF
Fe ₂ O ₃ †	4.41	3.51	3.92	2.11	3.38	4.04	3.20	0.35	–	
F	0.08	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.05	topaz/Kα,PC1
H ₂ O‡	1.51	1.52	1.55	1.55	1.57	1.55	1.58			
O=F	–0.03	–0.07	0.00	0.00	0.00	0.00	0.00			
Sum	100.46	99.75	99.26	99.49	100.67	100.65	99.37			
A sites										
Ca ²⁺	1.028	1.135	0.988	1.020	1.032	0.914	1.106	0.020		
Mn ²⁺	0.053	0.055	0.109	0.073	0.054	0.135	0.044	0.004		
Y ³⁺	0.053	0.127	0.121	0.060	0.094	0.088	0.112	0.019		
La ³⁺	0.008	0.017	0.003	0.010	0.007	0.009	0.007	0.001		
Ce ³⁺	0.158	0.214	0.080	0.116	0.080	0.137	0.125	0.021		
Pr ³⁺	0.057	0.055	0.037	0.042	0.033	0.063	0.051	0.005		
Nd ³⁺	0.411	0.242	0.312	0.361	0.330	0.430	0.337	0.031		
Sm ³⁺	0.153	0.076	0.180	0.195	0.220	0.143	0.131	0.012		
Gd ³⁺	0.058	0.043	0.109	0.093	0.112	0.049	0.062	0.006		
Tb ³⁺	0.005	0.004	0.012	0.007	0.008	0.004	–	–		
Dy ³⁺	0.011	0.015	0.027	0.009	0.014	0.009	0.016	0.003		
Er ³⁺	0.004	0.004	0.006	0.003	0.004	0.003	0.005	0.000		
Σ A site	1.999	1.987	1.984	1.989	1.988	1.984	1.996			
M sites										
Mg ²⁺	0.037	0.020	0.026	0.007	0.007	0.023	0.058	0.015		
Al ²⁺	1.757	1.966	1.821	1.952	1.879	1.763	1.897	0.028		
Fe ²⁺	0.885	0.780	0.880	0.899	0.884	0.930	0.808	0.035		
Fe ³⁺	0.321	0.248	0.286	0.153	0.244	0.294	0.229	0.024		
Σ M site	3.000	3.014	3.013	3.011	3.014	3.010	2.992			
T sites										
Si ⁴⁺	3.003	2.989	3.003	2.998	2.977	3.003	3.015	0.006		
Al ³⁺	0.000	0.011	0.000	0.002	0.023	0.000	0.000	0.000		
Σ T site	3.003	3.000	3.003	3.000	3.000	3.003	3.015			
F [–]	0.024	0.047	0.000	0.000	0.000	0.000	0.000	0.000		
H ⁺	0.976	0.953	1.000	1.000	1.000	1.000	1.000			
O ^{2–}	12.976	12.953	13.000	13.000	13.000	13.000	13.000			

Note: The formula was calculated on the basis of 8 cations and 13 anions. n.a. = not analyzed.

* Ask2b = single crystal used for structure refinement, an average of 7 point EMP analyses.

† The Fe²⁺/Fe³⁺ was calculated on the basis of the charge balance.

‡ Calculated on the basis of ideal stoichiometry.

temperature using a ⁵⁷Co(Rh) source. The isomer shift value was calibrated against an α-Fe foil. The spectrum was fitted with Lorentz functions using the computer program CONFIT2000 (Žák and Jirásková 2006). Considering the powdered character of the absorber (i.e., the Ask2a sample) and assuming a random orientation of all crystallites in the powder, we constrained the two components of the quadrupole doublets to have equal widths and equal intensities. The effects of non-ideal absorber thickness and variable recoil-free fractions for iron atoms in non-equivalent structural sites were expected to be within experimental errors (see Table 2). The acquired spectrum was fitted with two doublets corresponding to ⁶¹Fe³⁺ and three doublets of ⁶¹Fe²⁺ (Fig. 2), both in a high-spin state, with a Fe³⁺/Fe_{tot} ratio of 0.27.

Iron atoms are thought to occupy up to three independent octahedral sites in the allanite structure (e.g., Kartashov et al. 2002, and references therein). In our observed ⁵⁷Fe Mössbauer spectrum, Fe³⁺ was fitted using the two doublets of low intensities; this is in accord with structural data that suggest the presence of small amounts of Fe³⁺ in both M1 and M3 sites. The hyperfine parameters of these doublets are comparable to ferriallanite-(Ce) and åskagenite-(Nd) (cf. Kartashov et al. 2002; Chukanov et al. 2010). In previously published experimental ⁵⁷Fe Mössbauer studies (e.g., Dollase 1971, 1973) and computational work (e.g., Grodzicki et al. 2001) of epidote group minerals including allanite, the Fe³⁺ doublet with the largest quadrupole splitting value has been assigned to the M3 site. This is consistent with the fact that the quadrupole splitting for

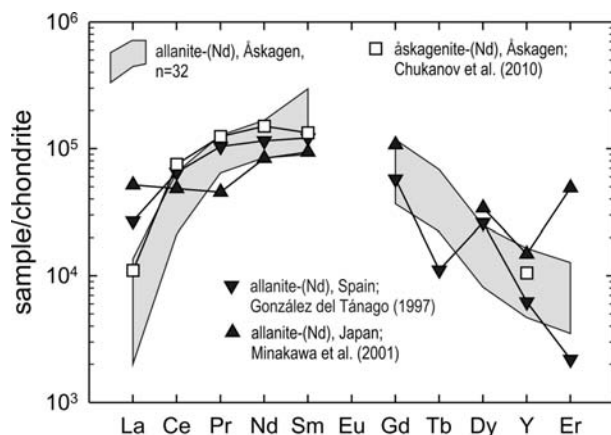


FIGURE 1. REE pattern of allanite-(Nd) normalized by chondrite (Taylor and McLennan 1985). Yttrium replaces Ho because of the similar ionic size, Pm is not shown. The gray area represents the field of the 32 analyses of allanite-(Nd) from Åskagen.

ferric iron increases with increasing site distortion and the M3 site in the epidote structure is generally much more distorted than both the M1 and M2 sites (Kartashov et al. 2002). The assignments for both ferric doublets of allanite-(Nd) Mössbauer spectrum are given in Table 2.

The three Fe^{2+} doublets in the ^{57}Fe Mössbauer spectrum of allanite-(Nd) indicate that ferrous iron atoms are present either exclusively in the most distorted M3 site (as previously suggested by Dollase 1973) with different next-nearest-neighbor configurations of atoms (i.e., M1, A1, T, and especially A2 sites with multiple different occupants and differing significantly in electron densities; cf. Ca vs. REEs) or in three independent M1, M2, and M3 sites. Taking into account the results of structure refinement (see below), the former interpretation is more prob-

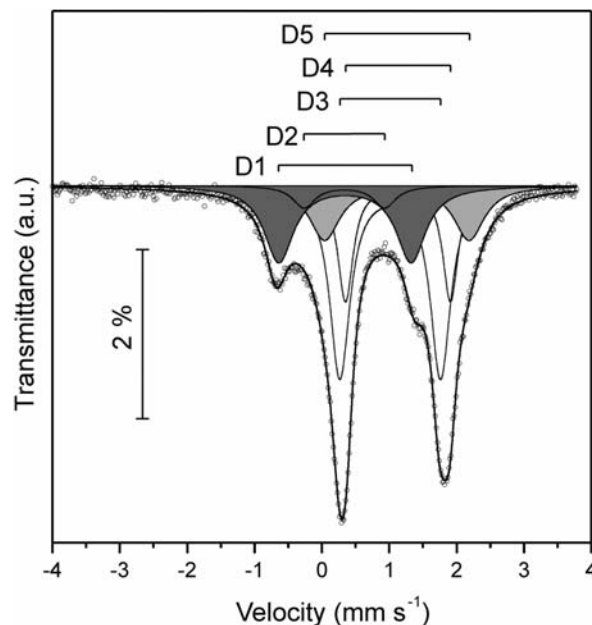


FIGURE 2. Room-temperature ^{57}Fe Mössbauer spectrum of allanite-(Nd). See the text and Table 2 for more details.

able at least for doublets D3 and D4 (Fig. 2). Averaged values of isomer shift $\delta = 1.07$ mm/s and quadrupole splitting $\Delta E_Q = 1.52$ mm/s for the D3 and D4 doublets are comparable to hyperfine parameters published for Fe^{2+} in the M3 site of ferriallanite-(Ce) (Kartashov et al. 2002). The last doublet of Fe^{2+} (D5, Fig. 2) has a quadrupole splitting value different from those of the D3 and D4 doublets. This could suggest the presence of Fe^{2+} also in other, less distorted octahedral sites (cf. McCammon 2004), such as the M1 or M2 sites. However, considering the absence of any other supporting data, the low fraction of this component in the whole spectrum (19%) and its significant overlap with other Fe^{2+} -doublets, we allocated this Fe^{2+} to the M3 site in the refined formula of allanite-(Nd) (see Table 2) in accordance with the structure refinement (see below).

Powder X-ray diffraction

The X-ray diffraction pattern of powdered allanite-(Nd) sample Ask2a was recorded on an X'Pert PRO MPD (PANalytical) instrument in Bragg-Brentano geometry with iron-filtered $\text{CoK}\alpha$ radiation (40 kV, 30 mA) and a solid-state X'Celerator detector. The sample was placed on a zero-background rotating single-crystal Si slide and continuously scanned in the 2θ range of $5\text{--}90^\circ$ with a step size of 0.017° . The positions of diffraction maxima were obtained by profile fitting performed with the XFit software. The resulting 60 reflections were indexed and the unit cell was subsequently refined using the Celref software (LMPG suite of programs).

Powder X-ray diffraction data are given in Table 3. Unit-cell parameters refined from the powder data are: $a = 8.873(2)$, $b = 5.729(1)$, $c = 10.077(2)$ Å, $\beta = 115.12(1)^\circ$, $V = 463.8(3)$ Å³. Using this technique, we also verified the absence of any mineral inclusions and/or crystalline phase impurities in the powdered sample of allanite-(Nd) used for Mössbauer spectroscopy.

TABLE 2. Room-temperature ^{57}Fe Mössbauer hyperfine parameters of the allanite-(Nd)

Iron valence	Parameter	Value	Assignment
Fe^{3+}	δ (mm/s)	0.35	D1
	ΔE_Q (mm/s)	2.05	M3 site
	Γ (mm/s)	0.43	
	RA (%)	18	
Fe^{3+}	δ (mm/s)	0.32	D2
	ΔE_Q (mm/s)	1.17	M1 site
	Γ (mm/s)	0.4	
	RA (%)	9	
Fe^{2+}	δ (mm/s)	1.01	D3
	ΔE_Q (mm/s)	1.49	M3 site
	Γ (mm/s)	0.34	
	RA (%)	34	
Fe^{2+}	δ (mm/s)	1.13	D4
	ΔE_Q (mm/s)	1.54	M3 site
	Γ (mm/s)	0.26	
	RA (%)	20	
Fe^{2+}	δ (mm/s)	1.11	D5
	$a\Delta E_Q$ (mm/s)	2.08	M3 site
	Γ (mm/s)	0.51	
	RA (%)	19	

Note: δ = isomer shift (± 0.02 mm/s), ΔE_Q = quadrupole splitting (± 0.02 mm/s), Γ = peak width (± 0.02 mm/s), and RA = relative area in the spectrum ($\pm 3\%$).

TABLE 3. Powder diffraction data for allanite-(Nd)

<i>l</i>	<i>d</i> _{meas}	<i>d</i> _{calc}	<i>h k l</i>	<i>l</i>	<i>d</i> _{meas}	<i>d</i> _{calc}	<i>h k l</i>
15	9.123(6)	9.124	0 01	20	2.399(4)	2.399	3 13
4	8.024(9)	8.033	1 00	15	2.323(2)	2.321	2 22
15	7.918(6)	7.924	1 01	18	2.281(2)	2.282	2 14
14	5.054(2)	5.058	1 01	21	2.278(1)	2.278	3 04
8	4.978(4)	4.977	1 02	35	2.1641(3)	2.164	4 01
11	4.847(4)	4.852	0 11	20	2.148(6)	2.148	3 11
5	4.669(6)	4.664	1 10	22	2.145(8)	2.146	4 03
15	4.651(2)	4.643	1 11	32	2.135(1)	2.137	2 21
13	4.563(3)	4.562	0 02	18	2.120(1)	2.12	2 23
11	4.014(3)	4.017	2 00	38	2.117(2)	2.117	3 14
8	3.963(3)	3.962	2 02	18	2.086(2)	2.085	0 23
13	3.756(2)	3.757	1 12	20	2.043(1)	2.043	2 03
10	3.572(4)	3.569	0 12	7	1.985(8)	1.984	1 04
46	3.5081(4)	3.507	2 11	19	1.895(3)	1.896	2 22
16	3.288(1)	3.289	2 10	26	1.880(3)	1.879	1 24
31	3.2091(5)	3.208	2 01	13	1.858(4)	1.858	1 30
9	2.910(1)	2.911	3 02	15	1.754(2)	1.754	2 31
100	2.8931(5)	2.895	1 13	11	1.726(1)	1.727	4 21
45	2.8652(3)	2.865	0 20	15	1.663(3)	1.663	2 23
21	2.800(2)	2.799	2 11	18	1.660(2)	1.66	1 33
60	2.698(1)	2.698	1 20	43	1.6594(4)	1.659	3 06
31	2.695(2)	2.694	1 21	18	1.629(1)	1.629	4 24
34	2.686(4)	2.686	0 13	19	1.600(2)	1.599	3 31
7	2.677(9)	2.678	3 00	13	1.573(2)	1.573	1 15
13	2.644(2)	2.641	3 03	15	1.547(1)	1.548	3 33
60	2.6072(5)	2.607	3 11	17	1.459(8)	1.459	5 24
28	2.530(4)	2.529	2 02	26	1.4358(6)	1.436	3 07
17	2.492(4)	2.493	1 21	10	1.376(2)	1.376	1 34
14	2.425(2)	2.426	0 22	6	1.360(2)	1.359	6 15
22	2.407(1)	2.406	2 21	12	1.301(1)	1.301	4 35

STRUCTURE OF ALLANITE-(Nd)

An optically anisotropic fragment of allanite-(Nd) was studied using a Oxford Diffraction KM-4/Xcalibur single-crystal X-ray diffractometer combined with a Sapphire2 CCD area detector. Data collection procedure and reduction details are summarized in Table 4. Data were corrected for Lorentz, polarization, and absorption effects. The structure model of allanite-(La) provided by Orlandi and Pasero (2006) was used as a starting model for the refinement. The structure was refined in monoclinic space group $P2_1/m$ using SHELXL-97 (Sheldrick 2008) with neutral atom scattering curves. The refined unit-cell parameters are: $a = 8.8897(5)$, $b = 5.7308(2)$, $c = 10.1010(6)$ Å, $\beta = 115.166(7)^\circ$, $V = 465.75(4)$ Å³, $Z = 2$.

During anisotropic refinement, site occupancies of all cation sites were refined as free variables. This lead to slight deviations from full occupancies only for the sites A1, A2, M1, and M3.

TABLE 4. Selected data for crystal-structure refinement, details of data collection, and refinement parameters

<i>a</i>	8.8897(5) Å	<i>b</i>	5.7308(2) Å
<i>c</i>	10.1010(6) Å	<i>V</i>	465.75(4) Å ³
β	115.166(7)°	<i>Z</i>	2
Cell, space group	monoclinic, $P2_1/m$		
Absorption coefficient	6.91 mm ⁻¹	<i>F</i> (000)	535
Crystal size	0.25 × 0.25 × 0.10 mm	Radiation	MoK α
2 θ _{max}	52.0°	Temperature	293 K
Measured reflections	5836	Independent reflections	1001
Reflections with $I > 2\sigma(I)$	874		
Refinement	Full matrix on F^2	$R1$ [$I > 2\sigma(I)$]	0.019
Weights	$w = 1/[\sigma^2(F_o^2) + (0.0275P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	wR_2	0.044
Refined reflections	1001	R_{int}	0.024
Refined parameters	125	Goodness of fit	1.03
$\Delta\rho_{max}$	0.69 e Å ⁻³	$\Delta\rho_{min}$	-0.40 e Å ⁻³

Therefore, the tetrahedral site and M2 were constrained to full occupancy. The occupancies for the A(1,2) and M(1,3) sites were refined using two major elements located in the respective sites, i.e., Ca vs. Mn in the A1 site, Nd vs. Ca in the A2 site, and Al vs. Fe in M(1,3) sites. The hydrogen atom was located in a difference Fourier map at the position reported by Orlandi and Pasero (2006). Final refinement resulted in $R = 0.019$; fractional atom coordinates and displacement parameters are listed in Tables 5 and 6.

The same crystal was subsequently analyzed using an EMP (Table 1). The calculated formula shows only slight deviations in occupancies for the A1, A2, M1, and M3 sites, within the range of analytical error. The empirical formula was assigned to the refined structure utilizing the bond-valence model (Brown and Altermatt 1985), the charge-distribution model of Nespolo et al. (1999), Mössbauer spectra of bulk allanite-(Nd), and the refined electron densities on individual sites. All Mn was placed on the A1 site, iron was treated as Fe³⁺ for M1 and as Fe²⁺ and Fe³⁺ for M3 sites, respectively. Charge and bond-valence values

TABLE 5. Fractional atomic coordinates and isotropic (*) or equivalent isotropic displacement parameters (Å²)

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{iso}^*/U_{eq}	Occ. (<1)
Ca1	0.75598(12)	0.75	0.14977(10)	0.0166(3)	0.872(12)
Mn1	0.75598(12)	0.75	0.14977(10)	0.0166(3)	0.128(12)
Nd2	0.59422(4)	0.75	0.43015(4)	0.01612(12)	0.712(3)
Ca2	0.59422(4)	0.75	0.43015(4)	0.01612(12)	0.288(3)
Al1	0	0	0	0.0111(4)	0.867(5)
Fe1	0	0	0	0.0111(4)	0.133(5)
Al2	0	0	0.5	0.0109(3)	
Fe3	0.30158(8)	0.25	0.21539(8)	0.0137(3)	0.831(6)
Al3	0.30158(8)	0.25	0.21539(8)	0.0137(3)	0.169(6)
Si1	0.33821(15)	0.75	0.03982(14)	0.0119(3)	
Si2	0.68558(15)	0.25	0.27747(14)	0.0123(3)	
Si3	0.18939(15)	0.75	0.32483(13)	0.0115(3)	
O1	0.2318(3)	0.9888(3)	0.0267(2)	0.0163(5)	
O2	0.3153(3)	0.9725(4)	0.3686(2)	0.0175(5)	
O3	0.7970(3)	0.0148(3)	0.3360(2)	0.0176(5)	
O4	0.0562(4)	0.25	0.1296(3)	0.0142(7)	
O5	0.0507(4)	0.75	0.1511(3)	0.0144(7)	
O6	0.0682(4)	0.75	0.4116(3)	0.0133(7)	
O7	0.5090(4)	0.75	0.1837(4)	0.0186(7)	
O8	0.5403(4)	0.25	0.3292(4)	0.0250(8)	
O9	0.6096(4)	0.25	0.0982(3)	0.0201(8)	
O10	0.0874(4)	0.25	0.4297(4)	0.0150(7)	
H10	0.072(7)	0.25	0.339(6)	0.029(16)*	

TABLE 6. Anisotropic displacement parameters (Å²)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca1	0.0243(6)	0.0125(5)	0.0167(6)	0	0.0125(4)	0
Mn1	0.0243(6)	0.0125(5)	0.0167(6)	0	0.0125(4)	0
Nd2	0.01462(18)	0.01892(18)	0.01285(19)	0	0.00393(13)	0
Ca2	0.01462(18)	0.01892(18)	0.01285(19)	0	0.00393(13)	0
Al1	0.0108(6)	0.0088(5)	0.0130(7)	-0.0004(4)	0.0044(5)	0.0002(4)
Fe1	0.0108(6)	0.0088(5)	0.0130(7)	-0.0004(4)	0.0044(5)	0.0002(4)
Al2	0.0108(6)	0.0082(6)	0.0127(7)	0.0000(5)	0.0042(5)	-0.0003(5)
Fe3	0.0118(4)	0.0122(4)	0.0136(4)	0	0.0019(3)	0
Al3	0.0118(4)	0.0122(4)	0.0136(4)	0	0.0019(3)	0
Si1	0.0125(6)	0.0103(6)	0.0123(7)	0	0.0048(5)	0
Si2	0.0131(6)	0.0106(6)	0.0126(7)	0	0.0050(5)	0
Si3	0.0113(6)	0.0109(6)	0.0121(7)	0	0.0049(5)	0
O1	0.0149(11)	0.0113(10)	0.0241(13)	0.0015(9)	0.0096(10)	0.0017(9)
O2	0.0177(12)	0.0175(11)	0.0178(13)	-0.0039(9)	0.0080(10)	-0.0011(9)
O3	0.0149(11)	0.0115(10)	0.0192(12)	0.0011(9)	0.0005(9)	-0.0017(9)
O4	0.0128(16)	0.0149(15)	0.0146(17)	0	0.0055(14)	0
O5	0.0137(16)	0.0150(15)	0.0153(18)	0	0.0070(14)	0
O6	0.0159(16)	0.0109(14)	0.0149(17)	0	0.0084(14)	0
O7	0.0155(17)	0.0185(15)	0.0184(18)	0	0.0040(14)	0
O8	0.0178(17)	0.0386(19)	0.0206(19)	0	0.0100(15)	0
O9	0.0214(18)	0.0247(17)	0.0157(19)	0	0.0094(15)	0
O10	0.0173(16)	0.0136(15)	0.0164(19)	0	0.0094(14)	0

TABLE 7. Bond-valence (BV) and charge distribution (CD) calculations for allanite-(Nd)

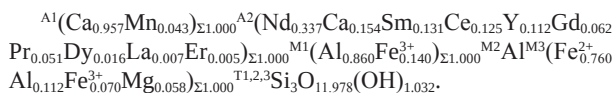
	Site occ.	e_{obs}	e_{for}	Charge	BV	CD	BV	CD
A1	$\text{Ca}_{0.957}\text{Mn}_{0.043}$	20.6	20.2	2	2.1	2	O1	-2 -2
A2	$(\text{REE}+\text{Y})_{0.846}\text{Ca}_{0.154}^*$	48.5	49.0	2.85	2.7	2.7	O2	-1.9 -2.1
M1	$\text{Al}_{0.86}\text{Fe}^{3+}_{0.14}$	14.7	14.8	3	2.9	3.1	O3	-2 -2.1
M2	Al	13	13	3	3.1	2.9	O4†	-1.7 -1.8
M3	$\text{Fe}^{2+}_{0.76}\text{Fe}^{3+}_{0.07}$	23.7	23.8	2.18	2.1	2.2	O5	-1.9 -1.9
	$\text{Al}_{0.112}\text{Mg}_{0.058}$							
Si1	Si	14	14	4	3.9	4.1	O6	-2 -1.9
Si2	Si	14	14	4	4	4.1	O7	-2 -2.1
Si3	Si	14	14	4	3.8	4		
							O8	-2 -1.9
							O9	-2.1 -1.9
							O10†	-1.3 -1.3

Note: e_{obs} = site electron density from structure refinement; e_{for} = site electron density calculated from refined formula. BV = bond valence (after Brown and Altermatt 1985), CD = charge density (Nespolo et al. 1999).

* (REE+Y) = $\text{Y}_{0.112}\text{La}_{0.007}\text{Ce}_{0.125}\text{Pr}_{0.051}\text{Nd}_{0.337}\text{Sm}_{0.131}\text{Gd}_{0.062}\text{Dy}_{0.016}\text{Er}_{0.005}$.

† Hydrogen bond donor (O10) and acceptor (O4).

of the refined formula are listed in Table 7. The resulting refined empirical formula of the type sample of allanite-(Nd) is:



There is a noticeable discrepancy between the interpretation of ^{57}Fe Mössbauer spectra (Table 2) and the structure refinement with respect to the allocation of the Fe^{3+} component. According to the interpretation of the ^{57}Fe Mössbauer spectrum, more ferric iron should occur in the M3 site, not fully occupied by divalent cations like Fe^{2+} , Mn^{2+} , and Mg^{2+} . However, the structure refinement unambiguously leads to the allocation of at least 0.14 apfu Fe into M1 site and bond-valence calculations show that Fe^{3+} fits better to the observed bond-length distances than Fe^{2+} (Table 7). Such discrepancies could be caused by combination of two factors: (1) uncertainty in obtaining correct proportions of respective iron fractions from both structure refinement and Mössbauer spectrum (i.e., determination of relative area in the Mössbauer spectrum within $\pm 3\%$, partially given by different recoilless fractions for iron atoms in non-equivalent structural sites), and (2) inhomogeneity of the studied sample of allanite-(Nd) (see Table 1) used for structure refinement and Mössbauer spectroscopy as well as differing volumes of the analyzed material.

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