

Hingganite-(Ce) and hingganite-(Y) from Tahara, Hirukawa-mura[†], Gifu Prefecture, Japan: The description on a new mineral species of the Ce-analogue of hingganite-(Y) with a refinement of the crystal structure of hingganite-(Y)

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Hingganite-(Ce), $\text{Ce}_2\Box\text{Be}_2\text{Si}_2\text{O}_8(\text{OH})_2$ or $\text{CeBeSiO}_4(\text{OH})$, occurs in a pegmatite at Hirukawa-mura, Gifu Prefecture, Japan. It is pale tan in color, vitreous and transparent, with a white streak. The Mohs hardness is 5–6, and the calculated density is 4.28 g/cm^3 . An electron microprobe analysis gave the empirical formula $(\text{Ce}_{0.82}\text{La}_{0.32}\text{Nd}_{0.13}\text{Pr}_{0.06}\text{Y}_{0.03}\text{Sm}_{0.01}\text{Gd}_{0.002}\text{Dy}_{0.001}\text{Ca}_{0.60})_{\Sigma 1.97}\text{Fe}_{0.24}\text{Be}_{2.02}\text{Si}_{2.02}\text{O}_{8.20}(\text{OH})_{1.52}$. The lattice parameters were determined by the Rietveld method coupled with the imaging plate Gandolfi XRD data: SG = $P2_1/a$, $a = 9.8973(11)$, $b = 7.6282(8)$, $c = 4.7505(6) \text{ \AA}$, $\beta = 90.416(8)^\circ$, $V = 358.64(7) \text{ \AA}^3$, and $Z = 2$ for $\text{Ce}_2\Box\text{Be}_2\text{Si}_2\text{O}_8(\text{OH})_2$. The three strongest lines in the powder XRD pattern [$d(\text{\AA})$, II_0 , hkl] are (3.14, 86, $\bar{2}11$ and 211), (2.85, 100, $\bar{1}21$ and 121) and (2.56, 46, $\bar{3}11$, 221 and 311). Hingganite-(Ce) is a new member of the gadolinite–datolite group of minerals. It is the Ce-analogue of hingganite-(Y), and ideally, is the Fe-free analogue of gadolinite-(Ce). A single crystal of hingganite-(Y) from the same locality showed a chemical composition of $(\text{Y}_{1.21}\text{Ca}_{0.28}\text{Nd}_{0.06}\text{Gd}_{0.06}\text{Dy}_{0.06}\text{Yb}_{0.05}\text{Er}_{0.04}\text{Ce}_{0.04}\text{Sm}_{0.03}\text{Ho}_{0.03}\text{Lu}_{0.02}\text{Pr}_{0.01}\text{Tm}_{0.01}\text{Tb}_{0.01}\text{La}_{0.01})_{\Sigma 1.92}\text{Fe}_{0.23}\text{Be}_{2.07}\text{Si}_{2.07}\text{O}_{8.19}(\text{OH})_{1.55}$. A negative anomaly was observed for Ho in the lanthanide distribution pattern of hingganite-(Y). A single crystal structure refinement of hingganite-(Y) converged to $R = 0.0329$ with the lattice parameters of: $a = 9.8830(16)$, $b = 7.6091(9)$, $c = 4.7423(9) \text{ \AA}$, $\beta = 90.342(14)^\circ$, and $V = 356.62(10) \text{ \AA}^3$.

Keywords: Hingganite-(Ce), Hingganite-(Y), New mineral, Crystal structure

INTRODUCTION

Hingganite-(Ce), $[\text{Ce}_2\Box\text{Be}_2\text{Si}_2\text{O}_8(\text{OH})_2$ or $\text{CeBeSiO}_4(\text{OH})]$, is a new member of the gadolinite–datolite group minerals, with a general formula of $A_2MT_2\text{Si}_2X_{10}$, where $A = \text{Ca}$, Y and the lanthanides, $M = \text{Fe}$ and vacancy, $T = \text{B}$ and Be , and $X = \text{O}$, (OH) , and F . It is the Ce-analogue of hingganite-(Y) $[\text{Y}_2\Box\text{Be}_2\text{Si}_2\text{O}_8(\text{OH})_2$ or $\text{YBeSiO}_4(\text{OH})]$ (Ding et al., 1984), and can also be expressed as the Fe-free analogue of gadolinite-(Ce) $(\text{Ce}_2\text{FeBe}_2\text{Si}_2\text{O}_{10})$ (Segalstad and Larsen, 1978) or the Ce–Be-analogue of datolite

$[\text{Ca}_2\Box\text{B}_2\text{Si}_2\text{O}_8(\text{OH})_2$ or $\text{CaBSiO}_4(\text{OH})]$. Hingganite-(Y) has been found at Hinggan, Julin Province, China, and was named after its type locality (Ding et al., 1984), prior to the discovery of the same mineral species at Tahara, Hirukawa-mura, Gifu Prefecture, Japan (Miyawaki et al., 1987).

Many pegmatites have been found in the Naegi granite body in the Tono and Kiso regions in the southeastern part of Gifu Prefecture and the southwestern part of Nagano Prefecture, and among these, the Tahara area is famous for the druse-type pegmatite. A Ce-analogue of hingganite-(Y) from Tahara has been already described as “hingganite-(Ce)” (Miyawaki et al., 1987) without the approval of the Commission on New Minerals and Mineral Names of the International Mineralogical Association, (IMA-CNMMN). The Ce-analogue shows a chemical composition with a slight Ce excess versus Y. During

[†]Hirukawa-mura has been merged into Nakatsugawa City as a part of the administrative reform of 13 February 2005.

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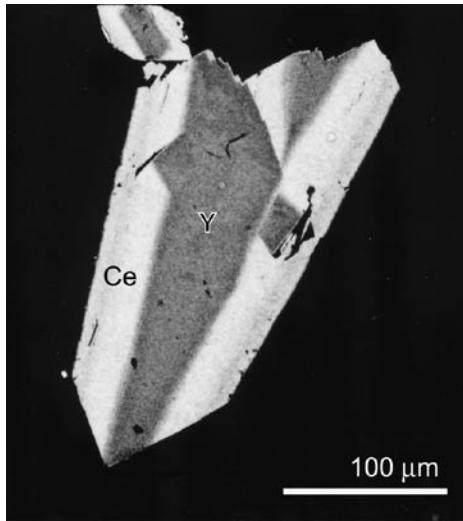


Figure 1. A back scattered electron image of a polished section of a fragment of hingganite-(Ce) and hingganite-(Y). Ce dominates the light gray parts and Y dominates the dark gray parts.

our continuing study on the rare earth silicates from Tahara, grains with a Ce content significantly in excess of Y were found in our samples. The mineral data and the name hingganite-(Ce), according to the Levinson rule, have been approved by the IMA-CNMMN, (IMA #2004-004). The type specimen is deposited at the National Science Museum, Tokyo under the registered number NSM-M28552. This report provides the formal description on hingganite-(Ce), a new mineral species approved by the IMA-CNMMN.

OCCURRENCE

Hingganite-(Ce) occurs in pegmatite in a quarry at Tahara, Hirukawa-mura, Gifu Prefecture, Japan. It occurs as the rim of euhedral prismatic crystals together with hingganite-(Y) (Fig. 1). The crystals are 1 to 5 mm in length. Associated minerals are; quartz, K-feldspar, albite, zinwaldite, cassiterite, stokesite, fluorite, chlorite, titanite, and an undetermined Ca-rich mineral related to hingganite-(Y). The surface of the prismatic crystals is often covered with needle-shaped crystals of the undetermined Ca-rich mineral belonging to the hingganite-group, showing parallel growth (Fig. 2).

PHYSICAL AND OPTICAL PROPERTIES OF HINGGANITE-(Ce)

Hingganite-(Ce) is transparent and pale tan in color with a vitreous luster. The streak is white. No fluorescence was observed under short and long wavelength UV light. The hardness is 5-6 on Mohs scale. Cleavage was not

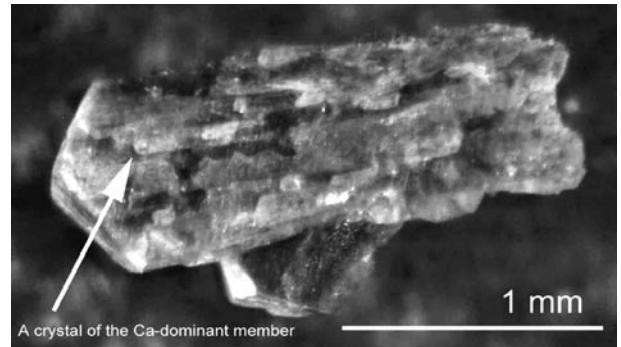


Figure 2. Photomicrograph of aggregates of hingganite-(Ce) and hingganite-(Y) covered with an undetermined Ca-dominant member of the hingganite group.

observed, and the density could not be measured due to the fine crystal size. The calculated density is 4.28 g/cm³ for the empirical formula, which is given in the subsequent section on chemical composition. Hingganite-(Ce) is optically biaxial positive with $2V = \text{large} (> 75^\circ)$. The refractive indices are $\alpha = 1.745(5)$ and $\gamma = 1.770(5)$.

CHEMICAL COMPOSITION

A quantitative analysis was carried out using a JEOL JXA-8800M WDS electron microprobe analyzer operating at 15 kV, an excitation current of 10 nA, and a beam size of 2 μm. The elements Be and H could not be determined, however, the dominant abundance of Be versus B has been confirmed by SIMS analysis of other grains of this mineral from the same locality (Miyawaki et al., 1987). The intensity ratio of ¹¹B/⁹Be in the mass spectra of ca. 1/1000 indicates that the B content in hingganite-(Ce) is negligible. The values for Be and H were calculated according to the general formula for the gadolinite-hingganite solid solution series, $\text{RE}_2(\text{Fe}_{x}\square_{1-x})\text{Be}_2\text{Si}_2\text{O}_8[\text{O}_x(\text{OH})_{1-x}]_2$, with the number of atoms of Be being set to be equal to that of Si.

The chemical composition of hingganite-(Ce) is shown in Table 1, together with those of the Y-dominant part and a single crystal of hingganite-(Y) from Tahara, which was the same crystal used in the X-ray single-crystal structure analysis. No other element with an atomic number greater than ten was detected in these analyses. The empirical formulae for hingganite-(Ce) and the two samples of hingganite-(Y) on the basis of 4 (RE + Ca + Si) cations per formula unit are, $(\text{Ce}_{0.82}\text{La}_{0.32}\text{Nd}_{0.13}\text{Pr}_{0.06}\text{Y}_{0.03}\text{Sm}_{0.01}\text{Gd}_{0.002}\text{Dy}_{0.001}\text{Ca}_{0.60})_{\Sigma 1.97}\text{Fe}_{0.24}\text{Be}_{2.02}\text{Si}_{2.02}\text{O}_{8.20}(\text{OH})_{1.52}$, $(\text{Y}_{1.22}\text{Ca}_{0.29}\text{Dy}_{0.09}\text{Yb}_{0.07}\text{Er}_{0.06}\text{Nd}_{0.02}\text{Gd}_{0.05}\text{Ce}_{0.01}\text{Sm}_{0.03}\text{Ho}_{0.01}\text{Lu}_{0.02}\text{Tm}_{0.01}\text{Tb}_{0.01})_{\Sigma 1.89}\text{Fe}_{0.12}\text{Be}_{2.09}\text{Si}_{2.09}\text{O}_{8.22}(\text{OH})_{1.77}$, and $(\text{Y}_{1.21}\text{Ca}_{0.28}\text{Nd}_{0.06}\text{Gd}_{0.06}\text{Dy}_{0.06}\text{Yb}_{0.05}\text{Er}_{0.04}\text{Ce}_{0.04}\text{Sm}_{0.03}\text{Ho}_{0.03}\text{Lu}_{0.02}\text{Pr}_{0.01}\text{Tm}_{0.01}\text{Tb}_{0.01}\text{La}_{0.01})_{\Sigma 1.92}\text{Fe}_{0.23}\text{Be}_{2.07}\text{Si}_{2.07}\text{O}_{8.19}(\text{OH})_{1.55}$,

Table 1. Chemical composition of hingganite-(Ce) and hingganite-(Y) from Tahara

Constituent	Hingganite-(Ce) ^a		Hingganite-(Y) ^a		Hingganite-(Y) ^b		Standard material
	Contents, wt% [†]	No. of atoms	Contents, wt% [†]	No. of atoms	Contents, wt% [†]	No. of atoms	
La ₂ O ₃	11.11(125)	0.32	trace	—	0.28(14)	0.01	LaP ₅ O ₁₄
Ce ₂ O ₃	28.32(74)	0.82	0.51(11)	0.01	1.58(95)	0.04	CeP ₅ O ₁₄
Pr ₂ O ₃	2.11(31)	0.06	trace	—	0.50(27)	0.01	PrP ₅ O ₁₄
Nd ₂ O ₃	4.70(39)	0.13	0.93(20)	0.02	2.48(106)	0.06	NdP ₅ O ₁₄
Sm ₂ O ₃	0.39(9)	0.01	1.21(14)	0.03	1.26(39)	0.03	SmP ₅ O ₁₄
Gd ₂ O ₃	0.08(7)	0.001	2.02(20)	0.05	2.56(51)	0.06	GdP ₅ O ₁₄
Tb ₂ O ₃	trace	—	0.57(8)	0.01	0.36(21)	0.01	TbP ₅ O ₁₄
Dy ₂ O ₃	0.05(6)	0.002	3.88(25)	0.09	2.51(43)	0.06	DyP ₅ O ₁₄
Ho ₂ O ₃	trace	—	0.25(24)	0.01	1.30(25)	0.03	HoP ₅ O ₁₄
Er ₂ O ₃	trace	—	2.83(22)	0.06	1.85(22)	0.04	ErP ₅ O ₁₄
Tm ₂ O ₃	trace	—	0.49(5)	0.01	0.41(11)	0.01	TmP ₅ O ₁₄
Yb ₂ O ₃	trace	—	3.28(22)	0.07	2.20(28)	0.05	YbP ₅ O ₁₄
Lu ₂ O ₃	trace	—	0.86(6)	0.02	0.95(13)	0.02	LuP ₅ O ₁₄
Y ₂ O ₃	0.72(31)	0.03	31.38(118)	1.22	31.11(238)	1.21	YP ₅ O ₁₄
CaO	7.07(48)	0.60	3.75(57)	0.29	3.57(73)	0.28	wollastonite
FeO	3.61(23)	0.24	1.92(89)	0.12	3.70(50)	0.23	Fe ₂ SiO ₄
SiO ₂	25.47(48)	2.02	28.72(55)	2.09	28.27(88)	2.07	wollastonite
BeO*	10.60(20)	2.02	11.96(23)	2.09	11.77(37)	2.07	
H ₂ O*	2.88(3)	1.52	3.63(28)	1.77	3.17(13)	1.55	
Total	97.10		98.17		99.83		

^a The core and rim of the same grain (see Fig. 2).^b The other grain used for the single crystal work.[†] The standard deviation is shown in the parentheses.^{*} Calculated value.

respectively. The simplified formula of hingganite-(Ce) is (Ce,Ca)₂(□,Fe)Be₂Si₂O₈[(OH)₂O]₂, and the ideal formula is Ce₂□Be₂Si₂O₈(OH)₂ or CeBeSiO₄(OH), which requires Ce₂O₃ 63.56, SiO₂ 23.27, BeO 9.69, and H₂O 3.49 wt%.

CRYSTALLOGRAPHY OF HINGGANITE-(Ce)

Powder X-ray diffraction data were obtained using a Gandolfi camera with a diameter = 114.6 mm employing Ni-filtered CuK α radiation. The sample of hingganite-(Ce) was scraped from the surface of the Ce-dominant part in the thin section used for the chemical analysis, using a stainless-steel sewing needle under a binocular microscope. The powder X-ray diffraction data of hingganite-(Y), which was used for the subsequent single-crystal work, was also obtained using the Gandolfi camera for comparison. The sample was adhered to the edge of a 10 μ m diameter glass fiber using epoxy resin. Two sets of measurements were carried out for each sample. The first run was carried out without a standard material, and the second run of the sample was carried out with the NBS 640b Si-standard reference material on the surface of the sample. The data were recorded on an imaging

plate (IP) and processed using a Fuji BAS-2500 bio-imaging analyzer and a PC software program written by Nakamura (1999).

The β angle in the monoclinic system was very close to 90°, which made it difficult to index the reflections of the powder X-ray diffraction data. Single-crystal work could not be carried out for hingganite-(Ce) because of the small dimensions of the crystals. The lattice parameters were determined using the Rietveld method (RIETAN-2000; Izumi and Ikeda, 2000) employing the IP-Gandolfi data of hingganite-(Ce) and the Si-internal standard. The least-square calculation of atomic positional and isotropic displacement parameters of hingganite-(Ce) did not give a feasible interatomic geometry. It may be caused by the low quality of the XRD data using Ni-filtered CuK α radiation from an X-ray tube. Therefore, the lattice parameters of hingganite-(Ce) and the isotropic displacement parameter of Si of standard were refined together with the fundamental parameters for diffraction profile, scale factors, background and zero-point shift in our calculation. The atomic positional and isotropic displacement parameters of hingganite-(Ce) were fixed to those of hingganite-(Y), which were ob-

Table 2. Powder X-ray diffraction data obtained using a Gandolfi camera and an imaging plate^a

<i>h</i>	<i>k</i>	<i>l</i>	Hingganite-(Ce) ^a			Hingganite-(Y) ^b			<i>h</i>	<i>k</i>	<i>l</i>	Hingganite-(Ce) ^a			Hingganite-(Y) ^b		
			<i>I</i>	<i>d</i> _{obs.}	<i>d</i> _{calc.} [†]	<i>I</i>	<i>d</i> _{obs.}	<i>d</i> _{calc.} [‡]				<i>I</i>	<i>d</i> _{obs.}	<i>d</i> _{calc.} [†]	<i>I</i>	<i>d</i> _{obs.}	<i>d</i> _{calc.} [‡]
1	1	0	42	6.06	6.04	33	6.01	6.03	1	3	2	6	1.705	{1.708 1.707}	9	1.706	{1.705 1.706}
2	0	0	15	4.96	4.95	11	4.93	4.94	4	0	2						
0	0	1	24	4.75	4.75	30	4.74	4.74	4	1	2	13	1.678	1.678	13	1.674	1.674
2	1	0	15	4.15	4.15	11	4.14	4.14	2	4	1						
1	1	1	37	3.74	{3.74 3.73}	32	3.73	{3.73 3.72}	4	1	2						
1	1	1							2	4	1	21	1.663	{1.668 1.666 1.665}	23	1.662	{1.664 1.661}
1	2	0	28	3.56	3.56	22	3.55	3.55	4	3	1						
2	0	1	34	3.44	{3.44 3.41}	35	3.43	{3.43 3.41}	4	3	1						
2	0	1							5	2	1						
2	1	1	86 ^{**}	3.13	{3.14 3.12}	100 ^{**}	3.12	{3.13 3.11}	6	0	0	23 ^{**}	1.644	{1.650 1.644}	16	1.647	{1.648 1.647}
2	1	1							5	2	1						
3	1	0	23	3.03	{3.03 3.02}	19	3.02	{3.02 3.01}	2	3	2						
2	2	0							2	3	2						
0	2	1	26	2.98	2.97	28	2.97	2.97	0	0	3	5	1.583	1.583	5	1.580	1.581
1	2	1	100	2.85	{2.85 2.84}	84	2.84	{2.85 2.84}	6	0	1	9	1.558	{1.562 1.555}	16	1.555	{1.559 1.553}
1	2	1							6	0	1						
3	1	1							3	3	2	4	1.534	1.533			
2	2	1	46	2.56	{2.55 2.55}	70	2.55	{2.55 2.54}	6	2	0	6	1.512	{1.514 1.511}	12	1.509	{1.508 1.507}
3	1	1							2	0	3	6	1.512	{1.510}			
4	0	0	11	2.48	{2.47 2.46}	10	2.47	{2.47 2.46}	4	4	0	2	1.479	1.476	5	1.480	1.474
1	3	0							2	1	3	4	1.479	1.476			
0	0	2	10	2.38	2.38	9	2.37	2.37	1	2	3				15	1.443	{1.445 1.443}
4	1	0	14	2.36	2.35	15	2.35	2.35	1	2	3						
2	3	0	23	2.26	2.26	15	2.26	2.26	4	4	1						
0	3	1	12	2.24	2.24	7	2.24	2.24	1	5	1				6	1.434	{1.434 1.433}
3	2	1				31	2.20	2.21	1	5	1						
1	1	2	33	2.21	{2.21 2.20}	11	2.19	{2.20 2.20}	2	4	2				4	1.421	{1.423 1.420}
3	2	1							2	4	2						
4	0	1							5	2	2				3	1.413	1.414
2	0	2	8	2.14	2.14	7	2.13	2.13	5	2	2	7	1.408	{1.408 1.407}			
4	1	1	9	2.10	{2.11 2.10}	10	2.10	{2.11 2.10}	3	1	3				5	1.404	{1.404 1.398}
4	1	1							3	1	3	5	1.397	1.399	7	1.397	1.398
2	3	1	18	2.04	{2.04 2.04}	13	2.04	{2.04 2.04}	3	5	1	10	1.329	{1.330 1.328}	10	1.325	{1.327 1.325}
2	3	1							3	5	1						
3	3	0	10	2.02	2.01	3	2.01	2.01	7	2	1						
1	2	2	30	1.976	{1.978 1.973}	35	1.972	{1.974 1.970}	7	2	1	5	1.273	{1.275 1.271}	7	1.274	{1.273 1.268}
1	2	2							0	6	0						
5	1	0							6	4	0	6 ^{**}	1.247	1.248	3 ^{**}	1.245	1.245
0	4	0	11 ^{**}	1.908	1.907	4	1.901	1.902	8	1	0						
3	1	2	20	1.875	{1.875 1.873}	23	1.871	{1.871 1.868}	1	6	1	6	1.219	{1.219 1.218}	5	1.216	{1.216 1.216}
1	4	0							0	4	3						
3	1	2	18	1.864	1.863	20	1.860	1.861	3	5	2	7	1.195	{1.198 1.195}	9	1.195	{1.195 1.192}
0	4	1	28	1.771	1.770	15	1.768	1.766	3	5	2						
5	2	0	14	1.756	1.757	16	1.754	1.754									

^aThe rim of the sample is shown in Figure 2.^bThe other grain used for the single crystal work.[†]Based on the Rietveld data of hingganite-(Ce): $a = 9.8973(11)$, $b = 7.6282(8)$, $c = 4.7505(6)$ Å, $\beta = 90.416(8)^\circ$, $V = 358.64(7)$ Å³.[‡]Based on the single crystal data of hingganite-(Y): $a = 9.8830(16)$, $b = 7.6091(9)$, $c = 4.7423(9)$ Å, $\beta = 90.342(14)^\circ$, $V = 356.62(10)$ Å³.^{*}The data were calibrated using an internal Si standard reference material (NSB 640b).^{**}Estimated from data using the external standard reference material due to overlap with the diffraction of Si standard.

tained from the single-crystal structure analysis as described below. A virtual chemical species was applied to the rare earth site (the *A* site) as 0.7Ce + 0.3Ca, in accordance with the chemical composition of hingganite-(Ce). The occupancy parameter of the Fe site was fixed at 0.2. The final reliability factors and goodness-of-fit indicator were as follows: $R_{wp} = 0.0246$, $R_p = 0.0180$, $R_R = 0.2570$,

$R_e = 0.0197$, and $S = 1.2499$. The diffraction data and refined lattice parameters of hingganite-(Ce) are listed in Table 2. The data of hingganite-(Y) from Tahara, which was used for subsequent single crystal structure analysis, with the lattice parameters and calculated *d*-spacing values based on the data from the four-circle diffractometer, are shown for comparison.

Table 3. Crystallographic data of hingganite-(Y) and experimental details

<i>a</i> (Å)	9.8830(16)
<i>b</i> (Å)	7.6091(9)
<i>c</i> (Å)	4.7423(9)
β (°)	90.342(14)
<i>V</i> (Å ³)	356.62(10)
Space group	<i>P</i> 2 ₁ / <i>a</i>
<i>Z</i>	2
Formula	Y _{1.3} Dy _{0.4} Ca _{0.3} Fe _{0.24} Si ₂ Be ₂ O _{9.6} (OH) _{0.4}
<i>D</i> _{calc} (g/cm ³)	4.06
μ (cm ⁻¹)	15.5
Crystal dimension (mm)	0.10 × 0.07 × 0.05
Diffractometer	Rigaku AFC-7R
Radiation	MoK α (graphite-monochromatized)
Scan mode, rate (°/min in ω)	2θ- ω , 4
2θ range (deg.)	5–65
Reflection range	-14 ≤ <i>h</i> ≤ 14 0 ≤ <i>k</i> ≤ 11 -7 ≤ <i>l</i> ≤ 3
No. of measured reflections	1541
No. unique reflections	1299
No. of observed reflections [<i>I</i> > 2σ(<i>I</i>)]	1129
<i>R</i> _{int}	0.0330
No. of variable parameters	80
<i>R</i> 1 [<i>I</i> > 2σ(<i>I</i>)], <i>R</i> 1(all reflections)	0.0329, 0.0448
w <i>R</i> 2 (all reflections)	0.1418
Weighting parameters, <i>a</i> , <i>b</i>	0.1, 0
Goodness of fit	1.151
Final Δ <i>ρ</i> _{min} (e/Å ³)	-2.126
Final Δ <i>ρ</i> _{max} (e/Å ³)	1.509

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{0.5}$$

$$w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$$

$$P = [2F_c^2 + F_o^2] / 3$$

A REFINEMENT OF THE CRYSTAL STRUCTURE OF HINGGANITE-(Y)

The crystal structure of hingganite-(Y) was refined using a single crystal from Tahara, Gifu Prefecture, Japan, to confirm the previous analysis of hingganite-(Y)[‡] (Yakubovich et al., 1983) before application of the atomic parameters of hingganite-(Y) in the Rietveld calculations of the lattice parameters of hingganite-(Ce). The intensity data of the single crystal of hingganite-(Y) with dimensions of 0.10 × 0.07 × 0.05 mm³ were collected with a Rigaku RASA-7R four-circle diffractometer using graphite monochromatized MoK α radiation (50 kV, 200 mA). Experimental details pertaining to the collection of the single crystal diffraction intensity data are given in Table 3; along with the lattice parameters determined by a least-squares refinement of the 2θ values of 25 strong reflections. The data reductions to F_o^2 with corrections for

Lorentz, polarization, and absorption (ψ -scan procedure) were carried out using software written by Dr. Kazumasa Sugiyama of the University of Tokyo (personal communication). The refinement was started with the atomic positional parameters of gadolinite-(Y) (Miyawaki et al., 1984) as the initial parameters referring to those of hingganite-(Y) (Yakubovich et al., 1983). The SHELXL-97 software package (Sheldrick, 1997) was employed for the refinement of the crystal structure. Scattering factors for the neutral atoms and anomalous dispersion factors were taken from the International Tables for Crystallography, Volume C (1992). Full-matrix least-squares refinement was performed by refining the positional parameters, scale factor, and displacement parameters.

The occupancy of the rare earth site was fixed as 0.65Y + 0.20Dy + 0.15Ca, according to the result of our chemical analysis. The occupancy parameter of the octahedral Fe site with a vacancy was refined. The refinements using the anisotropic displacement parameters for all of the crystallographic sites converged with *R*1 = 0.0329 [*I* > 2σ(*I*)]. The final refinement data are summarized in Table 3. The final positional parameters, equiva-

[‡] Although Yakubovich et al. (1983) described their specimen as hingganite-(Yb), the predominant rare earth element is yttrium in this sample, and therefore, it should be described as hingganite-(Y).

Table 4. Final atomic coordinates and displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
Y*	0.33238(4)	0.10918(5)	0.00084(8)	0.00755(18)	0.0073(2)	0.0080(2)	0.0073(2)	0.00140(11)	-0.00025(15)	-0.00077(11)
Si	0.08004(13)	0.27531(18)	0.5193(3)	0.0054(3)	0.0047(5)	0.0062(5)	0.0053(5)	-0.0001(4)	0.0003(4)	-0.0008(4)
Be	0.3368(6)	0.4148(8)	0.4443(14)	0.0049(9)	0.006(2)	0.005(2)	0.004(2)	0.0034(19)	-0.0014(17)	-0.0004(18)
Fe*	0	0	0	0.0061(13)	0.0062(19)	0.0056(18)	0.0065(19)	0.0045(13)	0.0010(12)	0.0006(13)
O1	0.0324(4)	0.4113(5)	0.7605(9)	0.0099(7)	0.0122(16)	0.0102(15)	0.0074(16)	-0.0023(12)	-0.0008(12)	0.0010(12)
O2	0.4517(4)	0.2866(5)	0.3281(8)	0.0098(6)	0.0079(14)	0.0132(16)	0.0082(14)	-0.0008(12)	-0.0025(11)	0.0021(13)
O3	0.1973(4)	0.3457(6)	0.3053(8)	0.0104(6)	0.0058(15)	0.0146(16)	0.0109(16)	0.0034(13)	0.0011(11)	0.0001(12)
O4	0.1473(4)	0.1068(5)	0.6864(9)	0.0107(7)	0.0120(18)	0.0100(16)	0.0102(17)	0.0000(11)	-0.0015(13)	0.0020(12)
O5	0.3318(4)	0.4115(6)	0.7845(9)	0.0115(7)	0.0107(16)	0.0168(17)	0.0072(15)	-0.0010(13)	0.0004(13)	-0.0023(14)

* Occupancy: Y: 0.65Y + 0.20Dy + 0.15Ca; Fe: 0.242(8)Fe

Table 5. Interatomic distances (\AA)

Y — O1	2.293(4)	Si — O1	1.614(4)
— O1	2.306(4)	— O2	1.625(4)
— O4	2.353(4)	— O3	1.635(4)
— O2	2.366(4)	— O4	1.645(4)
— O5	2.440(4)	<Si—O>	1.630
— O3	2.492(4)		
— O5	2.519(4)		
— O3	2.670(4)	Be — O4	1.595(7)
<Y—O>	2.430	— O2	1.598(7)
		— O3	1.613(7)
Fe — O5	2.059(4) x2	— O5	1.614(8)
— O4	2.240(4) x2	<Be—O>	1.605
— O2	2.301(4) x2		
<Fe—O>	2.200		

lent isotropic displacement parameters and anisotropic displacement parameters, are given in Table 4. The selected interatomic distances are summarized in Table 5. The F_o - F_c table (Table 6) was deposited at the editorial office, and is available on the website indicated at the end of this paper.

DISCUSSION

The replacement of Ce by Ca in hingganite-(Ce) suggests a solid solution towards calciogadolinite, $\text{YCaFe}^{3+}\text{Be}_2\text{Si}_2\text{O}_{10}$, or datolite, $\text{CaBSiO}_4(\text{OH})$. The brownish tint in color suggests that a part of the Fe in hingganite-(Ce) may be trivalent. In addition, the concentration of boron in hingganite-(Ce) is negligible. These observations indicate a solid solution towards calciogadolinite rather than datolite. The solid solution towards calciogadolinite for gadolinite mentioned by Ito and Hafner (1974) was confirmed for hingganite-(Ce). The low totals of the analysis of hingganite-(Ce) (Table 1) may derive from the estimation of oxidation state of Fe as being divalent and the lack of determination of the trace amounts of lanthanides, such as Tb, Ho, Tm, Yb, and Lu.

Hingganite-(Ce) is much richer in Ce, and is poorer in Y than hingganite-(Y) (Table 1). Figure 3 shows the chondrite-normalized lanthanide distribution patterns of hingganite-(Ce) and hingganite-(Y) from Tahara. The

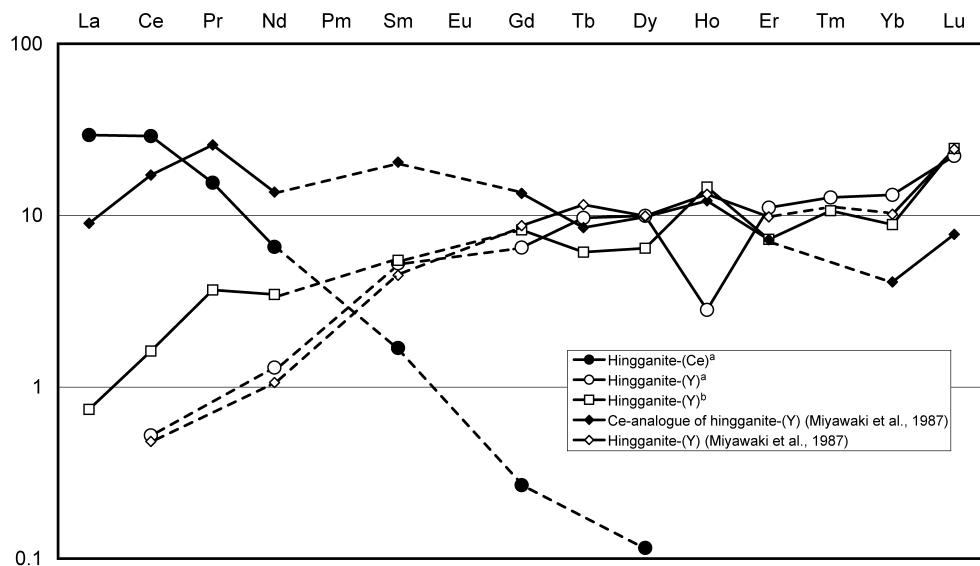


Figure 3. Chondrite-normalized lanthanide distribution patterns of hingganite-(Ce) and hingganite-(Y) from Tahara. The sample names, hingganite-(Ce), hingganite-(Y)^a, and hingganite-(Y)^b correspond with those given in Table 1.

lanthanide distribution pattern of hingganite-(Ce) is distinct from those of hingganite-(Y). The downward-sloping indicates abundances in the Ce-group rare earth elements with larger ionic radii in the pattern of hingganite-(Ce) (Fig. 3). It is worth noting that two different patterns, downward-sloping for hingganite-(Ce) and upward-sloping for hingganite-(Y), are observed within the same grain. The sharp boundary between hingganite-(Ce) and hingganite-(Y) (Fig. 1) indicates a marked change rather than a gradual fluctuation in the chemical composition of the source hydrothermal fluid in the druse of pegmatite.

The lanthanide distribution pattern of hingganite-(Y) associated with hingganite-(Ce) within the same grain shows a negative anomaly as a spike at Ho, whereas such an anomaly was not observed for other crystals of hingganite-(Y) and the Ce-analogue of hingganite-(Y) described by Miyawaki et al. (1987) (Fig. 3). Among the lanthanides, the ionic radius of Ho is the closest to that of Y, and Ho is usually concentrated in Y-dominant minerals. Consequently, a positive anomaly for Ho is sometimes observed in the lanthanide distribution pattern of Y-dominant minerals, e.g., gadolinite-(Y) (Miyawaki et al., 1984). The negative anomaly for Ho in the lanthanide distribution pattern of hingganite-(Y) is a specific feature of the specimen.

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Depository item (Table 6) is linked to the online version of the paper at <http://www.jstage.jst.go.jp/browse/jmps>

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