Hizenite-(Y), $\text{Ca}_2\text{Y}_6(\text{CO}_3)_{11} \cdot 14\text{H}_2\text{O}$, a new mineral in alkali olivine basalt from Mitsukoshi, Karatsu, Saga Prefecture, Japan

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Hizenite-(Y), ideal formula $\text{Ca}_2\text{Y}_6(\text{CO}_3)_{11} \cdot 14\text{H}_2\text{O}$, occurs in druse of alkali olivine basalt at Mitsukoshi, Karatsu, Saga Prefecture, Japan. It occurs as a platy crystal and forms spherical aggregates. Hizenite-(Y) closely associates with lokkaite-(Y), tenerite-(Y), and kimuraite-(Y). It is orthorhombic, $a = 6.295(1) \text{ \AA}$, $b = 9.089(2) \text{ \AA}$, $c = 63.49(1) \text{ \AA}$, $V = 3632(1) \text{ \AA}^3$, $Z = 4$. Hizenite-(Y) is white in color with vitreous to silky luster. The density is 2.98 g/cm^3 (calc), and there is a perfect cleavage on $\{001\}$. The strongest lines in the X-ray powder diffraction pattern are [d (I/I_0) hkl] 10.63 (100) 006, 6.384 (77) 0·0·10, 3.962 (51) 0·0·16, 3.821 (27) 029, 1·0·13, 2.060 (23) 306, 0·4·13, 15.57 (20) 004.

Keywords: Hizenite-(Y), Mitsukoshi, Higashimatsuura basalt, New mineral

INTRODUCTION

During a mineralogical investigation of rare earth (RE) minerals in the alkali olivine basalt, Mitsukoshi, Karatsu, Saga Prefecture, Japan, a white druse mineral was identified in the alkali olivine basalt. The occurrence of the mineral is similar to that of tenerite-(Y) and lokkaite-(Y), but the X-ray powder diffraction pattern and chemical composition showed it to be a new hydrous Ca-Y carbonate. The lattice parameters and chemical composition of the mineral showed that it is a member of tenerite family.

The name ‘Hizen’ is for the classic country name of the locality of the mineral. It had existed in northwest Kyushu (Saga and Nagasaki Prefecture) since the 7th century to the 16th century, and now, it remains as the name of town in Karatsu city. The mineral and mineral name have been approved by the International Mineralogical Association, Commission on New Minerals, Nomenclature and Classification (No. 2011-30). The type specimen is deposited in Kitakyushu Museum of Natural History and Human History, Kitakyushu, Japan, under the registered number KMNHM000001.

OCCURRENCE

Hizenite-(Y) occurs in a small druse in the alkali olivine basalt at Mitsukoshi, Karatsu, Saga Prefecture, Japan, called the Higashimatsuura basalt. This locality is the type locality of kozoite-(La) (Miyawaki et al., 2003). The Higashimatsuura basalt is a Neogene alkali olivine basalt and consists of five stages, based on volcanic activities (Ishibashi, 1971). The most recent stage has yielded three new minerals: kimuraite-(Y) (Nagashima et al., 1986),

Figure 1. Micrograph of hizenite-(Y) showing its occurrence mode.

kozoite-(Nd) (Miyawaki et al., 2000) and kozoite-(La).

Hizenite-(Y) occurs in a small platy crystal (25–50 μm in size, 0.04–0.2 μm in thickness), forming radial aggregates up to 1 cm in druse (Figs. 1 and 2). Hizenite-(Y) usually closely associates with lokkaite-(Y), tenerite-(Y) and kimuraite-(Y).

Figure 2. Secondary electron image of hizenite-(Y).

OPTICAL AND PHYSICAL PROPERTIES

Hizenite-(Y) is white in color and translucent to transparent. It has vitreous to silky luster on the cleavage plane which is perfect on {001}. The streak is white. The calculated density is 2.98 g/cm^3 . Because of the small size of the mineral, the other optical and physical properties could not be measured.

CHEMICAL COMPOSITION

Quantitative chemical analysis was carried out using a scanning electron microscope with energy dispersive X-ray spectroscopy (SEM-EDS; JEOL JSM-5800LV, Oxford ISIS, 20kV and 0.5 nA). The content of H_2O and CO_2 were analyzed by a CHN analyzer (Perkin Elmer 2400 II) in Kitakyushu Museum of Natural history and Human history. The analysis was carried out in five points and the results of analysis are given in Table 1. The empirical formula, on the basis of 47 O structural atoms, is $\text{Ca}_{1.76}(\text{Y}_{4.08}\text{Nd}_{0.58}\text{Gd}_{0.35}\text{Dy}_{0.28}\text{Sm}_{0.16}\text{Er}_{0.14}\text{La}_{0.11}\text{Pr}_{0.07}\text{Eu}_{0.07}\text{Ho}_{0.04}\text{Tb}_{0.02}\text{Yb}_{0.01}\text{Tm}_{0.00})_{\Sigma 5.91}(\text{CO}_3)_{11.2} \cdot 13.9\text{H}_2\text{O}$, and the simplified and ideal formulae are $\text{Ca}_2(\text{Y}, \text{Nd}, \text{Gd}, \text{Dy})_6(\text{CO}_3)_{11} \cdot 14\text{H}_2\text{O}$ and $\text{Ca}_2\text{Y}_6(\text{CO}_3)_{11} \cdot 14\text{H}_2\text{O}$, respectively.

Table 1. Chemical composition of hizenite-(Y)

n = 5	wt%	Range	No. atoms(O=47)
Y_2O_3	27.61	26.20 - 29.60	4.08
La_2O_3	1.11	0.95 - 1.41	0.11
Pr_2O_3	0.65	0.00 - 0.89	0.07
Nd_2O_3	5.80	4.69 - 6.72	0.58
Sm_2O_3	1.68	1.04 - 1.97	0.16
Eu_2O_3	0.73	0.00 - 1.56	0.07
Gd_2O_3	3.82	2.85 - 4.70	0.35
Tb_2O_3	0.24	0.00 - 0.79	0.02
Dy_2O_3	3.10	2.75 - 3.54	0.28
Ho_2O_3	0.47	0.00 - 0.93	0.04
Er_2O_3	1.58	1.02 - 1.83	0.14
Tm_2O_3	0.04	0.00 - 0.22	0.00
Yb_2O_3	0.10	0.00 - 0.51	0.01
CaO	5.93	5.28 - 6.42	1.76
CO_2	29.55	28.78 - 30.32	11.21
H_2O	15.03	14.85 - 15.21	27.88
Total	97.44		

CRYSTALLOGRAPHY

Single-crystal X-ray diffraction studies could not be carried out because of the small crystal-size. Unit cell parameters were determined from electron diffraction pattern observed by a transmission electron microscope (TEM). X-ray powder diffraction pattern was indexed using these cell parameters, and refined it.

TEM analysis data were obtained using a JEOL 200CX microscope (Kyushu University HVEM Laboratory). The electron diffraction pattern observed from normal to the cleavage plane showed periodicities of 6.3 Å (100) and 9.1 Å (010) (Fig. 3). Furthermore, the electron diffraction pattern observed from parallel to the cleavage plane showed a periodicity of 63.7 Å (001). The specimen was prepared using a focused ion beam (FIB) in Kyushu University HVEM Laboratory. The simulated diffraction pattern conforms closely to the observation data (Fig. 4). The simulated model was assumed that alternated layer structure consists of kimuraite-(Y) and lokkaite-(Y) on one to one relation along the *c* axis (Fig. 5). The single crystal structure analyses of kimuraite-(Y) and lokkaite-(Y) have not been made, but those models are estimated from the chemical composition and cell parameters (Miyawaki and Nakai, 1987). Kimuraite-(Y) consists of an Y-corrugated sheet and a Ca-H₂O layer on one to one relation along the *c* axis, and lokkaite-(Y) consists of two to one relation. On the simulated model of hizenite-(Y), the Ca-H₂O layer was simplified because there are no detailed models on kimuraite-(Y) and lokkaite-(Y), and the Y-corrugated sheet was referred the crystal structure of tenerite-(Y) (Miyawaki and Matsubara, 2004).

Powder X-ray diffraction data (Table 2) were ob-

tained using a diffractometer (BRUKER AXS M18X-HF22-SRA, MXP18) with $\text{CuK}\alpha$ radiation generated at 40 kV and 100 mA, and monochromated with graphite. The reflections of hizenite-(Y) could be indexed with an orthorhombic cell, but the space group could not be determined. A preferred orientation effect due to the perfect $\{001\}$ cleavage is present. The unit cell parameters refined from the powder data: $a = 6.295(1)$, $b = 9.089(2)$, $c = 63.49(1)$ Å, $V = 3632(1)$ Å³ and $Z = 4$.

RELATIONSHIP TO OTHER MINERALS

Hizenite-(Y) is the member of tenerite family [tenerite-(Y) (Miyawaki and Matsubara, 2004), kimuraite-(Y) and lokkaite-(Y) (Nagashima et al., 1986)]. The relationships of the lattice parameters, chemical formula and other data of those minerals are shown in Table 3. The dimensions of the a and b axes of hizenite-(Y) are similar to those of tenerite family minerals. Hizenite-(Y) has an alternated structure of kimuraite-(Y) and lokkaite-(Y) on one to one relation along the c axis (Fig. 5). This structure model was supported by the chemical formula of hizenite-(Y) which just between kimuraite-(Y) and lokkaite-(Y).

Figure 3. TEM image and electron diffraction pattern of hizenite-(Y) observed from normal to the cleavage plane $\{001\}$. (a) Bright field image. (b) Electron diffraction pattern observed from the c axis. (c) Enlarged pattern of (b) with indications of index.

Figure 4. TEM image and electron diffraction pattern of hizenite-(Y) observed from parallel to the cleavage plane $\{001\}$. (a) Bright field image. (b) Electron diffraction pattern observed from the a axis. (c) Enlarged pattern of (b) with indications of index. (d) Simulated diffraction pattern.

Table 2. X-ray powder diffraction data for hizenite-(Y)

<i>h k l</i>	<i>d</i> _{obs} Å	<i>d</i> _{calc} Å	<i>I</i> / <i>I</i> ₀	<i>h k l</i>	<i>d</i> _{obs} Å	<i>d</i> _{calc} Å	<i>I</i> / <i>I</i> ₀
	19.62		4*	3 1 12	1.908	1.908	6
0 0 4	15.57	15.86	20	3 2 3		1.898	
0 0 6	10.63	10.58	100	3 1 13		1.886	
	7.653		5**	1 2 29	1.882	1.882	7
0 0 10	6.384	6.346	77	0 1 33		1.881	
	5.873		4	0 4 19		1.879	
	4.630		5	1 3 25		1.859	
0 0 16	3.962	3.966	51	0 3 27	1.857	1.857	1
0 2 9	3.821	3.820	27	2 3 18		1.856	
1 0 13		3.858		0 4 20		1.848	
1 2 3	3.632	3.631	2	2 1 27	1.845	1.844	1
1 2 7	3.411	3.414	1	2 4 0		1.843	
	3.230		4*	0 5 0		1.818	
	3.010		2*	0 2 32	1.818	1.818	2
1 0 19		2.951		0 4 21		1.816	
2 1 3	2.946	2.946	9	2 4 6		1.815	
1 2 13		2.941		2 4 7		1.806	
1 3 0		2.730		1 4 19	1.801	1.801	0
1 0 21	2.724	2.724	1	0 0 36	1.764	1.763	3
2 1 10		2.694		1 2 32		1.747	
0 2 19	2.692	2.692	1	3 1 19		1.744	
1 3 4		2.691		1 0 35		1.743	
0 2 20	2.600	2.602	3	2 3 22	1.741	1.741	3
2 2 4		2.554		1 5 3		1.741	
1 2 18	2.549	2.548	3	2 2 27		1.740	
1 3 9		2.546		2 0 32	1.679	1.678	2
0 1 25		2.445		1 1 37		1.628	
0 0 26	2.445	2.441	16	2 3 26	1.629	1.627	2
0 2 22		2.436		1 2 35		1.627	
1 1 23		2.435		3 3 13		1.627	
	2.422		3*	0 4 29		1.576	
1 3 18	2.157	2.159	7	1 0 39		1.576	
2 3 8	2.103	2.105	1	2 5 0		1.574	
0 4 13	2.060	2.060	23	4 0 0	1.573	1.574	3
3 0 6		2.059		4 0 1		1.574	
3 0 8		2.029		2 4 21		1.573	
3 1 4	2.027	2.028	2	4 0 3		1.570	
1 4 10		2.026		4 0 4		1.566	
3 1 7	1.995	1.995	1	3 4 8	1.511	1.514	3
3 0 10		1.993		1 3 35		1.511	
0 0 32		1.983		0 4 32		1.494	
1 2 27	1.980	1.982	4	2 4 25	1.489	1.491	2
3 1 8		1.980		1 2 39		1.489	
2 0 25		1.976		4 2 0		1.487	

* Lokaite-(Y). ** Tengerite-(Y).

Table 3. Comparative data for tenerite family minerals

	Tengerite *	Lokkaite **	Kimuraite **	Hizenite this study
Chemical formula	$\text{Y}_2(\text{CO}_3)_3 \cdot 2\text{-}3\text{H}_2\text{O}$	$\text{CaY}_4(\text{CO}_3)_7 \cdot 9\text{H}_2\text{O}$	$\text{CaY}_2(\text{CO}_3)_4 \cdot 6\text{H}_2\text{O}$	$\text{Ca}_2\text{Y}_6(\text{CO}_3)_{11} \cdot 14\text{H}_2\text{O}$
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
<i>a</i>	6.0815	6.104	6.0433	6.295
<i>b</i>	9.1596	9.26	9.2545	9.089
<i>c</i>	15.0956	39.35	23.976	63.49
<i>Z</i>	4	4	4	4
<i>V</i>	840.89	2224.18	1340.9	3632
Density (obs)	3.12	2.92	2.6	
Density (calc)	3.11	2.92	2.98	2.98

* Miyawaki and Matsubara., 2004. ** Nagashima et al., 1986.

Figure 5. Schematic illustrations of the layer structure models of hizenite-(Y) and tenerite family minerals. These models of tenerite-(Y), kimuraite-(Y) and lokkaite-(Y) are modified from Miyawaki and Nakai (1987).

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