

## Sb-bearing Dugganite from the Kawazu mine, Shizuoka Prefecture, Japan

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**Abstract** Sb-bearing dugganite occurs as minute crystals in cavities of quartz vein from the Kawazu mine, Shizuoka Prefecture, Japan. It is trigonal with lattice parameters,  $a=8.490$ ,  $c=5.216$  Å, and  $V=325.6$  Å<sup>3</sup>. An electron microprobe analysis gave the empirical formula as  $\text{Pb}_{2.96}(\text{Zn}_{2.83}\text{Cu}_{0.19})_{\Sigma 3.02}(\text{Te}_{0.72}\text{Sb}_{0.30})_{\Sigma 1.02}(\text{As}_{1.51}\text{Si}_{0.23}\text{P}_{0.15}\text{Sb}_{0.11})_{\Sigma 2.00}\text{O}_{13.00}[\text{O}_{0.54}(\text{OH})_{0.46}]_{\Sigma 1.00}$  on the basis of  $\text{Pb}+\text{Zn}+\text{Cu}+\text{Te}+\text{Sb}+\text{As}+\text{Si}+\text{P}=9$  and the calculated (OH) with a charge balance. The crystal occurs as pale aquamarine blue hexagonal prisms up to 0.2 mm long. The mineral has approximately 30% joëlbruggerite mole of the solid solution between dugganite and joëlbruggerite.

**Key words** : dugganite, joëlbruggerite, Kawazu mine

### Introduction

Dugganite,  $\text{Pb}_3\text{Zn}_3(\text{TeO}_6)_x(\text{AsO}_4)_{2-x}(\text{OH})_{6-3x}$ , was first described by Williams (1978) from Tombstone, Arizona, USA, in association with two other new minerals, khinite and parakhinite. In 1988 Kim et al. reported the second occurrence of dugganite from Yakutia, USSR and proposed the ideal formula as  $\text{Pb}_3\text{Zn}_3\text{Te}(\text{As},\text{V},\text{Si})_2(\text{O},\text{OH})_{14}$ . Successively, Kim et al. (1990) described a new mineral, chermnykhite which is a V-analogue of dugganite, and at that time they corrected the ideal formula of dugganite to be  $\text{Pb}_3\text{Zn}_3\text{TeO}_6(\text{AsO}_4)_2$ . Finally, Lam et al. (1998) concluded the ideal formula as  $\text{Pb}_3\text{Zn}_3\text{TeAs}_2\text{O}_{14}$ , after their crystal structure analysis. Joëlbruggerite,  $\text{Pb}_3\text{Zn}_3(\text{Sb},\text{Te})\text{As}_2\text{O}_{13}(\text{OH},\text{O})$ , recently found from the Black Pine mine, Montana, USA (Mills et al., 2009) corresponds to the antimony analogue of dugganite. During the survey on the secondary minerals from the Kawazu mine, Shizuoka Prefecture, Japan, we have found Sb-bearing dugganite. The present paper deals with the first occurrence of this mineral in Japan and discussion on the relation between dugganite and joëlbruggerite.

### Occurrence

There are many hydrothermal gold-silver-copper-manganese vein deposits at the Kawazu mining area. The veins are developed in propyrite, rhyolitic tuff breccia and tuff of the Pliocene age. The geological setting of the ore deposits around the Kawazu mine, Shimoda City, Shizuoka Prefecture, Japan were summarized by Shimizu et al. (1988). Also the deposits are famous for the occurrences of tellurium, kawazulite, and the secondary Te-bearing minerals such as tellurite, paratellurite, kinichilite, spiroffite, rajite, emmonsite, teineite, sonoraite, and poughite. The present dugganite was collected from one of dumps in the Kawazu mine. Although the dump is composed of rocks and ores from some deposits, we estimate the specimen to be derived from Sarukui deposit due to the assemblage of elements. The present dugganite occurs as minute hexagonal prismatic crystals up to 0.2 mm long in cavities of quartz vein (Fig. 1). It is transparent and pale aquamarine blue in color with vitreous luster.



Fig. 1. Microphotograph of the aggregate of dugganite crystals. Field view: approximately  $1.6 \times 1.2$  mm.

### X-ray Crystallography

The X-ray diffraction pattern of dugganite was obtained by using a Gandolfi camera, 114.6 mm in diameter, employing Ni-filtered Cu- $K\alpha$  radiation. This diffraction pattern resembles that of joëlbruggerite from the Black Pine mine rather than dugganite from Arizona (Table 1). The unit cell parameters calculated in the trigonal system are as follows:  $a=8.490$ ,  $c=5.216$  Å and  $V=325.6$  Å<sup>3</sup>. Compared with the unit cell parameters of Arizona dugganite,  $a=8.472$ ,  $c=5.208$  Å and  $V=323.7$  Å<sup>3</sup> (Williams, 1978), the both axes of the present dugganite are distinctly longer due to the partial replacement of Sb with Te. Also compared with those of joëlbruggerite,  $a=8.4803$ ,  $c=5.2334$  Å and  $V=325.94$  Å<sup>3</sup> (Mills et al., 2009), the both axes of Kawazu dugganite are distinctly shorter due to lower content of Sb.

### Chemical Composition

Chemical analyses of the present dugganite were carried out using a Link Systems energy dispersive X-ray spectrometer (QX-2000) for Pb, Zn, Cu, Te, Sb, As, P and Si (15 kV, 1 nA, 3 μm beam diameter). The standard materials used were PbSO<sub>4</sub> for Pb, Zn for Zn, chalcopyrite for

Cu, TeSe for Te, InSb for Sb, InAs for As, GaP for P and wollastonite for Si, respectively. Table 2 shows the representative result for the Kawazu dugganite compared with data of the two Arizona dugganites, Yakutia dugganite and joëlbruggerite. The empirical formula of the present dugganite is  $\text{Pb}_{2.96}(\text{Zn}_{2.83}\text{Cu}_{0.19})_{\Sigma 3.02}(\text{Te}_{0.72}\text{Sb}_{0.30})_{\Sigma 1.02}(\text{As}_{1.51}\text{Si}_{0.23}\text{P}_{0.15}\text{Sb}_{0.11})_{\Sigma 2.00}\text{O}_{13.77}$  on the basis of total cations = 9 excluding H<sub>2</sub>O. This dugganite distinctly has higher Sb content than three known dugganites and the component extends the ideal component of joëlbruggerite,  $\text{Pb}_3\text{Zn}_3\text{SbAs}_2\text{O}_{13}(\text{OH})$ .

### Discussion

When we presented the mineralogical properties of dugganite from the Kawazu mine at the Annual Meeting of Mineralogical Society of Japan, we estimate that a Sb-analogue of dugganite exists and it has H<sub>2</sub>O as an essential component (Matsubara et al., 2004). The discovery of a new mineral, joëlbruggerite, as the Sb-analogue of dugganite by Mills et al. (2009) proves our estimation to be correct. Therefore, the empirical formula of the Kawazu dugganite after consideration to H<sub>2</sub>O is  $\text{Pb}_{2.96}(\text{Zn}_{2.83}\text{Cu}_{0.19})_{\Sigma 3.02}$

Table 1. Powder X-ray diffraction data for dugganite and joëlbruggerite.

<i>h</i>	<i>k</i>	<i>l</i>	1			2		3	
			<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
0	0	1	5.21	5.22	20	5.2	40	5.236	6
0	1	1						{	22
1	1	0	4.24	4.25	26	4.23	40		
2	0	0	3.67	3.68	17	3.67	30	3.674	14
1	1	1	3.29	3.29	100	3.28	100	3.298	100
2	0	1	3.00	3.00	80	2.997	80	3.008	89
2	1	0	2.78	2.78	30	2.773	50	2.783	20
0	0	2	2.61	2.61	10	2.603	40	2.619	5
0	1	2						{	36
1	2	1							
3	0	0	2.45	2.45	40	2.446	60		
1	1	2						{	11
3	0	1	2.22	2.22	18	2.215	40		
2	0	2	2.13	2.13	12	2.121	40	{	12
2	2	0							
3	1	0	2.04	2.04	22	2.03	40	2.041	13
2	2	1	1.966	1.966	4	1.963	5		
2	1	2						{	39
3	1	1	1.901	1.899	40	1.896	60		
4	0	0						{	17
3	0	2	1.786	1.786	18	1.783	40		
0	0	3	1.738	1.739	2	1.734	5		
1	0	3						{	2
3	2	0	1.686	1.687	5	1.687	10		
2	2	2	1.648	1.646	2	1.644	10		
1	1	3						{	30
3	1	2	1.606	1.606	35	1.603	60		
3	2	1							
4	1	0							
2	0	3	1.572	1.572	8	1.569	30	1.576	1
4	1	1	1.533	1.534	2	1.530	5		
2	1	3						{	1
5	0	0	1.471	1.471	4	1.46	20		
3	0	3						{	12
3	2	2							
5	0	1	1.415	1.415	15	1.413	30		
3	3	0							
4	2	0	1.389	1.390	2	1.387	10	1.392	3
4	1	2	1.367	1.367	2	1.364	10		
2	2	3						1.345	4
4	2	1	1.343	1.343	7	1.341	20		
3	1	3	1.323	1.323	5	1.321	30	1.328	5
0	0	4	1.304	1.304	4	1.303	10	1.303	10
1	0	4						{	7
5	0	2	1.281	1.281	8	1.279	30		
5	1	1							
						1.242	10		
4	2	2	1.227	1.226	8	1.225	30		
3	2	3	1.211	1.211	8	1.209	40		
4	1	3				1.177	50		

1: Dugganite from the Kawazu mine.  $a=8.490$ ,  $c=5.216$  Å (This study)2: Dugganite from Arizona.  $a=8.472$ ,  $c=5.208$  Å (Williams, 1978)3: Joëlbruggerite from the Black Pine mine.  $a=8.4803$ ,  $c=5.2334$  Å (Mills et al., 2009)

Table 2. Chemical compositions of dugganite and Joëlbruggerite.

Wt.%	1	Cations as $\Sigma\text{cations}=9^*$	Ideal cations	2	3	4	5
CaO	0			~0	nd	0.24	nd
PbO	50.09	2.96	3	55.3	51.47	53.13	50.72
CuO	1.12	0.19		1.2	0	1.06	nd
ZnO	17.46	2.83	3	17.6	18.82	17.25	15.98
FeO	0			nd	nd	nd	0.97
Al <sub>2</sub> O <sub>3</sub>	0			nd	nd	0.07	nd
SiO <sub>2</sub>	1.07	0.23		nd	0.96	1.06	0.70
P <sub>2</sub> O <sub>5</sub>	0.78	0.15		nd	0.70	4.90	1.05
V <sub>2</sub> O <sub>5</sub>	0			nd	3.61	0.03	nd
As <sub>2</sub> O <sub>5</sub>	13.17	1.51	2	10.4	12.16	8.28	13.02
Sb <sub>2</sub> O <sub>5</sub>	5.04	0.41		nd	0.07	nd	7.68
TeO <sub>3</sub>	9.55	0.72	1	14.0	12.61	13.48	5.78
H <sub>2</sub> O	0.32**	-0.46		1.5	nd	nd	0.44**
Total	98.60			100.0	100.40	99.50	96.34

\*: excluding H. \*\*: calculation

- 1: Dugganite from the Kawazu mine, Shizuoka Prefecture, Japan (This study)
- 2: Dugganite from the Emerald mine, Tombstone, Arizona, USA (Williams, 1978)
- 3: Dugganite from the Kuranakh deposit, central Aldan, Yakutia, Russia (Kim et al., 1988)
- 4: Dugganite from the Empire mine, Tombstone, Arizona, USA (Lam et al., 1998)
- 5: Joëlbruggerite from the Black Pine mine, Montana, USA (Mills et al., 2009)

Table 3. The ideal formula and crystal system of dugganite and Joëlbruggerite.

Mineral	Formula	Crystal system	Cell parameters (Å)	References
Dugganite	$\text{Pb}_3\text{Zn}_3(\text{TeO}_6)_x(\text{AsO}_4)_{2-x}(\text{OH})_{6-3x}$	Hex. ( <i>P6/mmm</i> )	$a=8.472(5)$ $c=5.208(5)$	Williams (1978)
Dugganite	$\text{Pb}_3\text{Zn}_3\text{Te}(\text{As}, \text{V}, \text{Si})_2(\text{O}, \text{OH})_{14}$	Orth. (C-cell)	$a=8.57(3)$ $b=14.84(5)$ $c=5.21(3)$	Kim et al. (1988)
Dugganite	$\text{Pb}_3\text{Zn}_3\text{TeAs}_2\text{O}_{14}$ $\text{Pb}^{[8]}_3\text{Zn}^{[4]}_3\text{Te}^{[6]}[\text{O}_6](\text{As}^{[4]}\text{O}_4)_2]$	Trig. ( <i>P321</i> )	$a=8.460(2)$ $c=5.206(2)$	Lam et al. (1998)
Dugganite	$\text{Pb}_3(\text{Zn}, \text{Cu})_3(\text{Te}, \text{Sb})(\text{As}, \text{Sb}, \text{Si})_2(\text{O}, \text{OH})_{14}$	Trig.	$a=8.490$ $c=5.216$	This study
Joëlbruggerite	$\text{Pb}_3\text{Zn}_3(\text{Sb}, \text{Te})\text{As}_2\text{O}_{13}(\text{OH}, \text{O})$ $\text{Pb}^{[8]}_3\text{Zn}^{[4]}_3\text{Sb}^{[6]}[\text{O}_5(\text{OH})](\text{As}^{[4]}\text{O}_4)_2]$	Trig. ( <i>P321</i> )	$a=8.4803(17)$ $c=5.2334(12)$	Mills et al. (2009)

$(\text{Te}_{0.72}\text{Sb}_{0.30})_{\Sigma 1.02}(\text{As}_{1.51}\text{Si}_{0.23}\text{P}_{0.15}\text{Sb}_{0.11})_{\Sigma 2.00}\text{O}_{13.00}[\text{O}_{0.54}(\text{OH})_{0.46}]_{\Sigma 1.00}$  on the basis of  $\text{Pb}+\text{Zn}+\text{Cu}+\text{Te}+\text{Sb}+\text{As}+\text{Si}+\text{P}=9$  and the calculated (OH) with a charge balance (Table 2). Also the excess Sb is assigned in the As-site in this formula. The composition of Kawazu dugganite corresponds to approximately 30% mole of the ideal component of joëlbruggerite,  $\text{Pb}_3\text{Zn}_3\text{SbAs}_2\text{O}_{13}(\text{OH})$ . Although the type specimen of joëlbruggerite has

only up to 63% mole of its ideal component, we consider the mineral more close to the end member to be found in future.

Although dugganite has been considered as hexagonal (Williams, 1978) or orthorhombic (Kim et al., 1990) system, the crystal structure of dugganite has been refined in the trigonal system (*P321*) by Lam et al. (1998). The crystal structures of dugganite and joëlbruggerite (Mills et

al., 2009) are isomorphous to each other. As we successfully indexed the diffraction peaks with the setting of cell, we conclude the crystal system of the Sb-bearing dugganite from the Kawazu mine to be trigonal (Table 3).

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