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Hexagonal prismatic garnet from Yamanoo pegmatite, Ibaraki, Japan

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Abstract Almandine–spessartine intermediate garnet occurs as hexagonal prismatic crystals from granitic pegmatite at Yamanoo, Ibaraki, Japan. This garnet is composed of 56% almandine and 44% spessartine. The crystal habit is dodecahedron consisting of *n* {110} and *d* {211}, and distinctly elongated to [111] direction.
Key words: intermediate garnet, almandine, spessartine, hexagonal prism, pegmatite

Introduction

During the examination for pegmatite minerals from Yamanoo, Ibaraki, Japan, an orange hexagonal prismatic garnet crystal was recognized. This specimen was collected by one of the authors, Fujiko Hayashi, in 1979. We identified that the garnet has intermediate composition of almandine and spessartine using X-ray diffractometer and EDS analyzer. Although a similar prismatic garnet crystal from Yamanoo is deposited in the Sakurai mineral collection of the National Museum of Nature and Science, Tokyo, under the name almandine (NSM-M39929), and another one also has been reported from same locality by Kuroishi (1989), the chemical composition and unit cell parameter of both specimens have not been examined. The present specimen is deposited in the mineral collection of the same museum (NSM-M46375).

Occurrence

Yamanoo is located at about 3 km east of the Makabe town, and at about 5 km north of Mt. Tsukuba, Sakura city, Ibaraki prefecture, Japan. The geology of this area is composed of metamorphosed sedimentary rocks of the Upper Paleozoic, gabbroic rocks and granitic rocks (e.g. Okada *et al.*, 1954). Granitic rocks of the area are classified into the Tsukuba, Inada and Kabasan-granites (Miyazaki *et al.*, 1996) based on their rock facies and intrusive relations. Recently, Koike and Tsutsumi (2017) determined the age of zircon in these three types of granitic rocks by the U–Th–Pb method using LA-ICP-MS, and the results are 62–80 Ma, 64 Ma and 64–81 Ma, respectively. The Yamanoo pegma-

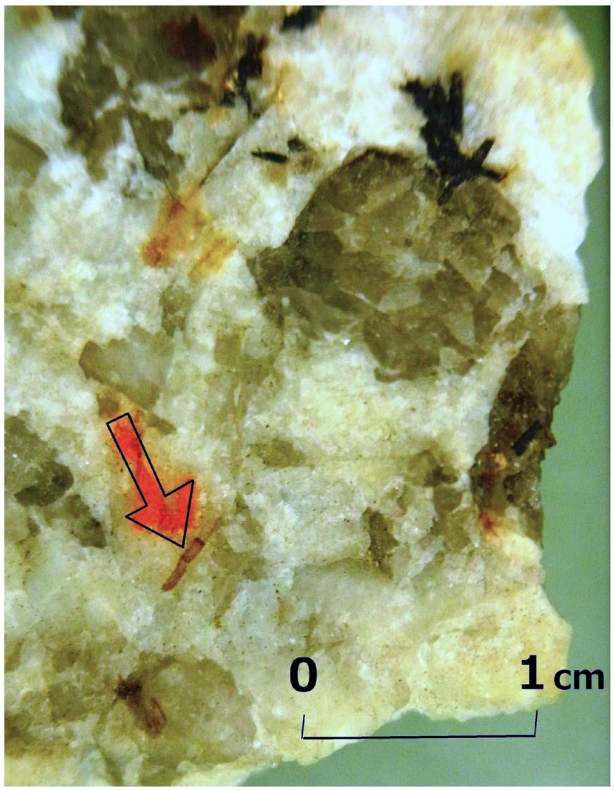

Fig. 1. Hexagonal prism of almandine (orange arrow) in the matrix. White is feldspars, gray is quartz and black is columbite-(Fe).

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titic dikes or lenses are observed in the fine-grained muscovite-bearing biotite granite of the Kabasan-granite. Many minerals are known in the pegmatites as follows: columbite-(Fe), monazite-(Ce), xenotime-(Y), almandine, zircon, uranophane-β, bertlandite, beryl, muscovite, quartz, opal, orthoclase, microcline, albite and laumontite. Especially beryl is blue like aquamarine, and almandine shows mainly reddish brown and trapezohedron crystal habit (Sakurai and Kato, 1972). The studied specimen was found from a small block of a pegmatitic dike. This is a transparent orange hexagonal prismatic crystal. It is associated with feldspars as well as with quartz, muscovite and columbite-(Fe) (Fig. 1).

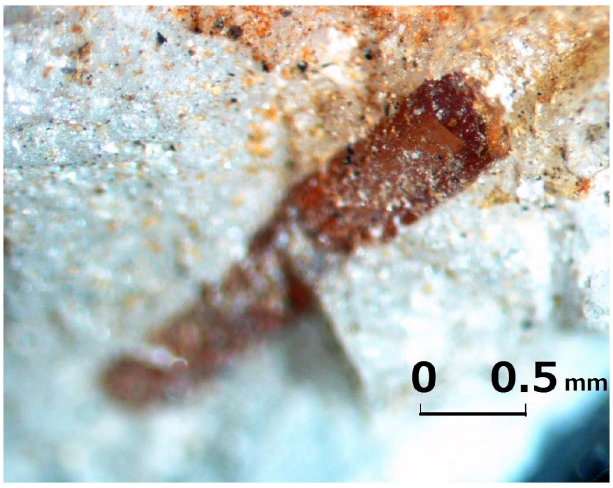

Fig. 2. Orange prismatic almandine in feldspars.

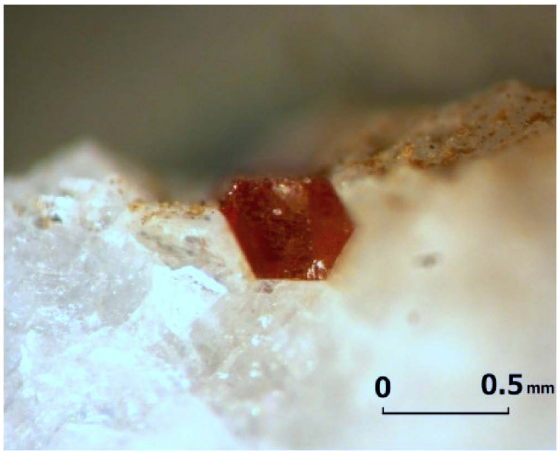

Fig. 3. The cross section of the hexagonal prism.

Crystal Habit and Optical Property

The specimen is a prismatic crystal with 3 mm in length and 0.5 mm in width included in feldspars (Fig. 2). The euhedral crystal showed hexagonal cross section (Fig. 3). The hexagonal prism shown in Fig. 3 was a half in size of the unbroken euhedral crystal. In the buried crystal, d {211} and n {110} faces are observed (Fig. 4).

The specimen is optically isotropic under polarizing microscope (Fig. 5) and there is no sign of optical anisotropy (e.g. grossular-andradite solid solu-

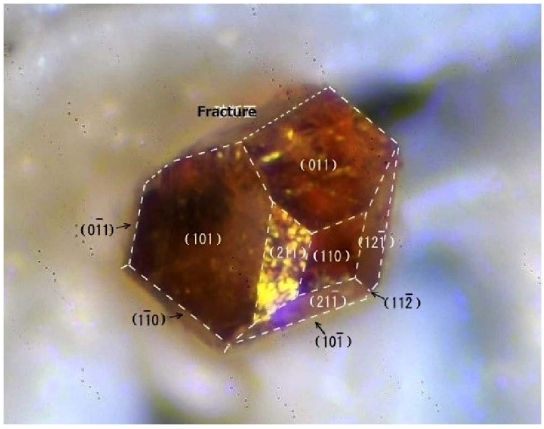

Fig. 4. Top of orange prismatic almandine.

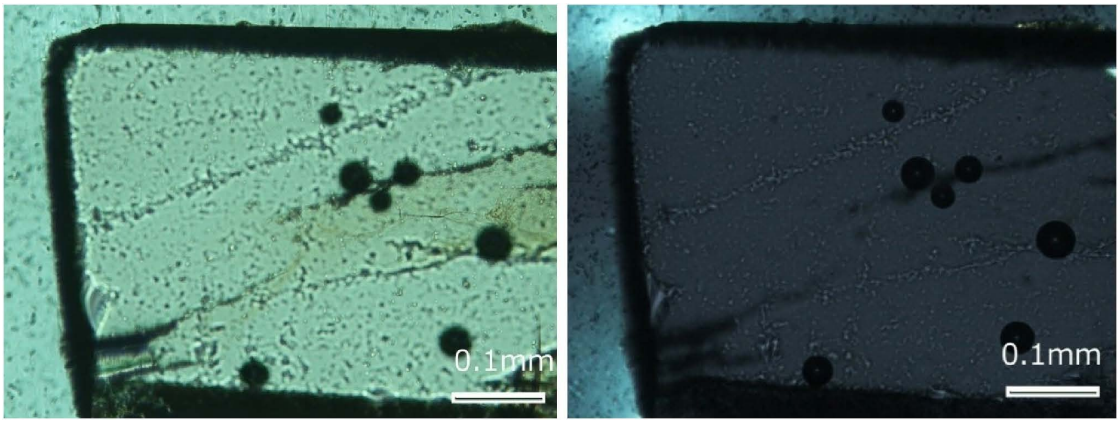

Fig. 5. Plane-polarized light image (left) and cross-polarized light image (right) of the thin section of sample.

Table 1. Chemical compositions of the sample normalized as total = 100%.

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
SiO_2	35.23	35.25	35.14	35.59	35.28	35.03	35.42	35.57	35.75	35.12
Al_2O_3	20.34	20.6	20.89	21.21	20.57	20.67	20.39	20.68	20.58	20.86
FeO	25.02	24.66	24.69	24.1	25.31	24.77	24.51	24.57	24.66	24.72
MnO	19.41	19.49	19.29	19.09	18.84	19.54	19.68	19.18	19.02	19.3

	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)	(19)	(20)
SiO_2	36.32	35.39	34.98	35.04	34.66	35.08	35.06	34.7	34.57	35.49
Al_2O_3	20.84	20.86	20.61	20.39	20.04	20.24	19.87	19.97	21.59	20.79
FeO	23.79	24.43	25.23	24.39	25.87	25.81	25.2	25.35	24.34	24
MnO	19.05	19.32	19.17	20.17	19.43	18.88	19.87	19.99	19.5	19.72

	Average of (1)～(20)
SiO_2	35.23
Al_2O_3	20.6
FeO	24.77
MnO	19.4

Mineral Species	
Almandine	56 mol%
Spessartine	44 mol%

Table 2. Details of the sample, data collection, and structural refinement.

Temperature	23.0°C
Radiation	Mo-Kα
Crystal size	0.37 × 0.23 × 0.13 mm
Space Group	Ia$\bar{3}$d (#230)
Unit cell dimension	a = 1.1570 (1) nm
Volume	V = 1.5487 (1) nm^3
Z	4
F(000)	1924
Diffractometer	Rigaku R-AXIS RAPID
Voltage, Current	50 kV, 40 mA
Detector Aperture	460.0 × 256.0 mm
Data Images	44 exposures
ω osclllation Range (χ = 45.0, ψ = 0.0)	130.0°–190.0°
Exposure Rate	100.0 sec./°
ω oscillation Range (χ = 45.0, ψ = 180.0)	0.0°–160.0°
Exposure Rate	100.0 sec./°
Detector Position	127.40 mm
Pixel Size	0.10 mm × 0.10 mm
Maximum 2θ	54.7°
No. of Reflections Measured	Total: 6391
Structure Solution	Direct Methods (SHELXT Ver.2014/4)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma w(Fo^2 - Fc^2)^2$
Least Squares Weights	$w = 1/[\sigma^2(Fo^2) + (0.0177 \cdot P)^2 + 2.0942 \cdot P]$
where	$P = (Max(Fo^2,0) + 2Fc^2)/3$
Residual: RI ($I > 2.00\sigma(I)$)	0.0159
Residual: R (All reflections)	0.0161
Residual: wR2 (All reflections)	0.0476

Table 3. Atomic coordinates and *B* iso/*B* eq and occupancy.

Site (atom)	x	y	z	*B* eq[1)]	Occ. assigned
M1 (Fe)	0.5	0.75	0.125	0.62 (13)	0.151340
M1 (Mn)	0.5	0.75	0.125	0.9 (2)	0.093850
Al	0.5	0.5	0	0.49 (3)	1/6
Si	0.5	0.75	−0.125	0.45 (2)	1/4
O	0.45158 (9)	0.65267 (8)	−0.03439 (9)	0.65 (3)	1

1) $B\ \mathrm{eq} = 8/3\pi 2(U11(aa^*)2 + U22(\mathrm{bb}^*)2 + U33(\mathrm{cc}^*)2 + 2U12(aa^*\mathrm{bb}^*)\cos\gamma + 2U13(aa^*\mathrm{cc}^*)\cos\beta + 2U23(\mathrm{bb}^*\mathrm{cc}^*)\cos\alpha)$

Table 4. Anisotropic displacement parameters.

Site (atom)	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
M1 (Fe)	0.0059 (17)	0.0059 (17)	0.012 (2)	−0.0022 (15)	0	0
M1 (Mn)	0.019 (4)	0.019 (4)	−0.005 (3)	0.002 (3)	0	0
Al	0.0062 (4)	0.0062 (4)	0.0062 (4)	0.00012 (18)	0.00012 (18)	0.00012 (18)
Si	0.0060 (3)	0.0060 (3)	0.0052 (4)	0	0	0
O	0.0093 (6)	0.0069 (5)	0.0086 (6)	0.0002 (4)	0.0010 (3)	0.0008 (4)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U11\mathrm{h}^2 + \mathrm{b}^{*2}U22\mathrm{k}^2 + \mathrm{c}^{*2}U33\mathrm{l}^2 + 2a^*\mathrm{b}^*U12\mathrm{hk} + 2a^*\mathrm{c}^*U13\mathrm{hl} + 2\mathrm{b}^*\mathrm{c}^*U23\mathrm{kl}))$

Table 5. Bond lengths (nm).

Atom	Atom	Distance	Atom	Atom	Distance
M1	O	0.22322 (10)	M1	O^1	0.22322 (10)
M1	O^2	0.22322 (10)	M1	O^3	0.22322 (10)
Al	O	0.18953 (9)	Al	O^4	0.18953 (9)
Al	O^5	0.18953 (9)	Al	O^6	0.18953 (9)
Al	O^7	0.18953 (9)	Al	O^8	0.18953 (9)
Si	O	0.16374 (10)	Si	O^9	0.16374 (10)
Si	O^1	0.16374 (10)	Si	O^{10}	0.16374 (10)

Symmetry Operators:
(1) $-X+1, -Y+1/2+1, Z$ (2) $Y, X+1, -Z+1$
(3) $-Y+2, -X+2, -Z+1$ (4) $-Z+1/2, -X+1, Y+1/2-1$
(5) $-Y+1, Z+1/2, -X+1/2$ (6) $-X+1, -Y+1, -Z$
(7) $Z+1, X, -Y+1$ (8) $Y, -Z+1, X$
(9) $Y+3/4-1, -X+1/4+1, -Z+3/4-1$ (10) $-Y+1/4+1, X+1/4, -Z+3/4-1$

Table 6. Bond angles (°).

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
O	M1	O^1	68.59 (4)	O	M1	O	115.42 (4)
O	M1	O^3	159.35 (4)	O^1	M1	O^2	159.35 (4)
O^1	M1	O^3	115.42 (4)	O^2	M1	O^3	68.59 (4)
O	Al	O^4	88.98 (4)	O	Al	O^5	88.98 (4)
O	Al	O^6	180.00 (6)	O	Al	O^7	91.02 (4)
O	Al	O^8	91.02 (4)	O^4	Al	O^5	88.98 (4)
O^4	Al	O^6	91.02 (4)	O^4	Al	O^7	180.00 (6)
O^4	Al	O^8	91.02 (4)	O^5	Al	O^6	91.02 (4)
O^5	Al	O^7	91.02 (4)	O^5	Al	O^8	180.00 (6)
O^6	Al	O^7	88.98 (4)	O^6	Al	O^8	88.98 (4)
O^7	Al	O^8	88.98 (4)	O	Si	O^9	114.20 (5)
O	Si	O^1	100.38 (5)	O	Si	O^{10}	114.20 (5)
O^9	Si	O^1	114.20 (5)	O^9	Si	O^{10}	100.38 (5)
O^1	Si	O^{10}	114.20 (5)	M1	O	Al	102.86 (5)
M1	O	Si	95.52 (4)				
Al	O	Si	132.40 (6)				

Symmetry Operators:
(1) $-X+1, -Y+1/2+1, Z$ (2) $Y, X+1, -Z+1$
(3) $-Y+2, -X+2, -Z+1$ (4) $-Z+1/2, -X+1, Y+1/2-1$
(5) $-Y+1, Z+1/2, -X+1/2$ (6) $-X+1, -Y+1, -Z$
(7) $Z+1, X, -Y+1$ (8) $Y, -Z+1, X$
(9) $Y+3/4-1, -X+1/4+1, -\mathrm{Z}+3/4-1$ (10) $-Y+1/4+1, X+1/4, -Z+3/4-1$

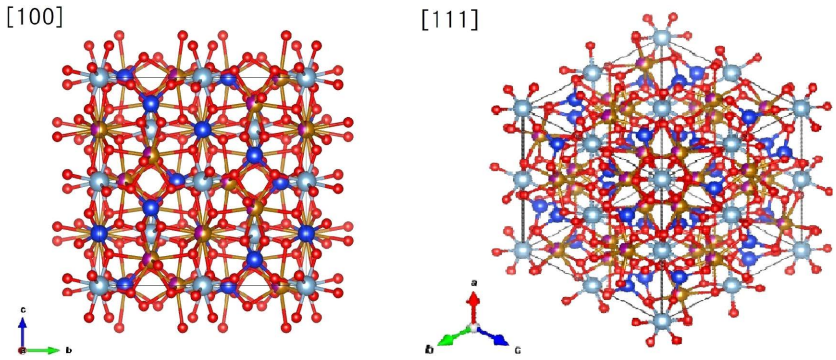

Fig. 6. Projections of the structure of intermediate garnet. Brown ball with magenta: M1 site (Fe and Mn), pale-blue: Al site, blue: Si site, red: O site. The structures were drawn with computer program VESTA (Momma and Izumi, 2011).

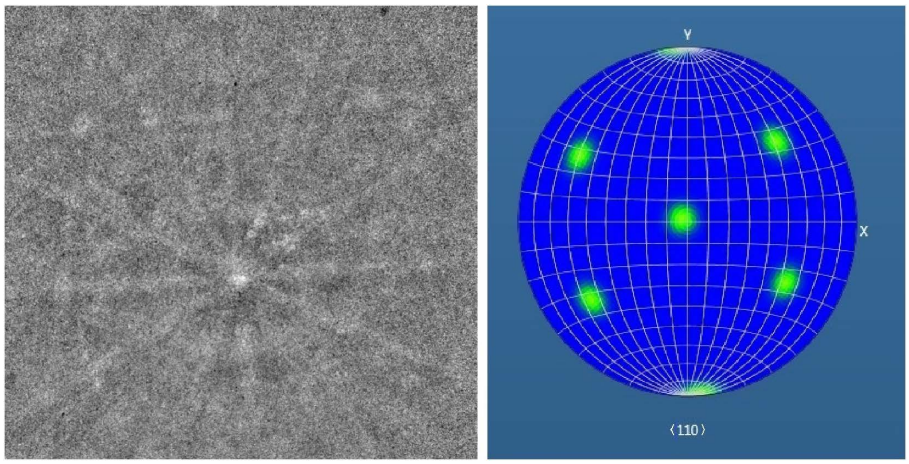

Fig. 7. The Kikuchi pattern (left) and a polar figure indicate direction of {110} and its equivalent reflections.

tion by Akizuki, 1989), twinning or zonal structure.

Chemical Composition

Chemical compositions of the sample were determined with a JEOL JSM-6360 scanning electron microscope (15 kV, 6 μA) and Oxford EDS system. Elements except Si, Al, Fe and Mn are scarcely detected by EDS measurement. The total weight percentage of all analyses is normalized to 100%. The results of the chemical analyses determine the chemical formula as $(Fe_{1.73}Mn_{1.37})_{\Sigma 3.10}Al_{2.02}Si_{2.94}O_{12}$, and indicate the present sample consisting of 56% almandine and 44% spessartine (Table 1). Consequently, the species name is determined almandine (Grew *et al.*, 2013).

X-ray Crystallography

Single-crystal X-ray diffraction data for the present orange prismatic crystal was collected with a Rigaku R-AXIS RAPID diffractometer using graphite monochromated Mo-Kα radiation. The crystal structure was refined to wR2 = 0.0476 under space group $Ia\bar{3}d$. The refined cell parameters were a = 1.1570 (1) nm, V = 1.5487 (1) nm^3. The initial structure model was obtained by direct method and missed sites were then located using differences Fourier techniques. All calculations were performed using SHELXL Version 2014/6 (Larson, 1970; Sheldrick, 2008, 2014). Details of data collection and refinement are given in Table 2. The crystallographic data (Tables 3–6) proves the sample to be a garnet (almandine-spessartine solid solution). Figure 6 shows the crystal structure of the garnet viewed along [100] and [110] drawn by VESTA (Momma and Izumi, 2011).

SEM-EBSD

The direction of the prismatic sample has been measured using electron backscatter diffraction (EBSD) with a scanning electron microscope (the SEM EBSD method). A Hitachi S-3400N scanning electron microscope (SEM) at Waseda University was used with following conditions: accelerating voltage 20 kV, working distance 30 mm, specimen tilted by 70°, low-vacuum mode (30 Pa), and uncoated samples. We used an HKL Nordlys detector (Oxford Instruments) to detect the electron backscatter patterns (EBSD) and HKL Channel 5 software (Oxford Instruments) to index the EBSD. Figure 7 shows the result of the measurement of the sample.

Discussion

Almandine–spessartine solid solution is ordinarily optically isotropic, and the most common crystal forms are dodecahedron or tetragonal trioctahedron. The present sample is optically isotropic and has an intermediate composition of 56% almandine and 44% spessartine. However, the crystal habit shows hexagonal prism elongated along [111]. The monoclinic crystal somewhat resembling augite with intermediate chemical composition of almandine–spessartine solid solution was named as partschinite (Dana, 1915), but was later considered spessartine by Strunz (1970).

Viewing from [111] direction, Al atoms in almandine-spessartine solid solution densely arrange (Fig. 6). The driving force for continuously supplying a solution of AlF_6^{3-} may crystallize the hexagonal prismatic almandine.

Acknowledgements

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