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2. A Mineral Romeite in Glass

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A mineral romeite in glass was observed and investigated the chemical composition, crystal chemistry and synthesized in laboratory.

Romeite was observed as a glass defect of CRT (cathode ray tube) face plate glass.

This crystal was small octahedral shape in Al_2O_3-rich glass knot. Chemical compositions are written in $(Ca_{2.04}Na_{0.30}Sr_{0.08})_{2.42}(Sb_{0.63}Ce_{0.55}Zr_{0.50}Ti_{0.32})_{2.00}O_{6.67}$, and crystal system is cubic, lattice constant : a is as follows.

$a=10.40\pm0.02$Å

1. Introduction

Romeite is a relatively rare mineral in natural occurrence ; firstly found in the Mn ore deposit of the Saint Marcel mine, Piemont, Italy, (Damour,1841). The chemical composition is written as $M_{1\text{-}2}Sb^{5+}{}_2O_6(O,OH,F)$ where monovalent or divalent cations, Ca, Na, Fe, Mn etc, can enter into M. The symmetry is cubic with space group Fd3m. Gozaisho mine, Fukushima Prefecture[1] is the first locality of the mineral in Japan.

The crystal structure of romeite was solved by Otto Zedlitz[2]. As expected from the chemical formulae, romeite has many chemical varieties. The crystal and chemical data of romeite are as follows :

Romeite[3]
$(Ca,Na,Fe^{2+}Mn^{2+})_{1\text{-}2}(Sb^{5+},Ti)_2O_6(O.OH.F)$
cubic, space group : Fd3m Z=8
lattice constant : 10.24-10.31 Å
octahedral crystal, color : yellow-transparent.

2. Romeite in glass

Romeite like crystals were found in face plate glass for cathode ray tube in the inspecting stage in a manufacturing plant. **Figure 1** shows the optical micrographs of such "romeite" crystals. Small octahedral crystals are found in this photograph. The sizes are about 1 to 10 μm. **Figure 2** shows

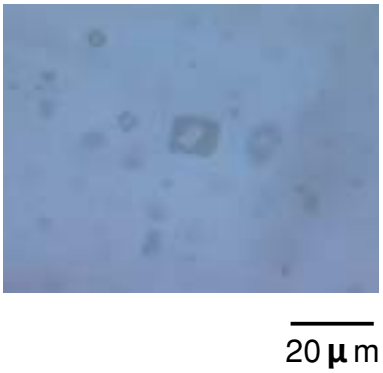

Fig. 1 Optical micrograph of romeite in glass.

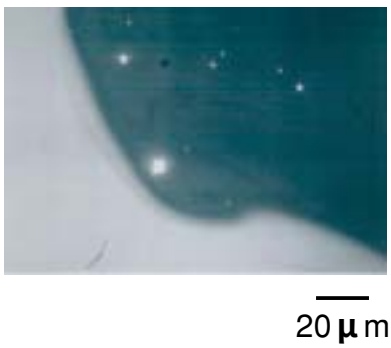

Fig. 2 Backscattered electron image of romeite in glass.

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Table 1 Chemical Compositions of Romeite in Glass and in Natural. (wt.%)

	1 [3]	2 [3]	3 [1]	4	5
Sb_2O_5	74.70	72.20	78.20	46.50	38.80
CaO	15.80	19.00	10.90	14.90	15.10
MnO	6.27	0.43	0.24	0.00	0.00
FeO	1.12	2.92	0.00	0.00	0.00
Na_2O	0.81	2.03	7.52	1.79	1.60
CeO_2				18.50	22.40
ZrO_2				12.10	12.20
TiO_2				4.47	6.09
SrO				1.11	0.78

1 St.Marcel, Italy　　2 Langban, Sweden
3 Gozaisho-mine, Japan
4 Crystal in glass　　5 Crystal in glass

the back scattered electron images of polished samples. Bright small "romeite" crystals are observed with surrounding dark colored phase. This phase is Al_2O_3-rich glass.

The outer zone of this phase is mother glass, that is face plate for cathode ray tube. The chemical composition of this crystal was determined with electron microprobe analysis. **Table 1** compares the compositions of crystals in glass and some natural minerals. The composition of romeite in glass is largely different from natural ones. It is reasonable that a question is raised whether or not romeite in glass is crystallographically the same as the natural ones.

The author, therefore, studied the origin and crystallographic identification of romeite in glass.

3. Synthesis of romeite

As mentioned above, it is doubtful that romeite in glass is isostructural with natural romeite. Unfortunately, it was difficult to study with X-ray diffraction because of too small size and amount of the specimens to measure diffraction intensities. Then the author attempted to synthesize romeite crystals with a similar composition to those in glass. The synthetic experiment was done in the following way.

1 Mixing of reagents in the same composition in **Table 1**, No.4 with an Al_2O_3 mortar.
2 High temperature synthesis at 1100℃ for 48hrs, followed by heating at 1500℃ for 2hrs in an Al_2O_3 crucible.
3 The synthesized powder samples were investigated with X-ray diffraction.

At first, Yellow powders were obtained after 1100℃ synthesis. The results of the X-ray powder diffraction measurements are shown in **Fig. 3**. As shown in **Fig. 3**, the main diffraction peaks agree well with those of natural one, which are marked by asterisks[1]. But, many diffraction peaks remain unidentified. It was considered at this stage that this material was intermediate to the last synthetic material. Then the re-synthetic experiment was done in high temperature heat treatment at 1500℃ using the same materials. White powders were obtained after 1500℃ synthesis. Powder X-ray diffraction pattern for the samples from the second heating was obtained as shown in **Fig. 4**. The diffraction lines marked with asterisks correspond to natural romeite[1]. In comparison both **Fig. 3** and **4**, we see that the reheating causes to diminish the unidentified peaks, resulting in that most recognizable peaks are identified to romeite. Referring to the powder diffraction data of natural romeite from Gozaisho Mine[1], the present indexing was done as shown in **Table 2**.

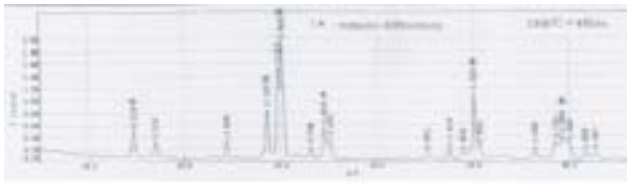

Fig. 3 X-ray powder diffraction pattern obtained from 1100℃ romeite synthesis.

Fig. 4 X-ray powder diffraction pattern obtained from 1500℃ romeite synthesis.

Table 2 X-ray Powder Diffraction Data Obtained from Synthetic Romeite.

This study		Gozaisho-mine[1]		
d(Å)obs.	Intensity	d(Å)obs.	Intensity	hkl
6.013	20	5.933	45	111
3.123	20	3.097	50	311
3.004	100	2.964	100	222
2.602	30	2.567	35	400
1.839	40	1.814	55	440
1.567	20	1.548	50	622
1.504	10	1.482	10	444

After indexing, the lattice constants were calculated using the least square method. The result is as follows :

a=10.40±0.02Å this study, which is compared with
a=10.265±0.002Å for the natural one (Matsubara et al.)[1]

The lattice constant of the present synthetic specimen is larger than the natural one. Ionic radii of Ce and Zr, which are contained in romeite in glass, are larger than Sb as shown in **Table 3**.

Table 3 Ionic Radius of Some Cations in Romeite Crystal after Shannon & Prewitt[4].

6-fold coordination		8-fold coordination	
Ti^{4+}	0.69	Na^{+}	1.24
Zr^{4+}	0.80	Ca^{2+}	1.20
Sb^{5+}	0.69	Mn^{2+}	1.01
Ce^{4+}	0.88	Fe^{2+}	0.86
		Sr^{2+}	1.33

Hence, we simply consider that the larger lattice constant of synthetic sample is the result of larger cationic sizes than in natural one. Taking this good agreement into account, it is reasonable to assume that romeite in glass crystallizes in cubic system. The chemical formula of romeite in glass is written as follows :

$$(Ca_{2.04}Na_{0.30}Sr_{0.08})_{2.42}(Sb_{0.63}Ce_{0.55}Zr_{0.50}Ti_{0.32})_{2.00}O_{6.67}.$$

This value is calculated on the basis of **Table 1**, No.4 crystal compositions and also assumed Sb+Ce+Zr+Ti=2.00. F atom content is not determined till now. But it is possible for F to exist in romeite in glass, because small amount of F is contained in glass. More accurately, it is necessary to solve the crystal structure of romeite by using single crystal X-ray diffraction. Unfortunately, we have not obtained the good single crystals so far. The author considers that romeite in glass is isostructural with natural romeite.

4. Conclusion

Romeite in glass was found in Al_2O_3-rich glass phase. Because of the chemical compositions and crystal habit, this crystal is considered to be romeite or its analogue. It was not possible to analyze crystallographic details about the sample.

—References—

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