Photon Factory Activity Report 2012 #30 (2013) **B**

BL-10A/2012G112

Single crystal X-ray diffraction experiments of a silica clathrate mineral chibaite

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1 Introduction

Chibaite is a new silica clathrate (clathrasil) mineral found from Late Miocene tuffaceous deposits in Boso Peninsula [1]. It has the MTN type framework structure with hydrocarbon molecules such as methane, ethane, propane, and 2-methil-propane contained in its cage-like voids. Space group symmetry of the MTN-type clathrasil at high temperature is $Fd\bar{3}m$, which is the highest symmetry of the framework topology, while its actual symmetry at room temperature is lower than that and depends on guest species [2]. In order to determine the actual symmetry of chibaite at room temperature and to reveal guest-host interactions that are affecting the symmetry, single-crystal X-ray diffraction study was performed.

2 Experiment

Single crystals of chibaite were picked up from thin sections of the samples under crossed-polar optical microscope. They were optically isotropic or nearly isotropic. Single-crystal X-ray diffraction study was performed using laboratory diffractometer equipped with imaging plate detector and focusing mirror (Rigaku R-AXIS RAPID-II with VariMax), and four-circle automated diffractometer at BL10A.

3 Results and Discussion

From Single-crystal X-ray diffraction experiments with R-AXIS, a space group $F4_132$ were suggested based on extinction conditions of reflections. However, this space group was not known as symmetry of MTN-type clathrasils at any temperature. Further experiments at BL10A revealed clear splitting of some diffraction profiles, demonstrating that the cubic $F4_132$ is not a true structure but the crystal is actually a pseudomerohedral micro twinning of a lower symmetry structure. On the other hand, another sample was found to be cubic $Fd\bar{3}$ or $Fd\bar{3}m$ at the experimental condition at BL10A, while 420 reflection, which violates extinction conditions of $Fd\bar{3}$ and $Fd\bar{3}m$, was observed at laboratory experiments. From these observations, it was found that tetragonal to cubit phase transition occurs near room temperature, around 20-30°C, and the exact transition temperature varies with samples. Details of data collection and the results of refinement for room temperature tetragonal phase are summarized in Table 1.

Epitaxial intergrowth of chibaite with DOH-type silica clathrate mineral was also confirmed by step scan measurements along reciprocal axes of chibaite. (111) plane of chibaite is oriented parallel with (001) of the DOH-type mineral, and $[1\bar{1}0]$ of chibaite is parallel with [110] of the DOH-type mineral.

Table 1. Summary of data collection and refinements.

Temperature	300(5) K
Radiation	0.7-1.0 Å, MoKa
Empirical Formula	$C_3H_{12}O_{34}Si_{17}$
Crystal size	0.06 x 0.04 x 0.03 mm
Space Group	$I4_1/a$ (#88)
Unit cell dimensions	a = 13.7474(3) Å
	c = 19.4428(5) Å
Volume	V = 3674.5(2) Å^3
Z	4
D_{calc}	1.933 g/cm^3
$F000$	2160
Absorption coefficient m	6.975 cm^{-1} (MoKa)
Max. and min. trans. factor	0.968 - 1.000
Diffractometer	R-AXIS RAPID
2θmax	60.0°
No. of Reflections Measured	22292
Independent reflections	Unique: 2767 (Rint = 0.0379)
Corrections	Lorentz-polarization, Absorption
Structure Solution	Charge flipping method
Refinement	SHELX97 [3]
No. Variables	128
Reflection/Parameter Ratio	21.62
Residuals: $R1$ (I>2.00s(I))	0.0684
Residuals: R (All)	0.0741
Residuals: $wR2$ (All)	0.2217
Goodness of Fit Indicator	1.808
Largest diff. peak and hole	0.60 e/Å^3 and -0.84 e/Å^3

References

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