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Single crystal X-ray diffraction experiments of silica clathrate minerals

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1 Introduction

Chibaite, the MTN-type silica clathrate (clathrasil) mineral and the DOH-type clathrasil mineral were found from Late Miocene tuffaceous deposits in Boso Peninsula [1]. These minerals consist of SiO_2 framework structures with cages-like voids containing hydrocarbon molecules such as methane, ethane, propane, and 2-methil-propane. While the highest possible space group symmetry of the MTN-type clathrasil is $Fd\bar{3}m$ at high temperature, the actual space groups of chibaite at room temperature is which is the highest symmetry of the framework topology, while its actual symmetry at room temperature is $Fd\bar{3}$ and $I4_1/a$. Space group of the DOH-type synthetic clathrasils is known to be *P6/mmm*. In order to determine the true space groups of chibaite and the DOH-type mineral at room temperature and to reveal guest-host interactions, single-crystal X-ray diffraction study was performed.

2 Experiment

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

3 Results and Discussion

From the single-crystal X-ray diffraction study, symmetry of some chibaite sample was found to be cubic, while that of most samples were tetragonal at room temperature. The tetragonal to cubic transition occurs at temperatures above around 20-30°C and the temperature varies with samples [2]. For the tetragonal phase, merohedral twinning was confirmed by peak splitting of {00l} and {hh0} reflections. For the DOH-type mineral, no indication of symmetry lowering from *P6/mmm* was observed. Epitaxial intergrowth of chibaite with DOH-type silica clathrate mineral was also observed 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.

Because large numbers of reflections have to be measured for single-crystal structure analyses, the following data collections for structure analyses were made by Rigaku R-AXIS RAPID-II. Electron density peaks corresponding to one methane molecule were found at the center of the small $[5^{12}]$ cage (common in chibaite and DOH) and $[4^3 5^{12} 6^3]$ cage of DOH, while in the $[5^{12}6^4]$ cage of chibaite and the $[5^{12}6^8]$ cage of DOH-type mineral, multiple numbers of electron density peaks were found at positions offset from the center of the cage. Details of data collection and the results of refinement for the DOH-type mineral are summarized in Table 1.

Table 1. Summary of data collection and refinements.

Temperature	293(2) K
Radiation	0.7 Å, Cu$K\alpha$
Empirical Formula	$Na_{0.01}(Si_{0.98}Al_{0.02})_{\Sigma 1.00}O_2 \bullet 0.50(CH_4)$
Crystal size	0.060 x 0.050 x 0.040 mm
Space Group	*P6/mmm* (#191)
Unit cell dimensions	a = 13.9020(3) Å
	c = 11.2802(2) Å
Volume	V = 1887.99(6) Å^3
Z	34
D_{calc}	2.02 g/cm^3
$F000$	1125.84
Absorption coefficient m	6.514 mm^{-1}
Max. and min. trans. factor	0.493 - 0.521
Diffractometer	R-AXIS RAPID
2θmax	136.4°
No. of Reflections Measured	22203
Independent reflections	739 (R_{int} = 0.0307)
Corrections	Lorentz-polarization, Absorption
Structure Solution	Charge flipping method
Refinement	SHELX97 [3]
No. Variables	67
Reflection/Parameter Ratio	11.03
Residuals: $R1$ [$I > 2.00\sigma(I)$]	0.0437
Residuals: R (All)	0.0445
Residuals: $wR2$ (All)	0.1359
Goodness of Fit Indicator: S	1.128
Largest diff. peak and hole	0.50 e/Å^3 and -0.35 e/Å^3

References

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