Ab initio structure determination of novel silica materials by high-resolution synchrotron powder diffraction

T. Ikeda*[1], H. Nakajima[2] and T. Nishide[2]
[1]Advanced Materials Laboratory, National Institute for Material Science, Tsukuba, 305-0044, Japan
[2]College of Engineering, Nihon University, Koriyama, 963-8642, Japan

Introduction

Recently, layered silicate compounds are noticeable for precursors of creating novel microporous materials[1]. These materials are usually obtained as a powder form, which include Si-O bonding framework, template organic molecule, alkali cation and H_2O. However, silica materials e.g. zeolites, clays are usually not easy to be obtained as a single crystal but powder form. Therefore, high-resolution powder diffraction data are indispensable for determining their structures. In this study, crystal structure of novel silicate named PhaseX: $Cs_4Si_8O_{24}{\cdot}nH_2O$, which has string type topology, has been analyzed by combination of the direct method and maximum-entropy method (MEM).

Experimental

Synthesis:

PhaseX is synthesized by a solid-state transformation method using mixture of silica sol, small amount of water, tetrabutylammonium: TBA ion and $CsCO_3$ solution. TBA molecule only plays a role in construction of silica framework as template, because TBA ion is not included in the final product. Chemical composition is calculated to be $Cs_4Si_8O_{24}{\cdot}nH_2O$ by ICP-analysis. Local structure of Si atoms is a Q^2-connection from ^{29}Si-MAS NMR.

High-resolution XRPD:

Sample, which has small crystalline size less than 5 μm, was sealed into a glass-capillary with an inner diameter of 1.0ϕ. The sample was mounted on the MDS diffractometer of BL-4B2 at Photon Factory. 6-arm detectors with Ge(111) analyzer are calibrated by NIST Si. Wavelength is selected to be 0.70696 Å. Scan range is from $3^o < 2\theta < 55^o$ with step width of 0.003^o and counting time was 14 s/step. Capillary was rotated with 60 rpm.

Result and Discussion

Indexing:

Obtained XRD pattern shows high crystallinity as shown in Fig.1. Indexing of reflections with TREOR90 built into PowderX indexing software gave an orthorhombic unit cell of a = 12.93662(12) Å, b = 8.81200(11) Å and c = 4.97878(6) Å with acceptable figures of merit: F_{30} = 42 and M_{20} = 11. Reflection conditions derived from the indexed reflections were $h + k = 2n$ for *hk0*, $k = 2n$ for *0k0* and $h = 2n$ for *h00*, affording space group *Pmmn* (No. 59) on the assumption that the PhaseX has a centrosymmetric space group.

Le-Bail extracting and model search:

Observed integrated intensities, $|F_o|^2$, of 433 reflections in a region of d > 0.92 Å were extracted by the Le Bail method with a versatile pattern-fitting system RIETAN-2000[2]. A split pseudo-Voigt function of Toraya was used as a profile function. Partial profile relaxation with a modified split pseudo-Voigt function was applied to 12 reflections in a region of 2θ lower than 21°, which significantly improved fits between their observed and calculated profiles. R factors were sufficiently low R_{wp} = 8.30% (R_e = 3.38%) and R_p = 0.64%.

Now, we search framework topology of PhaseX by a direct method using SIRPOW97 in EXPO and MEM program MEED. From Q^2-connection around Si atom, it is considered that framework has two type of topology. One model is closed ring of Si–O–Si network, and the other model is almost string network with silanol group at termination of string. Cs site is estimated to be one special position and one general position. However, the framework has not been determined as an unique model and the data analysis is in progress.

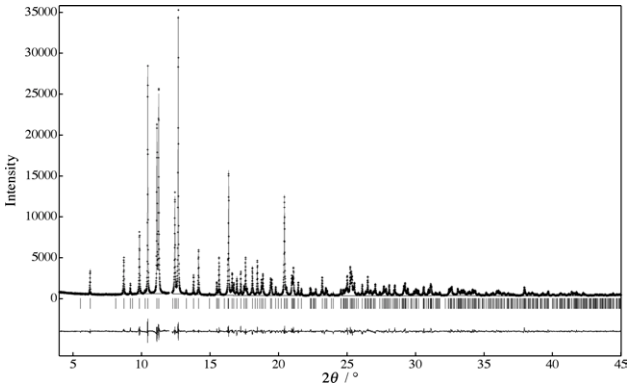

Figure 1 Result of Le Bail extraction of PhaseX

References

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* IKEDA.Takuji@nims.go.jp