

## Identification of high-pressure silica polymorphs using Raman and cathodoluminescence spectroscopy

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High-pressure silica polymorphs such as seifertite and stishovite are known in Martian and lunar meteorites and the existence and stability provide constraint on condition of shock pressure and post-temperature in impact event that the parent body have experienced. Transmission electron microscopy and Raman spectroscopy have been attempted to identify post-stishovite, whereas it was not successful to determine the structure due to potential vitrification or transition into other phase by the irradiation. Although cathodoluminescence (CL) spectroscopy has been also conducted, no characteristic signal was obtained from post-stishovite. Only XRD analysis allows us to identify the structure, where silica minerals are excavated with a focused ion beam (FIB) system from meteorite. Therefore, it is necessary for identification of micron-order high-pressure silica polymorphs in precious extraterrestrial materials to develop a new method without sample preparation. In this study, Raman and CL spectroscopy has been performed for synthetic and meteoritic silica minerals, the results of which can identify the polymorphs with high-spatial resolution as nondestructive analysis.

The block pieces of silica grains in Zagami, NWA2975 and NWA4734 meteorites, excavated with FIB system, were identified as seifertite, stishovite and cristobalite by a synchrotron X-ray at Spring-8 BL-10 and were employed for Raman and CL spectroscopy. Synthetic seifertite and stishovite were also analyzed as reference materials to compare their CL and Raman data with meteoritic silica polymorphs.

Reflected-light microscopy and backscattered electron image of synthetic seifertite show numerous polycrystalline grains (<50 micrometers in diameter) with two orthogonal sets of bright and dark lamellae. Wedge-shaped silica grains in the meteorites also display the tweedlike internal microstructure and are surrounded by radiating cracks extended from the surface to the neighbor maskelynite or clinopyroxene.

Raman spectra of synthetic seifertite consist of pronounced peaks at 380, 515, 564, 739 and 796  $\text{cm}^{-1}$  and weak peaks at 401, 496, 539, 547, 606 and 749  $\text{cm}^{-1}$ , of which the Raman shifts and relative intensities are corresponding to those calculated within the density-functional perturbation theory for seifertite. Similar Raman peaks are also obtained from silica grains in the meteorites, implying characteristic signals of seifertite. Synthetic and meteoritic seifertite has the distinct Raman peaks after the prolonged laser beam, X-ray and electron irradiation. Although seifertite was considered to be highly unstable phase and therefore the post-shock temperature of meteorite containing seifertite was supposed to be relatively low, it might survive post-shock thermal history with a higher temperature than the expected.

CL spectra of synthetic and meteoritic seifertite show emission bands at 330 and 380 nm in the UV region, which can be deconvoluted into emission components centered at 3.79 and 3.25 eV. The peak wavelengths are distinct from those obtained from other silica polymorphs such as stishovite (3.15 and 3.04 eV) and cristobalite (3.02 and 2.63 eV). CL images of synthetic seifertite exhibit polycrystalline grains with bright rim and vein-shaped luminescent interior on dull background, which may be caused by formation and elimination of lattice defect due to high pressure and dynamic recrystallization. The components, therefore, may be assigned to pressure-induced defect center. The emission intensities of the components centered at 3.79 and 3.25 eV appear to depend on the inferred shock pressure on the meteorites reported by previous studies and should be closely related to the defect density. Therefore, CL and Raman spectroscopy enables identification of silica polymorphs with high-spatial resolution and without destruction, and provides valuable information on impact history concerning shock pressure and post-temperature.

Keywords: Raman spectroscopy, Cathodoluminescence, High-pressure silica polymorphs, Seifertite, Stishovite, Meteorite