

The structural characteristics of the minerals crystallized at high pressure and ultrahigh pressure conditions

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Abstract

X-ray diffraction and Raman spectroscopy measurements were carried out on a number of silicate, oxide, and carbide minerals of high pressure (HP) and ultrahigh pressure (UHP) origin. They involve zircon, olivine, pyroxene, garnet, rutile and moissanite crystals recovered from basalt, peridotite, harzburgite and eclogite, and these rocks were derived from various geological terranes representing mantle environments.

Sharp to very sharp peak profiles in their X-ray diffraction and Raman scattering patterns indicate that all of these specimens are high quality, ideally imperfect mosaic crystals. Subsequent X-ray structural analyses also revealed a very small R factor (3~5%), and very small difference electron peaks and electron holes (less than ± 1 electron/ \AA^3). The most distinct structural feature in these high pressure or ultrahigh pressure minerals is the smaller cell parameters, in comparison with the low pressure counterparts crystallized from the Earth crust conditions. Although anisotropic characteristics play an important role in positioning the constituent atoms at high pressure and ultrahigh pressure conditions, the most rigid silicon-oxygen tetrahedra in the studied silicates display a smallest negative deviation relative to that of their low pressure Earth's crustal counterparts. The metal-oxygen bond distances are significantly smaller than those observed for the low pressure equivalent minerals formed in the crust environments.

UHP-Olivine vs HP-Olivine

The olivine crystal in the garnet-peridotite, referred to as UHP-olivine, with a composition of $(\text{Mg}_{1.83}\text{Fe}_{0.17})\text{SiO}_4$ was refined to a final R factor of 3.4% with a full-matrix least-squares method and 377 independent intensity data. The largest difference electron peak and hole are 0.694 and -0.582 e/ \AA^3 , respectively. A

mantle-derived high-pressure olivine crystal, $(\text{Mg}_{1.8}\text{Fe}_{0.2})\text{SiO}_4$, occurred in the xenolith of a Miocene basalt from Taiwan, referred to as HP-olivine, was also analyzed for structural comparison purpose. Both structures exhibit negative deviations in their unit cell parameters and interatomic bond distances, in comparison with the low-pressure crustal olivine structure. The mean Si-O distance in UHP-olivine (1.6379Å) are comparable to that of HP-olivine (1.6372Å). However, the cell dimensions and M1-O and M2-O bond lengths of UHP-olivine are slightly shorter than those of the HP-olivine crystals. All of the thermal ellipsoids of the constituent atoms in the UHP-olivine crystals are also consistently smaller than those in HP-olivine. The observed variations in the structural features suggest that at the time of crystallization of olivine, the UHP rocks might have been subjected to a slightly higher-pressure condition than the xenolith in the Miocene basalt. Raman scattering measurements indicate that the Raman peaks of UHP-olivine and HP-olivine are essentially identical, except that the Raman modes of UHP-olivine are slightly better in resolution than those of the HP-olivine crystals, especially in the 900 to 1000 cm^{-1} region.

UHP-Garnet

A pyrope-rich garnet, $(\text{Mg}_{2.09}\text{Fe}_{0.51}\text{Mn}_{0.03}\text{Ca}_{0.37})(\text{Al}_{1.87}\text{Cr}_{0.13})\text{Si}_3\text{O}_{12}$, in peridotite and a grossular-rich garnet, $(\text{Ca}_{2.03}\text{Fe}_{1.08})(\text{Al}_{1.90})\text{Si}_3\text{O}_{12}$, in rutile-eclogite were structurally refined to the final R factors of 5.4% and 2.1%, respectively. The pyrope itself is a high-pressure variety of garnet minerals. The grossular structure also displays a significant shortening effect in the cell parameter, 11.619Å versus 11.743Å. The latter value was theoretically calculated based on the garnet compositions and the associated end-member cell dimensions. The bond distances in the grossular structure are also showing negative deviations relative to the low-pressure counterpart, apparently due primarily to the crystallization pressure environment.

UHP-Rutile

Two rutile-eclogite specimens, from Mao-bei in the Su-lu ultrahigh pressure metamorphic belt, were studied with single crystal X-ray diffraction techniques. Two types of rutile crystals were recognized, one was occurred as inclusion in garnet grain and the other was free rutile. The structural analysis results suggest that the garnet-included rutile contains a significant amount of impure constituent. When Al impurity was deliberately introduced into the structural refinement cycles, the R factor decreased to 1.88% from 2.22% for assumed TiO_2 stoichiometric composition. The refined data indicate that the structural features of rutile, including the cell

parameters and bond distances, are quite ordinary. This is consistent with the fact that rutile is stable at a relatively wide range of temperature and pressure conditions. The presence of Al impurity might be a good indication that the rutile is of high pressure or ultrahigh pressure in origin.

HP-Zircon

Zircon crystals recovered as inclusions in chromite from Luobusa harzburgite in Tibet were analyzed with single crystal X-ray diffraction method. With a total of 112 independent X-ray intensity data, the zircon structure was refined to a final R factor of 1.65%. Final Difference Fourier analysis indicates that the largest difference peak and hole are 0.539 and -0.571\AA^{-3} , respectively. All the fundamental crystal data of this zircon are essentially similar to those of the crustal zircon. However, the mantle zircon exhibits a smaller unit cell parameters and the corresponding bond distances compared with the crustal counterpart. With the use of empirical equation based on high pressure work, the linear compressibilities, K_a and K_c were evaluated to be $1.6 \times 10^{-4} \text{ Kbar}^{-1}$. In other words, both the a and c axes of the mantle zircon display an identical compression behavior under pressure.

HP-Moissanite

Although silicon carbide is a common material widely used in various industrial applications, natural occurrence of moissanite is rather rare. Natural moissanites were reported to occur in kimberlite (Leung et al., 1990, 1996) as well as at the Trubka fumarole of Great Tolbachik Fissure Eruption of 1975-1976, Kamchatka, Russia (Jambor and Roberts, 1999). Polytypes of 3C, 6H, 15R and 33R have been recognized so far for kimberlitic moissanites. A 5H moissanite was found along the Dzoraget River in the Sevan-Amasii ophiolite zone (Fleischer et al., 1976). However, no detailed structural analysis for these moissanites have ever been undertaken. A number of moissanite crystals were recovered as inclusions in chromite from Luobusa harzburgite in Tibet. Single crystal X-ray diffraction study was carried out on such natural moissanite crystals. They are greenish blue in color, and three different polytypes, 6H, 15R and 33R, were identified based on X-ray analysis. With three-dimensional X-ray intensity data, the structures of 6H, 15R and 33R moissanite were refined with a least-squares method to the final R factors of 2.6%, 6.2% and 4.8%, respectively. The basic SiC_4 tetrahedral units in all the observed moissanite polytypes are essentially identical, and exhibit an ideal tetrahedral angles. However, the arrangement sequence of these tetrahedral groups varied in different polytypes, and resulted the c-axis as long as 83Å in the 33R structure. During the structural refinement processes for rhombohedral moissanites,

15R and 33R polytypes, a space group symmetry of R3m was used instead of reported R3.

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