

Radiation-damage-induced variations in Raman spectra of UHPM microdiamond

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Raman spectroscopy is a fundamental and very useful technique for characterization of metamorphic microdiamond. It is well known that microdiamonds from several UHP terranes have significant variations in their Raman spectra, which may reflect the difference of genesis (e.g., Perraki et al., 2009). However, Shimizu & Ogasawara (2014) compared Raman, photoluminescence (PL), and cathodoluminescence (CL) spectra of various diamonds in a tourmaline-rich quartzofeldspathic rock and demonstrated that some diamonds had suffered metamictization due to α -particle emission from host zircon. On the one hand, diamonds in maruyamaite (K-dominant tourmaline) had a sharp Raman band that is similar to that of diamonds with a high crystallinity [full width at half maximum (FWHM): 2-3cm⁻¹]. On the other hand, diamonds in U-rich zircon (up to 0.15 wt.% UO₂) showed broader and more downshifted Raman bands (FWHMs and peak positions varied up to 9.3 cm⁻¹ and 1328cm⁻¹, respectively), with additional small peaks at ~1490 and ~1630 cm⁻¹. The PL and CL studies also suggested that diamonds in U-rich zircon had been more metamictized. Therefore, it is emphasized that the effect of post-crystallization radiation damage should not be underestimated to discuss the genesis of microdiamond from its Raman spectra. To discuss whether radiation damage is a common phenomenon in metamorphic diamonds, a large number of Raman spectra of microdiamonds in various UHP rocks from the Kokchetav Massif, Kazakhstan were obtained. We report here that some diamonds in garnet also showed spectra with evidence of radiation damage.

Pelitic gneiss is the most abundant diamond-bearing rock in the Kumdy-Kol area of the Kokchetav Massif. Diamond in pelitic gneiss mainly occurs as inclusions in garnet, kyanite, and zircon. The main Raman peak of diamond in garnet and kyanite is broader and downshifted compared with that of non-irradiated diamond such as diamond in kimberlite or in maruyamaite (Shimizu & Ogasawara, 2014). FWHM of the main peak of diamond ranges 4-8 cm⁻¹ and shows various averages for different mineral composition of host rock. Most of peak positions are in the range of 1331-1332 cm⁻¹ but some microdiamonds have considerably upshifted peak up to 1334cm⁻¹. No correlation was found in FWHM vs peak position plots. This contrasts with that of some irradiated diamonds which show a negative linear trend (Orwa et al., 2000; Shimizu & Ogasawara, 2014). However, additional subtle peaks appeared at 1478 and 1637 cm⁻¹. In addition, a vacancy-related photoluminescence peak (at 637 nm; attributable to N-V⁻ center) was often observed in the Raman spectra. These facts indicate that some crystal defects derived from radiation also present in diamond in garnet, not only in diamond inclusion in actinide-rich mineral (e.g., zircon). Considering the absence of negative correlation between FWHM and peak position of the Raman peak, the Raman feature of diamond in garnet probably are controlled by combination effect of several factors such as radiation damage, residual pressure, and nitrogen impurities. It means that interpretation of spectroscopic characterization of metamorphic diamond is not quite simple. To adequately discriminate diamond populations by Raman spectroscopy, it is recommended to interpret Raman results in conjunction with other methods (FTIR, PL, CL, and TEM study, etc).

Keywords: microdiamond, radiation damage, Raman spectroscopy, ultrahigh-pressure metamorphism, crystal defect