Determination of laser induced damage threshold for graphite and low-maturity carbonaceous material using deep UV micro-Raman spectroscopy

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Micro-Raman spectroscopy is appropriate to assess the crystallinity of a small amount of carbonaceous material (CM). However, strong visible excitation lasers (e.g., 488nm or 532nm) during microanalysis result in serious laser-induced fluorescence from surrounding minerals and low maturity CM. The fluorescence makes it difficult to detect a weak Raman signal from the sample surface. In this study, we developed a new type of compact Deep-UV Raman system using a single monochromator with a front-illuminated cooled CCD and a 266 nm Micro-chip laser to overcome laser-induced fluorescence. The Raman spectra of CM in the first and second-order regions by deep UV Raman spectroscopy are much far from the fluorescence region (300 to 600 nm), therefore, it is easy to analyze the fluorescence free Raman spectra using a polish slab and a thin section. On the other hand, such deep UV laser may result in serious degradation and/or laser-induced heating on the sample surface, especially in microanalysis. We attempted to assess the laser-induced damage threshold for fluid deposited graphite and low-maturity CM (VRr = ˜0.5 %) to obtain correct Raman spectra from the spot size of ˜1 μm. For the fluid deposited graphite, there is no serious degradation on the sample surface between 0.10 and 2.50 J/cm^{-1} during deep UV micro-Raman spectroscopy. However, some sample surfaces become black after Raman measurements at the higher laser fluence of 1.96˜2.50 J/cm^{-1}, suggesting the possibility of irreversible damage (or photo-alteration?) by a deep UV laser. The Raman shift of G band after measurement displays the downshift of 6–8 cm^{-1} compared with other Raman spectra measured by low-laser fluence beneath 0.98 J/cm^{-1}. In addition, the G band FWHM also becomes bigger with increasing the laser fluence. Both changes in Raman spectra are well consistent with the Raman signature of laser-induced heating during micro-Raman analysis. We revealed that the laser heating by a deep UV laser is a more sensitive and serious effect than that by visible lasers previously reported. Lower laser fluences beneath ˜1.0 J/cm^{-1} should keep for avoiding the laser-heating of fully ordered graphite. For the low-maturity CM, a serious degradation on the polished surface even lower laser fluence region between 2.50 J/cm^{-1} and 0.34 J/cm^{-1} was observed. In addition, three samples irradiated by deep UV lasers of 0.16 to 0.10 J/cm^{-1} are also modified as a white halo, suggesting a photo-bleaching. On the other hand, the significant changes in Raman spectra were only observed at the laser fluence region between 2.5 J/cm^{-1} and 0.34 J/cm^{-1}. We found that the laser fluence beneath 0.16 J/cm^{-1} is required to obtain correct Raman spectra from the spot size of ˜1 μm by deep UV micro-Raman spectroscopy. In particular, the G and D band FWHM and their Raman shift values are widely applied for a reliable thermal indicator. We should keep in mind that such parameter is sensitively changed by even low laser fluence between 2.5 J/cm^{-1} and 0.34 J/cm^{-1}, especially in a deep-UV micro-Raman spectroscopy.

Keywords: Laser induced damage threshold, Deep UV micro-Raman spectroscpy, carbonaceous material

