Terahertz micro-Raman spectroscopy and its application to mineral sciences

*Masami Kanzaki[1]

1.Institute for Study of the Earth's Interior, Okayama University

The terahertz (THz) region in the Raman spectroscopy refers to 200 cm^{-1} or less in the relative wave number. This region has been measured for a long time by a Raman system with triple-monochromator. However, less expensive and compact Raman systems with notch filter + single-monochromator + cooled CCD detector have been used widely recently. The filters used for these systems hardly measure the THz region. Therefore, THz region is less and less measured in recent years. Although THz region is not particularly necessary for the identification of mineral phases, boson peaks in glasses and soft modes of phase transitions are present in this region, making important region for dynamical studies. This unfortunate situation is now over, as ONDAX developed a new filter which can go down to about 5 cm^{-1} (doi: 10.1063 / 1.3520137). We adopted this filter to our home-made micro-Raman system, and the THz region can now be observed routinely. In this talk, I will present details of our system, and also demonstrate some applications.
Our original system is backscatter geometry, and use a Raman edge filter of Semrock, and can measure down to 100 cm^{-1}. When measuring the THz region, the filter is replaced with the ONDAX's filter (SureBlock, 488 mm). Since single filter is about OD4, so two filters are necessary to observe Raman peaks. They must be tilted a few degrees with respect to the optical axis, so are mounted on the kinematic mounts of Thorlab. The intensity of the Rayleigh scattering is minimized by adjusting tilting angles. Since the transmittance is about 60%, one-third sensitivity drop is expected compared to original system.
Sulfur is measured first. Sulfur is known to have a Raman peak at 27 cm^{-1}. The peak was observed in both the anti-Stokes and Stokes sides. When silica glass was measured, a boson peak was observed as expected. Then, moganite phase of $AlPO_4$, which was reported before, was measured. Two new peaks in the THz region are found. Since moganite phase has a transition at high temperature like quartz phase, these peaks might be related to soft mode.
Alanine, one of the amino acids, were also measured. Alanine molecule has the chirality, and it is impossible to distinguished D- or L-alanine molecule by Raman spectroscopy. However, situation is different, if it crystallized. The D- or L-alanine and racemized DL-alanine now have different symmetry in crystalline states, which could now be distinguished by Raman spectroscopy. Since the difference is mainly reflected in the vibrations between the molecules, the difference is expected to appear at the THz region. Therefore, D-, L-, and DL-alanine crystals were measured and compared. It was found that D-, L-alanine and DL-alanine can be distinguished by Raman peaks in THz region. This could be used to study racemization process experimentally.

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