Phase transiton of $AlPO_4$-moganite: In-situ high-temperature Raman spectroscopic study

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Moganite-form of $AlPO_4$ has recently discovered as one of high-pressure phases (Kanzaki and Xue, 2012). Moganite is one of rare polymorphs of SiO_2, and its structure is closely related to twinned quartz. For SiO_2 -moganite, temperature-induced displasive transition has been reported (Heaney et al., 2007). However, pure phase sample is difficult to obtain, and accordingly quality of data by Raman or diffraction is not good. Although $AlPO_4$-moganite is easy to get pure phase, it is metastable at ambient pressure (moganite-SiO_2 is not stable phase ether). In this study, phase transition in $AlPO_4$-moganite was explored using in-situ high-temperature Raman spectroscopy up to 800 °C at ambient pressure. This transition was briefly mentioned in our 2011 this session talk, but completely new dataset, and additional low frequency data were obtained, and will be presented.

Used sample was same as that reported in our previous study (Kanzaki and Xue, 2012), and was synthesized at 5 GPa and 1500 °C. For heating, a wire heater was used (Kanzaki et al., 2012). Temperature was calibrated using 5~6 substances with known melting points. For Raman measurement, a home-built confocal micro-Raman system was used (488 nm laser, ~80 mW, 500 mm polychrometor, liquid N_2 cooled CCD detector). Initially, frequency region higher than 100 cm^{-1} was observed to 800 °C. Recently, our system is able to measure low frequency region, and two new peaks were identified at about 60 and 73 cm^{-1} at room temperature (see my talk last year). In order to check these peaks are soft mode or not, additional high-temperature study was conducted for < 100 cm^{-1} region. For the measurement, anti-Stokes and Stokes regions were observed simultaneously to identify true Raman peaks from the peaks originated from instrumental artifacts. The temperature is increased by 25 °C step, and increased up to 800 °C.

For the spectra measured above 100 cm^{-1}, several hard Raman modes displayed small shift to lower frequency with temperature. Above 425 °C, this trend was reversed or became nearly constant, and no discontinuity was observed. These results sugget that there is a displacive (higher order) phase transition at about 425 °C. For the region below 100 cm^{-1}, the 73 cm^{-1} peak showed significant temperature shift to lower frequency acompanyed with significant broadning on the peak width. The peak disappeared at 475 °C. From these results, this peak is considered as soft mode. The 60 cm^{-1} peak shifted just like the hard mode noted above, and still remained above 475 °C. At around 800 °C, berlinite (stable phase) was observed.

Our study confirmed that AlPO4-moganite indeed has the displacive transition, and identified soft mode. For SiO_2-moganite, only hard mode Raman was observed, and the transition temperature was determined as ~ 570 K (Heaney et al., 2007). No soft mode was reported to date. Our study suggests that soft mode for SiO_2-moganite may exist at lower frequency region not studied yet. There is some differences in the transition temperature between obtained from hard mode and from soft mode. This is likely due to thermal non-equlibrium in the sample as heating rate was faster for latter (low frequency run). Further study including remeasurement and measuremet at cooling process is in progress.

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