High temperature in situ Raman spectrum experiment of orthopyroxene

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In the Mg-rich portion of Mg2Si2O6-CaMgSi2O6 system, there had been the controversy about the appearance and stability of the Ca-poor orthopyroxene phase at high temperatures other than protoenstatite since the discovery by Foster and Lin (1975). Late in the 1980's, after going through the discussion on the relationship with Ca-free orthoenstatite, Carlson (1988) concluded that Ca-poor high temperature orthorhombic pyroxene (HT-Opx) was a thermodynamically distinct phase from Ca free orthoenstatite. However, there was no obvious experimental evidence that stands by his conclusion and there has been no direct observation of any transition into the HT-Opx. In recent years, Jackson et al. (2004) and Miyake et al. (2004) independently reported the transition to the high-temperature Ca-free orthoenstatite phase and described that this phase was same as HT-Opx. By using Ca-poor Opx, Ohi et al. (2006) described that the LT-HT phase transition of Opx was occurred at the temperature between 1170 and 1364 C by high temperature in-situ XRD. The aim of present study is to verify the temperature of this phase transition by using Raman spectroscopy.

The single crystal of Opx (Ca0.06Mg1.94Si2O6) was used in this study. The mixture of oxide in proportion of SiO2: CaCO3: MgO: V2O5 = 1.731: 8.003: 2.614: 0.095 (wt ratio) was kept at 1425 C for 24 h and then cooled at 0.5 C per hour to 1410 C. The single crystal was picked up from the synthesis sample for the present study.

The examinations of high temperature in-situ Raman spectroscopic analysis were carried out on a NRS-3100 (JASCO corporation) with a heating stage (Linkam TS1500), and the back-scattering spectra were obtained with the 514.5nm line from an argon ion laser. The laser power was ranging from 20 to 118.6 mW.

Raman spectra were sampled at 22, 400, 800, 900, 1000, 1100, 1140, 1180, 1220 and 1260 C on heating, and 1220, 1180, 1140, 1100, 1060, 1000 and 900 C on cooling. Because of the high intensity of back ground and peak broadening, it is hard to observe peaks at high temperature. The only three peaks, near 400, 650 and 1000 cm-1, could be observed in the Raman spectrum at 1260 C which was the maximum temperature in this study. Therefore, the peak shifts against temperature were mentioned about these three peaks.

The peaks were analyzed by fityk, peak fitting software. The peaks near 650 and 1000 cm-1 had binary peaks, which made the analysis difficult at high temperature. The peak near 400 cm-1 had a single peak and was easy to analyze. The wave number of the peak near 400 cm-1 decreased with increasing temperature. However, the variations of peak shift against temperature changed between 1100 and 1180 C. It showed that the LT-HT transition of Opx was occurred at the temperature between 1100 and 1180 C. It is consistent with the result of Ohi et al. (2006).