

Elastic geobarometry applied to omphacite: a Raman spectroscopy approach

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The widespread occurrence of omphacitic clinopyroxenes (a solid solution of jadeite, augite and aegirine, with the general chemical formula $(\text{Ca,Na})(\text{Mg,Fe}^{2+},\text{Al,Fe}^{3+})\text{Si}_2\text{O}_6$ in several geological settings and rock-types (e.g. high pressure eclogites, mantle xenoliths etc.), make them attractive to be exploited for Raman elastic geothermobarometry applications. Raman elastic geobarometry uses the deformation recorded by a mineral inclusion trapped in its host to retrieve the pressure and temperature conditions at which the inclusion has been entrapped [1], because Raman scattering is very sensitive to structural deformations in crystal structures developed upon heating or compression. Several host-inclusion systems have been studied so far, but clinopyroxene inclusions have not been thoroughly investigated yet. Therefore, the application of Raman elastic geobarometry to omphacites in various mineral hosts requires an accurate calibration of the Raman-peak positions against hydrostatic pressure. However, the Raman-peak positions and their pressure evolution depend also on the chemical composition. Besides, natural omphacite crystals can show a significant degree of cationic order related to the crystallization temperature, which can also affect the elastic behavior of omphacite.

To give an insight into the relation between the chemical order and pressure dependence of atomic dynamics, we have studied by in situ high-pressure Raman spectroscopy a series of crystals of omphacite from Münchberg Massif, Bavaria, Germany (peak conditions $P > 2$ GPa, $T = 600\text{--}650$ °C; [2]). The samples were free of iron, with compositions ranging between $\text{Jd}_{45}\text{Di}_{55}$ and $\text{Jd}_{52}\text{Di}_{48}$ and various degrees of cationic order achieved via isothermal annealing at different temperatures and for different times. We show that the pressure dependence of the wavenumber of the strongest Raman peak near 680 cm^{-1} is insensitive to the degree of chemical order, whereas the width of the same peak increases with cationic disorder and thus is indirectly related to closure temperature. To better understand the elastic behavior of the modes best suitable for elastic geobarometry, the Raman spectrum of a completely ordered omphacite of composition $\text{Jd}_{50}\text{Di}_{50}$, has been simulated at variable pressures with *ab initio* Hartree-Fock/Density Functional Theory simulations and compared with experimental spectra. The calculated data resulted to be in a good agreement with experiments and allowed us to understand changes in the pressure dependence of some modes. The experimentally obtained wavenumber-against-pressure trends can be potentially used to estimate the entrapment pressure of omphacite inclusions, assuming that they have the same chemical composition as the samples studied here. The dependence of Raman shifts on composition is planned as future work.

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