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Report:

Garnet and silicate spine1 are important phases in the Earths upper mantle and transition zone. The presence of Fe in these phases in natural samples such as inclusions recovered from diamonds has the potential of providing information about the oxidation state of the Earth's mantle, provided the thermodynamic properties of the redox reactions involving Fe^{2+} and Fe^{3+} are known. The major chemical component for Fe^{3+} in garnet corresponds to the chemical end-member named "skiagite", $Fe_3Fe_2Si_{3\,12}$, for which the reaction involving spine1 and pyroxene, $Fe_3Fe_2Si_3O_{12} = 4Fe_2SiO_4$ (spinet) + $FeSiO_3$ (pyroxene) + O_2,was recently calibrated as an oxygen barometer by Gudmundsson & Wood (1995) at low pressures. However, application of this reaction to the analysis of deep mantle samples, such as inclusions in diamond, requires consideration of the effects of pressure and temperature on the molar volumes of the components involved. We have therefore determined the room temperature equations of state of both skiagite and spine1 by high-pressure powder diffraction in diamond-anvil pressure cells.

Samples of skiagite and spine1 were synthesised from oxides at 1100°C and 9.7-9.0 GPa in a multi-anvil press at the Bayerisches Geoinstitut in Bayreuth. These samples were loaded in turn into diamond-anvil pressure cells of the BGI design (Allan et al., 1996), together with methanol:ethanol mixture as pressure medium, ruby as an indicator of approximate pressure and quartz to act as a precise internal pressure standard. Data were collected on ID30 with an A3-sized image plate located at approximately 30 cm from the sample position. A monochromatic wavelength of 0.51Å was chosen as it provides a reasonable compromise between diffraction signal to noise and resolution of the diffraction pattern. Care was taken to try and remove systematic errors from the experiment and thereby obtain accurate and precise unit-cell volumes at each pressure. Comparison of room pressure data from several different diamond-anvil cell mounts indicates that the precision of unit-cell volumes obtainable with this experimental configuration is 1 part in 2,000. This compares to a typical esd in volume obtained by fitting the diffraction patterns of 1 part in 5-10,000.

Data were collected from each samples at approximately 1 GPa intervals to a maximum pressure of 13 GPa. As expected, at pressures above 11 GPa diffraction patterns showed evidence of line-broadening due to non-hydrostatic stresses from the pressure medium; such data were discarded. Unit-cell parameters of the samples and the quartz were obtained by full-pattern (Le-Bail) refinement of l-dimensional intensity-28 plots obtained by integration of the images with Fit-2D. Pressures were determined by each data point from the measured unit-cell volume of the quartz and its equation of state (Angel et al., 1997). Equation of state parameters of spine1 and skiagite were obtained by a fully-weighted fit of a third-order Birch-Murnaghan EOS to the pressure-volume data. In all cases χ_w^2 of the fits were significantly greater than 1, indicating that the uncertainties in pressure (typically 0.01-0.02 GPa propagated from the esd of the unit-cell volume of quartz) and the esd of the volumes of the samples are both underestimated by esd's from pattern refinement alone.

For skiagite, a fit to 13 data points up to a maximum pressure of 11 GPa yields K_o = 157.4(3.0) and K' = 6.7(8). These results are comparable to majorite garnet ($MgSiO_3$) for which K_o - 160 GPa, and indicate that skiagite garnet is significantly more compressible than the major Al-bearing garnet endmembers almandine or pyrope (K, > 170 GPa). Two samples of spine1 with compositions intermediate between Fe_2SiO_4 and magnetite (Fe_3O_4) were measured. For X_{fay} = 0.60; Ko =172.6(4.3) and K' = 5.6(1.2) and for X_{fay} = 0.45; Ko = 174.0(9) and K' = 4.0(9). A combined fit to all the spine1 data (n=24) yields Ko = 168.9(1.2) and IS = 5.7(1.2). Constraining K' = 4 yields Ko = 175.5(1.4). The spine1 solid solutions have smaller bulk moduli compared with literature values for either magnetite or Fe_2SiO_4-spinel. The incorporation of Fe^{3+} into Al-rich garnet and silicate spine1 acts to reduce the isothermal bulk modulus of both phases.

References

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