1.4.26

Microscopic strain-macroscopic thermodynamic relationships in garnet solid solutions: A synchrotron study

M. DAPIAGGI[1], C. A. GEIGER[2] AND G. ARTIOLI[1]

[1] Dipartimento di Scienze della Terra, Università di Milano, via Botticelli 23, I-20133, Milano (Italy)
[2] Institut für Geowissenschaften, Universität Kiel, D-24098 Kiel (Germany) (chg@min.uni-kiel.de)

Pyrope-grossular ($Mg_3Al_2Si_3O_{12}$ - $Ca_3Al_2Si_3O_{12}$) solid solutions show marked positive deviations from thermodynamic ideality [1]. The enthalpic nonideality, i.e. $\Delta H^{mix} > 0$, is thought to result from microscopic elastic strain caused by the substitution of differently sized Ca and Mg atoms in the triangular dodecahedral site. Although progress has recently been made in demonstrating this [2,3], good experimental data measuring local structural strain are scarce to nonexistant. It is possible, however, to determine strain associated with substitutional solid solutions by means of peak shape analysis of high-resolution X-ray synchrotron powder diffraction data. This was done for the first time using nine well characterized synthetic Py-Gr garnets from data obained at the ESRF. Data were collected at temperatures between 5 K to 300 K. The low temperature data help minimize dynamic effects and enable the strain component to be measured better from the line profiles. The diffraction experiment intrinsically probes strain over length scales comparable to those of the crystal domains (10^3 Å).

The results show that the two end-members Gr and Py have the lowest strain, while the solid solutions display 'positive excess' structural strain across the join. This microscopic strain correlates well with the calorimetrically determined macroscopic $\Delta H^{mix} > 0$. The asymmetric ΔH^{mix} behavior can even be reproduced, where the largest deviations are at Py-rich compositions. It is concluded that positive enthalpies of mixing in Py-Gr garnets are largely due to local elastic strain energies arising from the Mg-Ca cation exchange. Synchrotron radiation provides a powerful experimental method to investigate the nature of strain density in a material and specifically the physcal reasons relating to thermodynamic nonideality in solid solutions. Diffraction measurements may even offer an alternative method for the evaluation of ΔH^{mix} when calorimetric measurements can not be undertaken.

References

[1] Geiger C.A. (1999) *Min Pet*, **66**, 271-299.
[2] Bosenick A., Dove M.T. and Geiger C.A. (2000) *PCM*, **27**, 398-418.
[3] Boffa Ballaran T., Carpenter M.A., Geiger C.A. and Koziol A., (1999) *PCM* **26**, 554-569.

1.4.28

Phase relations in the hematite-ilmenite series: Crucial in acquiring and preserving crustal magnetism

P. ROBINSON[1], R. J. HARRISON[2], S. A. MCENROE[1], F. LANGENHORST[3] AND F. HEIDELBACH[3]

[1] Geological Survey of Norway, N-7491, Trondheim, Norway (peter.robinson@ngu.no)
[2] Cambridge University, Cambridge, U.K.
[3] Bayerisches Geoinstitut, Universität Bayreuth, Germany

Phases studied are $R\bar{3}PM$ paramagnetic ilmenite, $R\bar{3}cPM$ titanohematite, CAF canted-antiferromagnetic hematite, and metastable $R\bar{3}FM$ ferrimagnetic ferri-ilmenite. CAF hematite is weakly magnetic. FM ferri-ilmenite can be strongly magnetic, if preserved by rapid cooling, but only at 280°C and below. None of these explain strong and stable remanent magnetizations, and high-T thermal stabilities up to 630°C, of slowly cooled, highly exsolved members of the series, shown by TEM to have lamellae down to 1-2 nm thick (one unit cell). Atomic simulations of lamellar contacts showing hybrid "contact layers" between ilmenite and hematite in intergrowths led to a theory of "lamellar magnetism" (LM). Single lamellae have a ferrimagnetic moment, 2Mc – 1 Mh, where Mc = contact layer moment, Mh = one unbalanced Fe^{3+} hematite layer moment. Magnetically and atomically simulations require even numbers of layers, and lamellae, odd numbers of layers including contact layers, constraining placement of lamellae in relation to magnetism. Moments of contact layers are antiferromagnetically coupled to adjacent hematite, so LM has hysteresis and thermal demagnetization properties of hematite, but can be stronger. Strong LM depends on stable or metastable reactions with high lamellar yield, production of abundant fine lamellae, and an external force causing lamellae to be magnetically in-phase. The earth's field is most effective in producing in-phase LM in rocks with a strong lattice-preferred orientation of 0001 planes parallel to the field. In nature, hematite with exsolved ilmenite could generate a saturated magnetic moment per unit volume of ~150 kAm^{-1} (magnetite: 480 kAm^{-1}).

LM is a chemical remanence produced at nucleation, where host or lamella is CAF hematite, at lower T than demagnetization in short experiments. One-atm. diagrams show where magnetic effects may be produced by combined stable/metastable equilibria. Natural sample analyses suggest effects of minor components, especially $MgTiO_3$, and questions about effects of pressure on miscibility gaps and magnetization T's. CAF hematite has a ferromagnetic moment 90° from the sublattice magnetizations of Fe^{3+} in octahedral layers. LM may also be spin-canted, but only where significantly out-of-phase. Moments of strong LM will be quasi-parallel to sub-lattice magnetizations and one *a*-crystallographic axis. These relationships are being tested on large hemo-ilmenite single crystals using a cryogenic magnetometer and electron-backscatter diffraction.