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Hard Mode Infrared Spectroscopy applied to the study of solid solutions

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During the last three decades Hard Mode Infrared Spectroscopy has been widely used as an analytical tool for the study of phase transformations. In fact information about the width of individual phonon bands can be used to follow variation of the order parameter for a phase transition quantitatively. Recent experience has shown that peak shifts and line-width variations of phonon spectra can be used to detect the structural response to any local changes associated not only with phase transformations but also with cation substitution. The underlying hypothesis is that the mechanism by which most materials accommodate atoms of different sizes involves elastic distortions. Non-ideal mixing in solid solutions can be therefore understood in terms of local strain heterogeneities arising from the replacement of a cation by another. We can, therefore, expect that such local distortions give rise to spectral line broadening. Typically IR powder-absorption spectra of silicate minerals are very complex and unambuguous fits of overlapping peaks are limited. However, given that any line broadening contains, in principle, information about the local structural properties, a more general method which makes use of the autocorrelation function [1] has been used to extract effective or average line widths and obtain new insight on the microscopic mechanism of solid solution formation.

Local strain fields in a variety of silicate solid solutions have now been characterised by IR spectroscopy. There are enough data to start showing systematic variations of line broadening with excess enthalpy of mixing. These in turn correlate semi-quantitatively with bulk modulus. In other words, the thermodynamics of solid solution formation probably can be understood in terms of essentially elastic effects. Solid solution mechanisms in carbonates and oxides are expected to be different, but there are, as yet, limited IR data for these.

Reference

[1] Salje E.K.H., Carpenter, M.A., Malcherek T.G.W., and Boffa Ballaran T. (2000) *EJM* **12,** 503-519.

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Local and macroscopic strain in the barium aluminate - strontium aluminate solid solution

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Phase transitions are commonly investigated in chemically pure materials. It is well known, however, that even minor impurities can significantly affect their transformation behaviour and that physical properties which depend on phase transitions can be tailored by careful selection of chemical substitutions across a solid solution. Common to these considerations is the role of strain. Spontaneous strains at phase transitions are associated with changes in elastic energy and the replacement of one atom by another in a solid solution can be understood in terms of elastic strain fields. The barium aluminate ($BaAl_2O_4$) – strontium aluminate ($SrAl_2O_4$) solid solution provides an opportunity to examine such strain effects as it displays three different displacive transitions, each with a different dependence on composition.

$BaAl_2O_4$ and $SrAl_2O_4$ belong to the large group of stuffed tridymite structures. The ionic radii of Ba^{2+} and Sr^{2+} differ by ~10% and the enthalpy of mixing of the solid solution is expected to have a positive deviation from ideality. The phase transitions which have been observed are a hexagonal – monoclinic (proper ferroelastic) transition at Sr-rich compositions, a hexagonal – hexagonal (improper ferroelectric) transition at Ba-rich compositions and a different hexagonal – hexagonal transition at intermediate compositions. The latter involves an increase of the *a* lattice dimension by a factor of $\sqrt{3}$. IR powder absorption spectra for samples with different compositions collected in-situ at a range of temperatures have been analysed using the autocorrelation method. The resulting line broadening parameters, Δcorr, confirm the positive deviation from ideal mixing but are also reduced as a consequence of the phase transitions. There is a correlation between the magnitudes of the spontaneous strains and the magnitudes of the changes in Δcorr. It appears that the breaking of symmetry at phase transitions allows additional mechanisms for local structural relaxations which help to relieve, at least in part, local strains in the solid solution due to cation substitutions.