Hard mode infrared spectroscopy of plagioclase feldspars

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Abstract: Local states of order and the character of phase transitions in a suite of natural and heat-treated plagioclase feldspars have been examined by Hard Mode Infrared Spectroscopy at room temperature. Autocorrelation analysis has been used to determine variations of average linewidths of groups of peaks in the primary IR spectra. Changes in frequency of selected peaks and an autocorrelation parameter from the frequency range 500–650 cm⁻¹ scale with the square of the macroscopic order parameter for the $C\bar{T} \leftrightarrow \bar{I}$ transition. Combining the autocorrelation data, which provide information relating to the local (unit-cell) scale behaviour, with lattice strain, which indicates the average macroscopic behaviour, leads to a qualitative differentiation between the two incommensurate phases, $e_1$ (An-rich) and $e_2$ (Ab-rich). Within individual domains of the $e_1$ structure in crystals of composition ~An70, the local homogeneity and Al/Si ordering conformation appear to be indistinguishable from $\bar{I}$ structural states. The degree of $\bar{I}$ order diminishes with increasing Ab-content and would extrapolate to zero somewhere between ~An40 and ~An50. The $e_2$ structures appear to relate to the Al/Si ordering of albite but retain a degree of heterogeneity on a phonon length scale which is comparable to that found in disordered $C\bar{T}$ crystals. On the length scale of the IR experiments, there is an abrupt cut off for the formation of $P\bar{T}$ domains between ~An86 and ~An90 as Ab-component is added to anorthite. Transitions of the type $C\bar{T} \leftrightarrow \bar{I}$, $\bar{I} \leftrightarrow P\bar{T}$ and $P\bar{T} \leftrightarrow e_1$ appear to be continuous as a function of composition at a local structural scale. Deviations from ideal mixing in the heat-treated series arise from Al/Si ordering at An-rich compositions.

Key-words: IR spectroscopy, plagioclase feldspar, phase transitions, Al/Si ordering.

Introduction

Plagioclase feldspars are among the most studied of minerals, due both to their abundance in the earth’s crust and to the complex nature of their subsolidus behaviour. An understanding of their thermodynamic properties would be of value to petrologists but, owing to the combination of chemical substitutions, displacive phase transitions, cation ordering and miscibility gaps found in natural and experimental samples, a comprehensive thermodynamic model for the solid solution remains elusive. A fundamental problem has been that the structural information obtained from X-ray diffraction studies represents some average over many unit cells and that the true local states of order, on a unit-cell scale, may be different.

The primary objective of the present study was to use Hard Mode Infrared Spectroscopy (HMIS) to investigate these local states of order and compare them with the known macroscopic behaviour. Particular focus has been on the local structural variations accompanying $C\bar{T} \leftrightarrow \bar{I}$, $C\bar{T} \leftrightarrow e_2$ and $\bar{I} \leftrightarrow e_1$ transitions, where $e_1$ and $e_2$ represent incommensurate phases of the plagioclase solid solution. A recent study of sodic pyroxenes has shown that a new technique for quantifying line broadening in IR spectra also provides a different perspective on the overall mixing behaviour of solid solutions (Boffa Ballaran et al., 1998). This technique, based on the autocorrelation function, is applied to plagioclase feldspars for the first time.

Significant advances have been made in the last few years in the use of HMIS as a probe for...