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Incommensurate to normal phase transition in malayaite

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Abstract

We report variable temperature X-ray diffraction (20 K < T < 295 K) and Raman scattering (90 K < T < 400 K) data of malayaite, the tin analog of the mineral titanite, aided by results from density functional perturbation theory. The phase transition from the normal to the incommensurately modulated crystal structure occurs at $T_c = 50 \pm 2$ K with an almost constant **q**-vector of 0.27**b***. Some first order satellite diffraction maxima are observable up to 55 K, where they increasingly broaden toward the main reflections. Softening of the lowest frequency transverse optical B_g phonon mode, dominated by antiparallel motion of Ca atoms, is observed on cooling from 400 to 90 K. This confirms the displacive character of the transition to the modulated structure, indicated by the instability of this phonon mode in the zero-temperature approximation of first principle computation. The transition to the incommensurately modulated phase is preceded by a temperature region of anomalous thermal expansion in the normal phase, marked by negative thermal expansion along [010] and consequently a change from hardening to softening phonon modes on cooling below 150 K. The modulated phase of malayaite highlights the potential of density functional perturbation theory for the discovery of hitherto unknown ground state structures of minerals.

Keywords: Phase transition, phonon softening, 1d-modulation, thermal expansion, synchrotron XRD