A high-resolution powder neutron diffraction study of the crystal structure of neighborite (NaMgF$_3$) between 9 and 440 K

KEVIN S. KNIGHT[1,2,*]

[1]ISIS Facility, STFC Rutherford Appleton Laboratory, Harwell Oxford, Didcot, Oxfordshire OX11 0QX, U.K.
[2]Department of Earth Sciences, The Natural History Museum, Cromwell Road, London SW7 5BD, U.K.

ABSTRACT

The temperature dependence of the unit-cell dimensions and the crystal structures of the fluor-perovskite neighborite, NaMgF$_3$ (analyzed in the *Pbnm* setting of the space group), have been determined at 88 temperatures between 9 and 440 K from high-resolution, time-of-flight, powder neutron diffraction data. Lattice parameters exhibit saturation at low temperatures, before developing linear thermal expansion coefficients at temperatures above ~350 K. The temperature dependence of each axis has been analyzed, and fitted, using a two-term expression related to an Einstein internal energy function. The unit-cell parameters *a* and *c* behave in a conventional manner, however, an unexpected, and previously unobserved, region of negative linear thermal expansion has been found for the *b* axis in the temperature interval $20 \leq T \leq 90$ K. Estimated, high-temperature axial thermal expansion coefficients derived from the lattice parameter fitting are in good agreement with those experimentally determined from an earlier synchrotron study, and indicate that high-temperature saturation has been achieved in neighborite by 440 K. The unit-cell volume varies smoothly and monotonically over the whole temperature interval, and the two-term Debye model of Barron has been successfully used to fit these data with characteristic temperatures of 369(2) and 1055(14) K. For the temperature interval 313.15–443.15 K, the thermodynamic Grüneisen constant has been determined using the Debye parameterization of the unit-cell volume, coupled with literature values of the isobaric molar heat capacity. The evolution of the crystal structure as a function of temperature is presented, and explained, in terms of the temperature dependence of the amplitudes of the seven symmetry-adapted basis-vectors of the aristotype phase that are consistent with the orthorhombic space group. The calculated temperature variations of the bond lengths are in excellent agreement with those experimentally determined. The primary order parameters for centrosymmetric, zone-boundary phase transitions in perovskite-structured compounds, i.e., the amplitudes of the basis vectors that transform as the irreducible representations R_4^+ (anti-phase tilt) and M_3^+ (in-phase tilt), have been fitted to a Landau free energy expansion that incorporates low-temperature saturation. Within the temperature range studied, the temperature dependence of the displacement corresponding to the anti-phase tilt is consistent with tricritical behavior. Experimental evidence is presented for a quadratic coupling of the in-phase tilt to the anti-phase tilt for temperatures greater than ~135 K, suggesting critical behavior at the orthorhombic–cubic transition is purely related to an instability at the R point of the pseudocubic Brillouin zone.

Keywords: Neighborite, Rietveld refinement, crystal structure, neutron diffraction