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

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**ABSTRACT**

The temperature dependence of the unit-cell dimensions and the crystal structures of the fluoroperovskite 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 $\sim$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 describe the temperature variation of the bond lengths. 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 $R_{\pm}^4$ (anti-phase tilt) and $M_{\pm}^3$ (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 $\sim$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

**INTRODUCTION**

For over 30 years, the thermoelastic, physical, and structural properties of the fluoroperovskite mineral neighborite (Chao et al. 1961), NaMgF$_3$, has been used as an isostructural, isoelectronic, easily synthesized stable phase to provide experimental insight into the potential behavior of mantle MgSiO$_3$ perovskite (O’Keeffe et al. 1979; O’Keeffe and Bovin 1979; Cheeseman and Angell 1981; Anderson et al. 1985; Zhao et al. 1993a, 1993b, 1994a, 1994b; Mitchell et al. 2007). In the original mineralogical description of neighborite (Chao et al. 1961), the space group setting $Pcmn$ of $Pnma$ was chosen by analogy with earlier work carried out on CaTiO$_3$ perovskite (Kay and Bailey 1957).

Subsequent crystallographic investigations of neighborite have settled on the alternative setting of the space group $Pnma$, space group $Pbnm$ (Zhao et al. 1993a, 1993b, 1994a, 1994b; Mitchell et al. 2007), and it is this setting that we use in the work to be described in detail below.

Experimental investigations of neighborite have included the determination of the elastic moduli (Zhao and Weidner 1993), the temperature dependence of the isobaric heat capacity above room temperature (Topor et al. 1997) and the equation of state (Liu et al. 2005; Martin et al. 2006). Contradictory experimental results were found for the presence of superionic conductivity in neighborite at high temperatures (O’Keeffe and Bovin 1979; Anderson et al. 1985), which remain to be resolved. The crystal structure of neighborite has been determined at high temperatures (Zhao et al. 1993a, 1993b), at low temperatures (Mitchell...