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A high-resolution neutron powder diffraction study of the low-temperature structural phase transitions in $RbCaF_3$ perovskite

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ABSTRACT

The temperature dependence of the crystal structure and thermoelastic properties of $RbCaF_3$ perovskite are reported from a high-resolution neutron powder diffraction investigation in the temperature interval 2–300 K. Two phase transitions have been identified from these data, the first from space group $Pm\bar{3}m$ to $I4/mcm$, at 200 K, has been well characterized in earlier studies, the second, from space group to $I4/mcm$ to $Pbnm$ has previously been less well understood. New results from the former transition show the order parameter evolves with a critical exponent of 0.284(5), and the phase is characterized by an Einstein temperature of 192(8) K, and a Debye temperature of 270(10) K. The temperature variation of the tetragonal spontaneous strain in this phase is consistent with an additional fourth order invariant in the Landau potential. The second phase transition is found to be strongly first order and a temperature dependent, and heating rate/cooling rate dependent phase coexistence is found at all temperatures below ~ 80 K on heating, and ~ 65 K on cooling. The evolution of the orthorhombic unit cell is atypical in the region of the phase transition, with a and b exhibiting strong negative linear thermal expansion, whilst the c axis behaves in the expected manner. The crystal structure of the $Pbnm$ phase at 2 K is reported from an unconstrained Rietveld refinement for the first time.

1. Introduction

Brillouin zone-boundary ferroelastic phase transitions in perovskite-structured compounds (ABX_3) remain a challenging problem crystallographically for 3 principal reasons. Firstly, in the majority of perovskite-structured compounds, the anion species (X) are generally light atoms, usually oxygen, less commonly fluorine, rarely heavier halogens, and in all cases the cations (A, B) are present in a pseudo-body-centred cubic array [1]. Secondly, in single crystals, the presence of twinning that arises due to symmetry descent from the aristotype phase (or an alternative higher symmetry phase) [2] can prove difficult to disentangle when the twin density is high due to limitations in instrumental resolution in direct space [3]. Finally, the structural phase transitions are frequently accompanied by the development of small spontaneous strains [4] that arise from the relative rotations of the corner-shared constituent BX_6 octahedra. As a result, X-ray powder diffraction data collected at modest resolution can appear to be derived from a pseudo-body-centred cubic phase, where the fundamental reflections are moderately line-broadened, and the diagnostic super-lattice reflections are weak, and difficult to characterize. The light atom sensitivity of neutron diffraction obviates the first of these problems, however it is still necessary to collect neutron diffraction data at as high a resolution as possible to derive the correct unit cell metric and to determine the nature of the spontaneous strains that develop. Despite the loss of information that arises from Bragg reflection overlap, powder diffraction techniques probably represent the optimum method for the initial structural characterization of perovskite-structured compounds. As a result, high resolution neutron-based powder diffraction reinvestigations of apparently well-studied materials can sometimes yield unexpected results; recent examples include the correct identification of the high temperature phases of $SrZrO_3$ [5], the resolution of the ambient temperature crystal structure of natural “sodium niobate” (lueshite) [6] and the recent observation that at room temperature, $NaTaO_3$ is in fact a mixed phase, pinning an intermediate phase at an incomplete high temperature structural phase transition [7].

The high electronegativity of fluorine (3.98, Pauling scale) results in different bonding environments in metal fluorides than that seen in the isoelectronic oxides (O, 3.44) resulting in subtle differences in the crystal chemistry and reactivity. The bulk moduli of fluoroperovskites are in general significantly smaller than those of the oxide equivalents, and hence phase transitions to higher density phases occur at lower,

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more experimentally accessible pressures. As part of a programme of work to study the structural crystallography of fluoroperovskites [8–13] as possible analogue phases for use in investigations of the perovskite-post-perovskite structural phase transition in lower mantle $MgSiO_3$, we have reinvestigated the structural crystallography of the low temperature phase transitions in $RbCaF_3$ using high resolution neutron powder diffraction.

At ambient temperature and pressure, $RbCaF_3$ is found in the perovskite aristotype structure, space group $Pm\bar{3}m$(Wyckoff positions: Rb 1*b*, Ca 1*a*, F 3*d*), with Modine and co-workers first determining the presence of low temperature structural phase transitions at temperatures of 198, 43, and 10 K [14]. Using quantitative optical birefringence and electron paramagnetic resonance (EPR) (Fe^{3+} doping for Ca), the 198 K transition was found to be associated with the condensation of a single component of the triply degenerate phonon mode with irreducible representation R_4^+ and an accompanying symmetry change to a tetragonal structure in space group $I4/mcm$ [15]. At temperatures close to the 198 K transition temperature ($1 < T/Tc \leq 0.85$, transition temperature Tc), the birefringence and the b_2^0 parameter for the fine-structure splitting were consistent with a critical exponent of $\beta = 0.25$ (tricritical behaviour), however at lower reduced temperatures, this value apparently increased to $\beta = 0.5$ (second order behaviour). The results from isobaric heat capacity measurements in the vicinity of the 198 K phase transition have not provided a definitive answer to the nature of this transition as they appear to be irreproducible, and hence could possibly be related to issues of sample purity [16,17]. Ho and Unruh [16] found a sharp spike in the isobaric heat capacity at the 198 K transition with the liberation of latent heat i.e. evidence of a first order, not tricritical transition; by contrast, Koussina et al. [17] only determined a broad maximum in the heat capacity at the same temperature.

The p – T phase boundary of the $Pm\bar{3}m - I4/mcm$ phase transition has been investigated at low pressures by EPR [18] and nuclear magnetic resonance (NMR) [19], and at higher temperatures and pressures, by neutron powder diffraction (NPD) [10,20]. A self-consistent Clapeyron slope of 33.7 K GPa^{-1} was found between the EPR [18] and the room temperature neutron diffraction measurements [10] (note a typographical error in the abstract of [10] for the units of the Clapeyron slope which reads 10^{-5} GPa K^{-1} rather than the correct value of 10^{-2} GPa K^{-1}). The NMR results are inconsistent with both these measurements, and, in addition, the full phase diagram [20] ($0 \leq p \leq 8$ GPa; $100 \leq T \leq 500$ K), and indicate an apparent Clapeyron slope of 272 K GPa^{-1}, a factor of ~ 8.5 too high. We have no explanation for the significantly different Clapeyron slope derived from NMR, when compared to EPR/NPD.

Further experimental evidence for the 198 K transition being weakly first order, rather than tricritical, is afforded by Rietveld refinement of NPD data [21], the spontaneous birefringence [22], high resolution X-ray double-crystal diffractometry [23], Raman hard mode spectroscopy [24], and the temperature dependence of superlattice reflections measured at the R point of the pseudocubic Brillouin zone [25]. The temperature dependence of the octahedral tilt angle (the primary order parameter) in the tetragonal phase showed critical behaviour with an exponent of 0.27 [21], not the expected value of 0.25. A higher value of the critical exponent than 0.25 was mirrored in the EPR measurements [14], the Raman hard modes [24], and the integrated intensities of the superlattice reflections [25]. Double crystal diffractometry indicated that a small, but measureable, lattice parameter discontinuity existed at the transition temperature [23], whilst optical measurements showed a similar discontinuity in the spontaneous birefringence [22]. The ambient temperature volume discontinuity between the cubic and tetragonal phases at the transition pressure of ~ 2.8 GPa is significantly higher [10] than that corresponding to the 198 K transition at ambient pressure [23]. Hence, the nature of the weakly first order $Pm\bar{3}m - I4/mcm$ phase transition clearly becomes more strongly first order with pressure at ambient temperature.

By contrast with the weakly first order structural phase transition at 198 K, the nature of the lower temperature structural phase transitions appears to be strongly first order. The lower-temperature phase transitions were observed as abrupt changes in the crystal field parameters derived from the EPR measurements [14], heat capacity anomalies [16,17], and peaks in the dielectric loss [14]; all experimental measurements indicated significant hysteresis at these phase changes. However, as observed in the 198 K transition, the heat capacities of the lower temperature transitions are irreproducible, with either a small cusp being found between 48 K and 52 K [16], or a broad excess heat capacity anomaly starting at ~ 61 K [17]. The nature of the 10 K transition, or even its existence, has yet to be satisfactorily confirmed or characterized by calorimetry.

The structural crystallography of $RbCaF_3$ below 70 K has been investigated by neutron powder diffraction [21] and a complete transition to a structure in space group *Pnma* (pseudocubic metric $2a = 2c \neq 2b$, $\alpha = \gamma = 90°$, $\beta \neq 90°$; Glazer notation $a^-b^+a^-$ [27]) was identified at temperatures below 11 K [26]. Due to instrumental resolution limitations, however, the crystal structure of this phase could not be accurately determined, and a set of strict constraints had to be applied for least squares convergence (pseudocubic metric fixed at $2a = 2b = 2c$, $\alpha = \beta = \gamma = 90°$, anion displacements fixed with Glazer notation $a^-a^+a^-$).

To enable a more detailed crystallographic investigation of $RbCaF_3$ at low temperatures, we have utilised a high resolution, neutron time-of-flight diffractometer with an approximately Q-independent resolution function ($Q = 4\pi\sin(\theta)/\lambda$).

2. Experimental

Close to phase-pure, polycrystalline $RbCaF_3$ was prepared from a stoichiometric mixture of RbF and CaF_2 which had been pre-dried at 473 K for 24 h. The reactants were intimately mixed, ground and pre-fired at 773 K for 6 h. After the initial calcination and grinding, the sample was heated at 973 K for 18 h with a number of intermittent coolings and re-grindings. Phase purity was confirmed by X-ray powder diffraction and Rietveld refinement of neutron powder diffraction data ($RbCaF_3$ 98.8 wt%, CaF_2 1.2 wt%).

Low-temperature neutron diffraction data were collected using the high resolution powder diffractometer HRPD of the ISIS neutron spallation source of the Rutherford Appleton Laboratory. A 1.5 cm thick aluminium sample container of slab geometry, equipped with vanadium front and back windows, was lightly filled with $RbCaF_3$ powder. Heat was supplied directly to the sample via a 100 W cartridge heater inserted into the side wall of the sample container; temperature control was provided by a Rh/Fe sensor inserted into the opposite side wall of the sample can. Thermal contact between sample can, sensor and heater was ensured using Jet Lube SS-30 copper anti-seize paste, thermal equilibration in the sample was achieved by 3 kPa of helium exchange gas. A gadolinium mask was used to avoid contaminant Bragg peaks in the collected data from either the sample container or the thermometry; locating screws were masked from the incident neutron beam by thin cadmium foils.

High resolution neutron powder diffraction data were collected using the single time-of-flight window of 30–130 ms, which corresponds to a *d*-spacing range of ~ 0.60 to ~ 2.60 Å in the high resolution backscattering detector bank, and ~ 0.86 to ~ 3.73 Å in the medium resolution, high count-rate 90° detector bank. The sample container was attached to a centre stick and placed in an AS Scientific "Orange" cryostat and cooled to 2 K using a Roots pump. Data were collected at 2 K, 10 K, and in 10 K steps to 70 K for data collection periods of 40 μA h, from 80 K to 190 K in 10 K steps for 20 μA h, from 192 K to 200 K in 2 K steps for 20 μA h, 205 K, 210–300 K in 10 K steps for 7 μA h. To investigate the low temperature hysteresis, the sample was then cooled to 65 K and data were collected in 10 K steps on cooling to 15 K in 10 K steps for 40 μA h. Finally a data set was collected at 5 K for 40 μA h. The sample was permitted to equilibrate at the set point temperature for 10