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Low temperature, high pressure thermo-physical and crystallographic properties of $KZnF_3$ perovskite

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HIGHLIGHTS

- 2-term Debye model for $KZnF_3$ perovskite proposed.
- New equation of state data presented.
- Consistency between ab-initio calculation, elastic constants and experimental bulk modulus found.

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ABSTRACT

The thermoelastic, and low temperature and high pressure crystallographic properties of the cubic perovskite $KZnF_3$ have been investigated at 41 temperatures between 7 K and 305 K, and at 19 pressures between 0.07 and 6.38 GPa. Using supplementary literature values of the low temperature isobaric heat capacity, the thermoelastic properties of $KZnF_3$ are well described by the two-term Debye model of Barron with characteristic temperatures 281 K, and 440 K, and mean Grüneisen constant of 1.43. The isothermal bulk modulus has been determined from a Birch-Murnaghan second order equation-of-state as 81.2 GPa, in excellent agreement with prior measurements of the elastic stiffnesses. The measured bulk modulus is consistent with the approximate linear trend with inverse molar volume that has been observed in other $A^IB^{II}F_3$ perovskite-structured compounds. Despite the simplicity implicit in the two-term model, the calculated phonon density of states has features in common with the full vibrational density of states calculated from the measured phonon dispersion curves.

1. Introduction

Fluorperovskites, $A^IB^{II}F_3$ perovskite-structured compounds, have been studied for many decades, initially as materials to investigate soft-mode phase transitions [1–4], but more recently as a host structure that permits the dilute substitution of a number of optically active divalent, or trivalent ions on to an octahedral site with perfect (or nearly perfect) $m\bar{3}m$ point group symmetry [5]. In particular, $KZnF_3$ has been studied to investigate the interaction of Cu^{2+}-Mn^{2+} pairs [6], laser action of V^{2+} [7], Co^{2+} [8], and Cr^{3+} [9], and the Jahn-Teller effect for Fe^{2+} [10] and Cr^{3+} [11]; a comprehensive set of references has been given in the recent study of the crystal fields in Ni^{2+} doped material [5].

The geophysical properties of the Earth's lower mantle are conditional on having a detailed knowledge of the thermophysical properties of $MgSiO_3$ in both perovskite, and post-perovskite phases [12]. In the latter phase, extremes of pressure are required for stabilization, and hence studies of analogue phases have been carried out where the perovskite-post perovskite phase transition occurs at more easily experimentally accessible temperatures and pressures [13]. Fluorperovskites have proved to be ideal analogue materials to study the geophysical properties of the mantle and the mantle-core boundary, for example, it is possible to quench some materials in the post-perovskite structure, and the seismic velocity changes observed in the D″ region of the lower mantle have been interpreted by reference to experimental studies of $NaNiF_3$, and $NaMgF_3$ [12,13]. Furthermore, the compounds $KZnF_3$ [14], $KCaF_3$ [15,16], and $NaMgF_3$ [17] have been used as analogue phases in

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studies of the viscosity and electrical conductivity of the mantle.

In this manuscript we re-investigate the thermophysical properties of $KZnF_3$ perovskite using neutron diffraction techniques carried out at low temperature at ambient pressure, and high pressure at ambient temperature. These data will be of potential value in spectroscopic studies of pressure induced level crossings [18], as a baseline measurement for lattice parameter saturation in investigations of structural phase transitions using Landau theory and as an alternative compound for making geophysical property measurements.

2. Experimental

Phase pure $KZnF_3$ was synthesised using standard solution techniques [19] from reactant aqueous solutions of KF and $ZnCl_2$ according to the reaction shown below.

$$3KF(aq) + ZnCl_2(aq) \rightarrow KZnF_3(s) + 2KCl(aq).$$

The filtered $KZnF_3$ precipitate was washed using de-ionised water and filtered a further three more times to remove any remaining soluble KCl, before being finally dried at 100 °C in a muffle furnace. The dried powder was then annealed at 600 °C under an argon atmosphere for 24 h, before being lightly ground to produce a sample suitable for neutron powder diffraction.

High resolution neutron powder diffraction data were collected on the HRPD (High Resolution Powder Diffractometer) instrument at the ISIS neutron spallation source using the single time-of-flight window of 30–130 ms, which corresponds to a *d*-spacing range of ~0.60–~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. An aluminium sample container of slab geometry, 1.5 cm thick, with vanadium front and back windows, was lightly filled with $KZnF_3$ powder. Temperature control was provided by a Rh/Fe sensor inserted into one wall of the sample can, with heat supplied by a 100 W cartridge heater inserted into the opposite wall; excellent thermal contact between can and thermometry was ensured by the use of Jet Lube SS-30 copper anti-seize paste. To avoid contaminant Bragg peaks in the collected data, from either the sample container or the thermometry, a thin gadolinium mask was fixed to the front window of the sample can. The sample container was attached to a centre stick and placed in a Sumitomo RDK-415D top loading close cycle refrigerator (CCR), and a set point temperature of 305 K was applied to the sample, with the set point to the CCR 50 K lower. The sample was then equilibrated at 305 K for 1 h before data collection commenced. Data were collected at 305 K, and in 10 K steps on cooling down to 105 K, thereafter in 5 K intervals to 10 K, with a single data collection made at 7 K, the sample base temperature using the CCR. For all sample temperatures down to 70 K, the CCR set point was 50 K lower; below 70 K, the CCR was permitted to cool to its own base temperature. A 5 min thermal equilibration period was applied once the sample had reached its set point temperature. Sample temperature stability was better than ±0.2 K of the set point temperature for all measurements made. Data collection times were 12 μAh (approximately 17 min) at all sample temperatures with the exception of the 7 K run which was measured for 100 μAh (approximately 2.5 h).

The time-of-flight data were normalised, corrected for detector efficiency and solid angle variations, and finally for self-shielding in slab geometry for the two detector banks ($N/V = 5.32 \times 10^{21}$ cm^{-3}, $\sigma_s = 18.145$ b, $\sigma_a = 3.239$ b at $\lambda = 1.798$ Å [20]). Two data sets in the time-of-flight range 32–120 ms for $2\theta = 168.33°$, and $2\theta = 90.00°$ were analysed in multi-bank Rietveld refinement using the GSAS suite of programs [21].

For the high pressure measurements, approximately 60 mm^3 of powdered $KZnF_3$ was loaded into a null scattering Ti-Zr alloy capsule gasket [22] with a small pellet of lead being placed in the centre of the sample to act as a pressure marker. To enable hydrostatic conditions, the sample was moistened with a few drops of perdeuterated 4:1 methanol-ethanol pressure transmitting fluid, before the gasket was closed. The capsule was placed in zirconia-toughened-alumina anvils [23] and the whole assembly was then loaded into a type-V3b Paris–Edinburgh press and finally located and aligned within the sample vacuum tank of the PEARL beamline neutron time-of-flight diffractometer [23] of the ISIS neutron spallation source. The sample pressure was varied by changing the load applied to the capsule assembly between the opposed anvils of the press.

Ambient-temperature, high-pressure neutron powder diffraction data for the *d*-spacing interval $0.46 < d < 4.1$ Å were collected using the main $2\theta = 90°$ bank of the PEARL diffractometer. Data sets suitable for Rietveld refinement were obtained after electronically focusing the individual detector element spectra, normalization of these summed patterns with respect to the incident beam monitor and the scattering from a standard vanadium sample. Finally, a correction for the wavelength and scattering-angle dependence of the neutron attenuation by the anvil and gasket materials [23] was applied. Data were collected at nineteen separate loads: ~9 tonnes (1 tonne = 1 Mg) load, 11, 13, 15, 17, 19, 21, 23, 25, 27, 28.5, 30, 35, 40, 45, 50, 55, 60 and 65 tonnes. Data collection times averaged approximately 1 h for a given data point.

3. Results

Convergence from the ideal aristotype crystal structure was rapid for all temperatures for a model of 1 lattice parameter, isotropic atomic displacement parameters for the cations, anisotropic atomic displacement parameters for the anion, 2 scale factors, and 10 Chebychev polynomials to describe the background functions (5 for each bank). The line shape parameters, the time-of-flight to Å calibration for the $2\theta = 90.00°$ bank, and the quadratic term for the $2\theta = 168.33°$ bank were determined from the 7 K refinement and fixed at these values for all the higher temperature measurements. Typical high and low temperature results are listed in Table 1, and the quality of fit shown is in Fig. 1 for the 7 K data set.

For the high pressure measurements, multi-phase Rietveld refinement was carried out for the sample, $KZnF_3$, the pressure marker, Pb, and contributions from the anvil materials, corundum, Al_2O_3, and tetragonal zirconia, ZrO_2. Convergence from a starting model of $KZnF_3$ derived from the 305 K data set was rapid, with typical results, in this case from the 30 tonne load, included in Table 1. The fit to these data are illustrated in Fig. 2.

Table 1
Structural parameters and Rietveld agreement factors for $KZnF_3$ at two temperatures and one pressure.

	7 K	305 K	1.59 GPa
a/Å	4.043312(5)	4.055541(7)	4.02770(6)
100 K u_{iso}/Å^2	0.482(13)	1.445(19)	1.25(6)
100 Zn u_{iso}/Å^2	0.296(10)	0.702(13)	0.42(4)
100 F u_{11}/Å^2	0.548(17)	0.866(23)	0.28(8)
100 F u_{22}, u_{33}/Å^2	0.758(10)	1.957(15)	1.79(5)
Rp	0.038[a]	0.051[a]	0.051[b]
Rwp	0.044[a]	0.051[a]	0.058[b]

Space group $Pm\bar{3}m$, K 1*b*, Zn 1*a*, F 3*d*.

[a] 6347 observations, 17 variables (5 crystallographic, shown above, 2 scale factors, 10 Chebychev polynomial background terms) – low temperature measurements.

[b] 3634 observations, 32 variables (5 crystallographic shown above, 4 scale factors, 15 Chebychev polynomial background terms, 3 profile terms, 5 additional lattice parameters) – high pressure measurements.