Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Solid State Chemistry 177 (2004) 654–659
JOURNAL OF SOLID STATE CHEMISTRY
http://elsevier.com/locate/jssc

High-temperature powder synchrotron diffraction studies of synthetic cryolite Na_3AlF_6

Qingdi Zhou and Brendan J. Kennedy*

School of Chemistry, The Centre for Heavy Metals Research, The University of Sydney, Sydney 20006, Australia

Received 3 June 2003; received in revised form 28 July 2003; accepted 6 August 2003

Abstract

A high-resolution synchrotron diffraction study of the structures of a synthetic sample of cryolite Na_3AlF_6 from room temperature to 800°C is reported. At room temperature Na_3AlF_6 is monoclinic and the structure is described in space group $P2_1/n$. Heating the sample to 560°C results in only minor changes to the structure. A first-order transition from this monoclinic structure to a high-temperature cubic structure is observed near 567°C. The cubic $Fm\bar{3}m$ structure is characterized by disorder of the fluoride atoms.

Keywords: Perovskite; Cryolite; Phase transition

1. Introduction

Compounds whose structures are based on the ABX_3 perovskite motif are of considerable interest over a wide range of scientific and technical fields. The vast majority of interest has been focused on the oxide perovskites as a consequence of the array of electronic and magnetic properties displayed by these oxides [1,2]. In comparison the fluoride perovskites, most of which have a double perovskite ($A_2BB'X_6$) type structure and are isostructural with elpasolite, K_2NaAlF_6, have historically been of interest mainly as hosts in spectroscopic studies of various lanthanide ions. Such studies have revealed the halide containing perovskites display an array of structural phase transitions [3].

The cubic elpasolite structure is on a double perovskite cell $a_e \approx 2a_p$, where a_e and a_p are the cubic cell parameters of elpasolite and perovskite. In the cubic double perovskite or elpasolite structure all the cations lie on special positions. The Al^{3+} ions occupy a face-centered cubic (fcc) lattice and each ion is octahedrally surrounded by six F^- ions located at a distance $\pm x$ along the three four-fold crystal axes. The Na^+ ions occupy similar octahedral sites and together they form a simple cubic lattice. The AlF_6 and NaF_6 octahedra are corner connected in three dimensions (see Fig. 1). The K^+ ions are surrounded by 12 F^- ions. The Al–F and Na–F distances are then given by the lattice parameter and the value of x. The cell doubling observed in elpasolite is a result of a rock-salt like ordering of the two different B-type cations, Fig. 1. The ordering of the two B-type cations, Al and Na, arises from differences in their size and bonding properties.

In the ABX_3 perovskites changes in the ratio of the sizes of the A and B type cations may result in tilting or rotations of the BX_6 octahedra, lowering their symmetry from cubic [4]. Indeed the mineral perovskite ($CaTiO_3$) is actually orthorhombic space group *Pnma* [5] as is neighborite, $NaMgF_3$ [6]. Similar tilts occur in the double perovskites. For example elpasolite is cubic at room temperature but replacing the two K cations with Na to give cryolite, Na_3AlF_6, results in a lowering of symmetry to monoclinic [3]. Increasing the temperature inevitably results in a reduction of the tilting of the BX_6 octahedra in the ABX_3 perovskites [5]. In numerous cases this leads to structural transitions to higher symmetry structures (5, 7–10). Similar events occur for the double perovskites [3]. In their early work Steward and Rooksby [11] showed cryolite undergoes a phase transition near 550°C; they concluded the structure of the high-temperature form was cubic and it was

*Corresponding author. Fax: +61-2-9351-3329.
E-mail address: b.kennedy@chem.usyd.edu.au (B.J. Kennedy).

0022-4596/$ - see front matter
doi:10.1016/j.jssc.2003.08.012

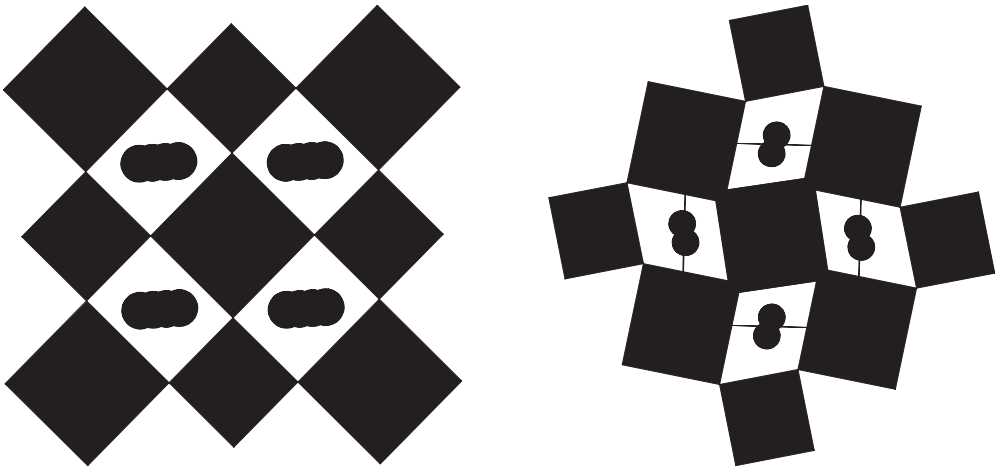

Fig. 1. Representation of the structure of cryolite, Na_3AlF_6 in both the high-temperature cubic and low-temperature monoclinic forms. The smaller hatched octahedra are the AlF_6 octahedra and the unshaded octahedra the larger NaF_6 groups. The perovskite A-type Na cations are represented by the spheres.

isostructural with elpasolite. Yang and co-workers [12] however suggested the high-temperature structure is in fact orthorhombic in space group *Immm*.

The current paper describes high-resolution synchrotron diffraction studies of a synthetic sample of Na_3AlF_6, with particular emphasis on the high-temperature phase transition. We find, in agreement with the early work of Steward and Rooksby [11] and in contrast to that of Yang et al. [12], that the high-temperature phase is cubic. We observe unusual cation disorder in the high-temperature cubic phase.

2. Experimental

Room temperature and variable temperature (100–800°C) synchrotron X-ray diffraction patterns were recorded on the Debye–Scherrer diffractometer at beamline 20B, the Photon Factory Japan [13]. The synthetic sample (Aldrich) was finely ground and housed in a 0.3 mm dia quartz capillary for the measurements. Data were collected over the angle range $5 \leqslant 2\theta \leqslant 70°$ using two image plates as the detector with an incident wavelength of $\lambda = 0.75$ Å. Data were collected in two stages, firstly from 100 to 800°C in 25° steps. Then a second sample was investigated from 500 to 600°C in 5° steps.

2.1. Structural analysis

Structures were refined using the Rietveld method implemented in the program Rietica [14] where the instrumental parameters were refined using a Pseudo–Voigt profile shape function. The background was estimated by interpolation of up to 40 points. A number of weak peaks were observed due to scatter from the furnace and the regions in the diffraction patterns affected by such peaks were excluded in the refinements.

3. Results and discussion

3.1. Room temperature structure

The refinement of the structure of Na_3AlF_6 at room temperature was performed in space group $P2_1/n$ using the structural parameters reported by Hawthorne and Ferguson [15] as a starting model. In Glazers [16] notation the structure has an $a^-b^-c^+$ tilt pattern. The in-phase or tilts give rise to R-point reflections whereas the out-of-phase (+) tilts give rise to M-point reflections. The ordering of the Na and Al cations also gives rise to R-point reflections in the diffraction pattern. The appropriateness of this space group was confirmed by the appearance of both R- and M-point reflections, together with the obvious monoclinic splitting of the appropriate Bragg reflections in the diffraction patterns. The refinement was straightforward and the refined structural parameters and bond distances are in excellent agreement with those obtained by in the early study of Hawthorne and Ferguson [15] from a single crystal of a natural cryolite sample, Table 1, as well as in the later studies of Yang et al. [12] and Ross et al. [17]. The very small differences between these various studies possibly arises from the presence of various other trace elements in the natural cryolite samples used. The rotations of the MF_6 octahedra result in Na_3AlF_6 having a $\sqrt{2}a \times \sqrt{2}b \times 2c$ superstructure relative to that of the prototype ABX_3 perovskite cell.

As an aside Na_3AlF_6 is an interesting compound for diffraction studies since the three ions are all isoelectronic. Whilst the identity of the atoms at the various sites cannot be confirmed the refined bond distances

make chemical sense and thus vindicate the choice of the locations of the Na and Al atoms in the two B-type positions. The difference in size and charge of the two cations results in ordering of these. Clearly it is not possible to comment on the possibility of incomplete ordering of the Na and Al cations. It is possible that the extent of ordering in our synthetic sample is different to that found in the various naturally occurring cryolite samples.

3.2. High-temperature structure

The synchrotron diffraction patterns recorded at or above 570°C could all be indexed on the basis of a primitive cubic cell with $a \approx 7.93$ Å. A LeBail type analysis of the profiles assuming space group $Fm\bar{3}m$ satisfactorily accounted for all the observed Bragg reflections and it was concluded that the cubic phase has an undistorted elpasolite, double perovskite, structure in which the rock-salt type ordering of the Na and Al cations persists. Attempts to refine the structure in this model resulted in unusually poor fits to the observed data and the displacement parameters for the F atoms were anomalously high. The other structural parameters appeared reasonable although surprisingly the displacement parameters for the Al reduced from 2.0(1) $Å^3$ at 550°C to 0.6(1) $Å^3$ at 600°C. The orthorhombic *Immm* model proposed by Yang et al. [12] was also unsatisfactory and in this case the refined lattice parameters always indicated the structure to be metrically cubic.

Examination of the diffraction patterns demonstrated the calculated intensity, in $Fm\bar{3}m$, of some peaks to be systematically underestimated, whereas others were overestimated. A Fourier difference map showed extra off-center scattering density around the F site indicating static displacive disorder. Attempts to model this using anisotropic displacement parameters for the F atoms were unsuccessful, and so a model in which the fluorides were disordered away from the 24*e* sites was sought. A number of models in which disorder of the fluoride atoms was allowed were then considered together with the possibilities of both cation and anion vacancies. The best fit was obtained when the F anions were allowed to move from the 24*e* sites at 00 z, $z \approx 0.28$ to a nearby 96*k* site at (x x z) $x \approx 0$ $z \approx 0.28$ but with an occupancy of 25%. This resulted in a dramatic improvement in the quality of the fit as seen both by the R-factors, Table 2 and by visual examination of the profiles, Fig. 2. The inclusion of either cation or anion vacancies did not significantly improve the quality of fit and it was concluded that Na_3AlF_6 retains its composition at the temperatures studied. This model is displayed in Fig. 3.

The static disorder of the F anions is apparently a consequence of unfavorable bonding contacts in the cubic phase. The refined Al–F and Al–F bond distances in the monoclinic phase at 550°C are not significantly different to those observed at room temperature, Table 3. However at 600°C the refined Al–F distance becomes unreasonably small, 1.717 Å and the Na–F distance (2.254 Å) within the NaF_6 octahedra is smaller than expected. Conversely the average Na–F distance for the 8-coordinate Na cations is somewhat larger than expected. The displacement of the F atoms by 0.53 Å along the (110) direction has the effect of significantly increasing the Al–F distance whilst the Na–F distances within the NaF_6 octahedra also increase. The average Na–F distance for the second Na cations in the perovskite A-type sites decreases somewhat as a result of the fluoride atoms being disordered over the 96*k* site, Table 3. In this regard the movement of the F anions has the same effect as tilting of the octahedra around the undersized A-type cations. We note that the earlier study of Yang et al. also revealed unusually large atomic displacement parameters in the high-temperature phase which they ascribed to "considerable temporal as well as spatial fluctuation" [12]. These apparent fluctuations are well modeled by the disordered model presented here.

Table 1
Positional and thermal parameters for synthetic cryolite Na_3AlF_6 at room temperature

Atom	Site	x	y	z	B
Al1	2*a*	0	0	0	1.2(1)
Na1	2*b*	0	0	0.5	0.8(1)
Na2	4*e*	0.5140(7)	0.9492(3)	0.2480(6)	1.5(1)
F1	4*e*	0.1043(4)	0.0471(4)	0.2197(5)	0.7(1)
F2	4*e*	0.7265(7)	0.1773(7)	0.0488(6)	1.1(1)
F3	4*e*	0.1645(6)	0.2746(7)	0.9368(5)	0.9(1)

The figures in parenthesis are the standard errors. R_p 2.33, R_{wp} 2.15, χ^2 3.28%. $a = 5.3956$ (2), $b = 5.5821(2)$, $c = 7.7568(2)$, Å $\beta = 90.181(1)°$.

Table 2
Positional and thermal parameters for synthetic cryolite at 600°C

Atom	*Ordered model* R_p *5.0* R_{wp} *6.8*				*Disordered Model 2* R_p *3.3* R_{wp} *4.3*			
	Site	$x = y$	z	B	Site	$x = y$	z	B
Na	4*a*	0	0	4.4(3)	4*a*	0	0	3.7(1)
Al	4*b*	0.5	0.5	0.6(1)	4*b*	0.5	0.5	2.0(1)
Na	8*c*	0.25	0.25	5.5(2)	8*c*	0.25	0.25	6.3(1)
F	24*e*	0	0.2838(7)	9.2(3)	96*k*	0.0468(4)	0.2828(3)	2.5(2)

The differences between the ordered and disordered models are explained in the text.

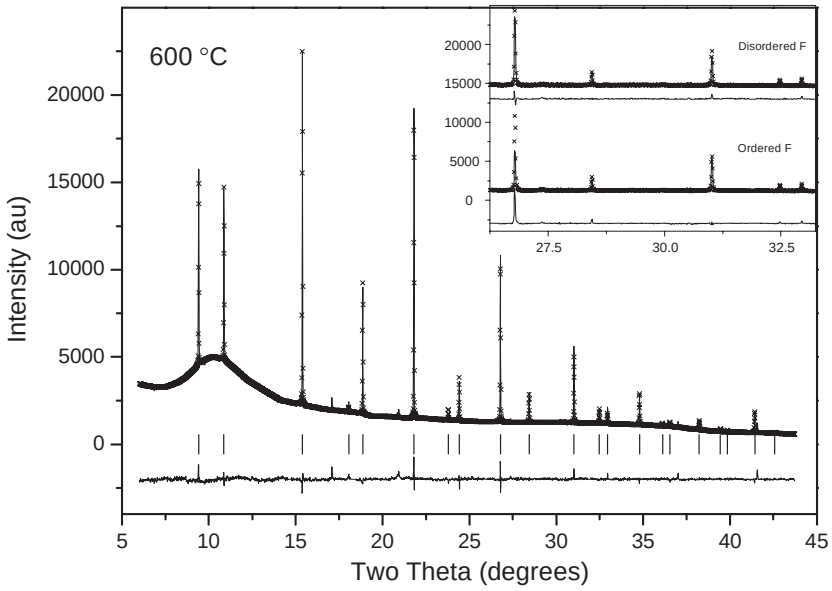

Fig. 2. Observed, calculated and difference synchrotron profiles for Na_3AlF_6 at 600°C. The inset shows the notably better fit obtained when the F atoms are disordered on a 96k site at x, x, z with $x \approx 0$ and $z \approx \frac{1}{4}$.

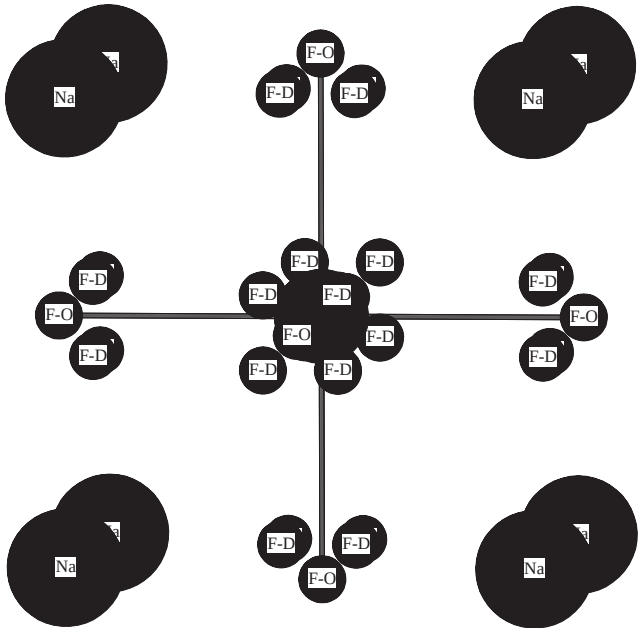

Fig. 3. Representation of the disorder of the F atoms in the high-temperature cubic phase. The F atoms in the ordered structure are at the 24*e*(00*z*) site and are labeled F–O and the disordered F at the 96*k* site are labeled F–D.

Static disorder has been observed in a number of ABX_3 perovskites, most noticeably in $PbZrO_3$ [18]. Its occurrence in double perovskites is less well known. Marx and Ibberson [19] found disorder of the Li atoms in Li_6NBr_3 that has the anti-elpasolite structure (i.e. the N and one type of Br anions are at the center of the rock salt octahedra). In this case they placed the Li onto a 96*j* site at *x y 0* with $x \approx 0.25$ and $y \approx 0$. The *R*-factors do not distinguish between this model and that proposed here for the high-temperature cubic cryolite phase, although we note that the displacement parameters for the F remains somewhat higher in the Marx and Ibberson (19) model (3.6 $Å^3$) than when the F is at the 96*k* site (2.5 $Å^3$).

Table 3
Bond distances (Å) for synthetic cryolite at selected temperatures

Bond	25°C monoclinic	550°C monoclinic	600°C cubic ordered model	600°C cubic disordered model
Al–F	1.768(5)	1.764(6)	1.717(6)	1.803(3)
	1.799(5)	1.782(9)		
	1.828(4)	1.801(6)		
	1.798	**1.782**		
Na(1)–F	2.299(4)	2.297(8)	2.254(6)	2.307(3)
	2.219(5)	2.282(6)		
	2.271(5)	2.314(7)		
	2.263	**2.298**		
Na(2)–F	**2.506**	**2.604**	2.820(1)	2.297(4)
				2.868(1)
				2.583

The differences between the ordered and disordered models are explained in the text. Where necessary the average bond distances are given in bold.

3.3. Phase transition

Fig. 4 shows the temperature dependence of the lattice parameters for Na_3AlF_6. These results are consistent with the description of Steward and Rooksby in their earlier study [11]. The most striking feature is the sharp discontinuity near 567°C indicative of a first-order phase transition. Prior to this the nearly linear thermal expansion of the unit-cell lengths is unexceptional and

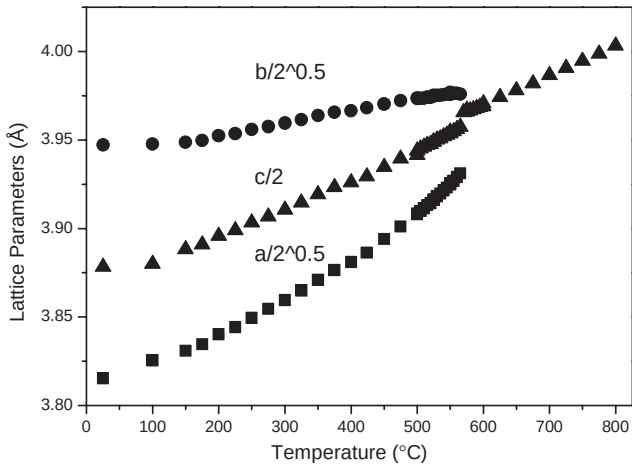

Fig. 4. Temperature dependence of the lattice parameters for Na_3AlF_6 showing the presence of a first-order monoclinic to cubic phase transition near 567°C. In the monoclinic phase the cell parameters have been reduced to the equivalent perovskite vales as follows: $a = \sqrt{2}a_p$, $b = \sqrt{2}a_p$ and $c = 2a_p$. In the cubic phase an equivalent reduction has been imposed $a = 2a_p$. In all cases esds of the cell parameters are smaller than the symbols.

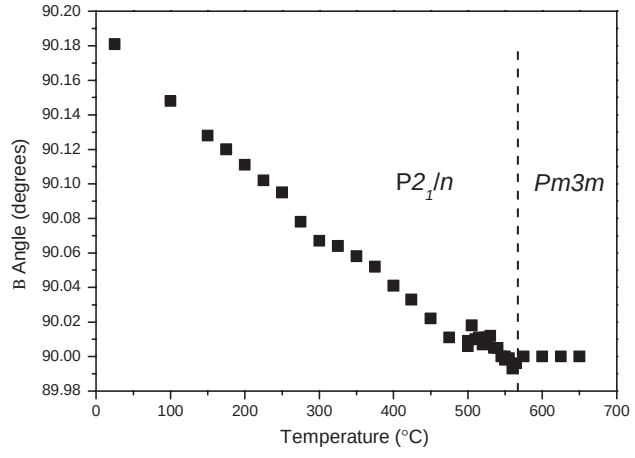

Fig. 5. Temperature dependence of the monoclinic beta angle as the temperature. The dashed vertical line shows the position of the first-order phase transition.

is good agreement with that found in earlier studies [11,12]. It is noteworthy that the monoclinic angle, which exhibits an almost linear decrease as the temperature is increased to 500°C, Fig. 5 becomes equal, within the precision of the present refinements to 90° near 500°C, some 50 or so degrees below the first-order phase transition. It is clear from Fig. 4 that the lattice parameters remain noticeably different so that the symmetry of the Na_3AlF_6 is at least orthorhombic. Comparison of the profiles recorded at 450°C and 550°C, that is above and below the point at which the refined monoclinic angle becomes equal to 90° did not show the loss of any reflections and it was concluded that both the in-phase and out-of-phase tilts persist above 550°C and that the structure remains face centered.

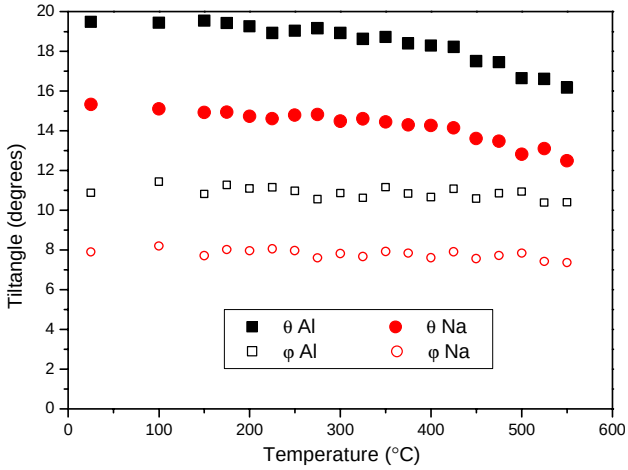

Fig. 6. Temperature dependence of the octahedra tilt angles for Na_3AlF_6 calculated form the refined atomic coordinates. The tilt about the, cubic, four-fold axis is given by φ and that about the two-fold axis by θ.

We then considered the possibility of a continuous phase transition from the monoclinic $P2_1/n$ structure to an orthorhombic phase as suggested by Yang [12]. Using group theory Howard and co-workers have recently identified possible sequences of phase transitions in double perovskites with rock-salt like ordering and by comparison with this work [20] we cannot identify any candidate phases. Yang [12] concluded that the *Immm* phases exists as a consequence of a simultaneous application of two modes, Γ_4^+ and Y_2^+ from low-temperature monoclinic $P2_1/n$ phase. There is no simple distortion that would allow the transition from *Immm* to the parent cubic structure in $Fm\bar{3}m$. We believe our hypothesis of a direct first-order transition from $P2_1/n$ to $Fm\bar{3}m$ is the more reasonable. There are a number of examples in the perovskite literature where the diffraction patterns apparently indicate one metric cell, but the structure actually has lower symmetry [6,7,21]. This appears to be the case for Na_3AlF_6 between 500°C and 565°C.

As indicated previously the monoclinic structure has an $a^-b^-c^+$ tilting pattern and following Groen [22] the refined atomic co-ordinates have been used to calculate the magnitude of the tilts about the 0 1 1 (φ) and 1 1 0 (θ) axis of the cubic aristotype. For simple ABX_3 perovskites it has been found [5,7–10] that continuous transitions to a higher symmetry structure involve the progressive removal of one or more of the tilts. The temperature dependence of the tilts in Na_3AlF_6 are illustrated in Fig. 6 and from these it is clear that an continuous transition to a higher symmetry structure is still somewhat distant. As described by Mitchell [1] the tilts of the smaller AlF_6 octahedra are smaller than those of the larger NaF_6 octahedra.

Consequently we believe that Na_3AlF_6 remains monoclinic up to the point of the first order phase

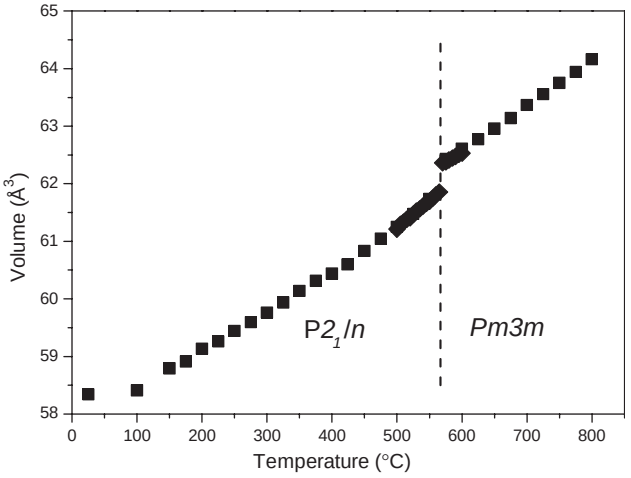

Fig. 7. Temperature dependence of the cell volume for Na_3AlF_6 showing the presence of a first-order monoclinic to cubic phase transition near 567°C. For ease of comparison the volumes equivalent to that of the parent perovskite are plotted.

transition. As seen in Fig. 7 this phase transition is accompanied by a noticeable increase in the cell volume as the structure becomes cubic.

4. Conclusion

We have demonstrated that very accurate and precise structures of the double perovskite, Na_3AlF_6, can be obtained using high-resolution synchrotron powder diffraction methods. The structure of this synthetic sample of cryolite has been found to be monoclinic from room temperature to 560°C. Just above this a first-order phase transition to a cubic structure is observed. The monoclinic phase is characterized by large in-phase and out-of-phase tilts of the AlF_6 and NaF_6 octahedra. As for the simple ABX_3 perovskites these tilts in Na_3AlF_6 are believed to be a consequence of the less than optimal size of the Na^+ ions on the perovskite A-type site. Although the magnitude of these tilts is progressively reduced as the temperature is increased they remain relatively large over the entire temperature range. It can be concluded that any continuous phase transition involving a loss of tilting is still remote at 565°C. The high-temperature cubic phase is characterized by static displacive disorder of the F anions. The effect of this disorder on the local bond distances is similar to that of the tilts and is necessary to stabilize the cubic structure.

Acknowledgments

This work performed at the Australian National Beamline Facility was supported by the Australian Synchrotron Research Program, which is funded by the Commonwealth of Australia under the Major National Research Facilities program. BJK acknowledges the support of the Australian Research Council and numerous helpful discussions with Dr. C.J. Howard. The assistance of Dr. James Hester at the ANBF is gratefully acknowledged.

References

[1] R.H. Mitchell, Perovskites—Modern and Ancient, Almaz Press, Thunder Bay, Ontario, 2002.
[2] M.T. Anderson, K.B. Greenwood, G.A. Taylor, K.R. Poeppelmeir, Prog. Solid State Chem. 22 (1993) 197.
[3] I.N. Flerov, M.V. Gorev, K.S. Aleksandrov, A. Tressaud, A. Grannec, M. Couzi, Mater. Sci. Eng. R 24 (1998) 81.
[4] C.J. Howard, H.T. Stokes, Acta Crystallogr. B 54 (1998) 782; C.J. Howard, H.T. Stokes, Acta Crystallogr. erratum B 58 (2002) 565.
[5] Y. Zhao, D.J. Weidner, J.B. Parise, D.E. Cox, Phys. Earth. Planet Interiors 76 (1993) 17.
[6] B.J. Kennedy, C.J. Howard, B.C. Chakoumakos, J. Phys. C: Condens. Matter 11 (1999) 479.
[7] C.J. Howard, K.S. Knight, B.J. Kennedy, E.H. Kisi, J. Phys.: Condens. Matter 12 (2000) L677.
[8] B.J. Kennedy, B.A. Hunter, J.R. Hester, Phys. Rev. B 65 (2002) 224103.
[9] B.J. Kennedy, A.K. Prodjosantoso, C.J. Howard, J. Phys. C: Condens. Matter 11 (1999) 6319.
[10] B.J. Kennedy, C.J. Howard, G.J. Thorogood, J.R. Hester, J. Solid State Chem. 161 (2001) 106.
[11] E.G. Steward, H. Rooksby, Acta Crystallogr. 6 (1953) 49.
[12] H. Yang, S. Ghose, D. Hatch, Phys. Chem. Minerals 19 (1993) 528.
[13] T.M. Sabine, B.J. Kennedy, R.F. Garrett, G.J. Foran, D.J. Cookson, J. Appl. Crystallogr. 28 (1995) 513.
[14] C.J. Howard, B.A. Hunter, A computer program for Rietveld analysis of X-ray and neutron powder diffraction patterns, Lucas Heights Research Laboratories, NSW, Australia, 1998, pp. 1–27.
[15] F.C. Hawthorne, R.B. Ferguson, Canad. Mineral 13 (1975) 377.
[16] A.M. Glazer, Acta Crystallogr. B 28 (1972) 3384; A.M. Glazer, Acta Crystallogr. A 31 (1975) 756.
[17] K.C. Ross, R.H. Mitchell, A.R. Chakhmouradian, J. Solid State Chem. 172 (2003) 95.
[18] D.L. Corker, A.M. Glazer, J. Dec, K. Roleder, R.W. Whatmore Acta Crystallogr. B 53 (1997) 135.
[19] R. Mark, R.M. Ibberson, J. Alloys Compd. 261 (1997) 123.
[20] C.J. Howard, B.J. Kennedy, P.W. Woodward, Acta Crystallogr. B 59 (2003) 463.
[21] C.J. Howard, R.L. Withers, B.J. Kennedy, J. Solid State Chem. 160 (2001) 8.
[22] W.A. Groen, F.P.F. Van Berkel, D.J.W. Ijdo, Acta Crystallogr. C 42 (1986) 1472.