Thermal expansion and phase transitions of α -AlF₃

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Graphical abstract:

α -AlF₃ has a rhombohedrally distorted ReO₃-type structure at ambient conditions and displays strongly positive volume thermal expansion that is highly anisotropic; the material becomes cubic on heating above ~713 K and continues to show positive thermal expansion.

ABSTRACT

ReO_3 -type materials are of interest for their potential low or negative thermal expansion. Many metal trifluorides MF_3 adopt the cubic form of this structure at elevated temperatures, which rhombohedrally distorts upon cooling. The rhombohedral form displays strong positive volume thermal expansion, but cubic MF_3 display much lower and sometimes negative thermal expansion. The expansion behavior of $\alpha\text{-AlF}_3$ was characterized via synchrotron powder diffraction between 323 and 1177 K. $\alpha\text{-AlF}_3$ is rhombohedral at ambient conditions and displays strongly anisotropic thermal expansion. The volume coefficient of thermal expansion (CTE), α_v , at 500 K is $\sim 86 \text{ ppm}\cdot\text{K}^{-1}$, but the linear CTE along the c -axis, α_c , is close to zero. $\alpha\text{-AlF}_3$ becomes cubic on heating to $\sim 713 \text{ K}$ and continues to show positive thermal expansion above the phase transition ($\alpha_v(900 \text{ K}) \sim 25 \text{ ppm}\cdot\text{K}^{-1}$).

1. INTRODUCTION

The simple cubic ReO_3 structure (Figure 1), consisting of metal-centered octahedra that share anions at their corners, is of interest because of its potential for low or negative thermal expansion (NTE). This structure is related to that of perovskites, ABX_3 , with a vacant A site and hence significant empty volume, and has been used to illustrate how NTE can arise from the transverse thermal motion of bridging atoms and the resulting rocking of relatively rigid units.^{1,2} Rhenium trioxide itself displays low thermal expansion at ambient conditions,³⁻⁶ but members of this structural family, including fluorides and oxyfluorides, have coefficients of thermal expansion (CTE) ranging from strongly positive to strongly negative.⁷⁻¹²

Figure 1. The cubic ReO_3 structure, with the unit cell outlined in red. Green spheres represent metal ions, while blue spheres represent anions.

Many metal trifluorides (MF_3 ; $M = \text{Al}, \text{Cr}, \text{Fe}, \text{Ga}, \text{In}, \text{Ti}, \text{V}$) are only cubic at elevated temperatures; upon cooling, they adopt a rhombohedrally distorted form of the ReO_3 structure (VF_3 -type).¹³⁻¹⁵ This phase transformation involves the coupled rotation of the constituent MF_6 octahedra. The thermal expansion of some ReO_3 -type MF_3 has been studied. The unfolding of the rhombohedral phase on heating is accompanied by strongly positive thermal expansion (PTE), while the cubic phase shows much lower or even negative thermal expansion. Notably, cubic ScF_3 displays pronounced NTE over a wide temperature range (at least 10 to 1100 K).¹⁰ TiF_3 is cubic above ~ 340 K,^{12,14,15} and its CTE is slightly positive just above the phase transition but then becomes slightly negative above ~ 400 K.¹² We have recently explored the control of thermal expansion in ScF_3 -based materials by forming $\text{Sc}_{1-x}\text{M}_x\text{F}_3$ ($M = \text{Ti}, \text{Y}$) solid solutions. Solid solutions of ScF_3 and TiF_3 display CTEs ranging between those of the end members;¹² however, in cubic $\text{Sc}_{1-x}\text{Y}_x\text{F}_3$, where the size mismatch between the two cations is quite large, the CTE is largely independent of composition.¹¹

α -AlF₃ also has ReO₃-type connectivity. At room temperature, the material is rhombohedral, becoming cubic at ~730 K.¹⁶ Although the rhombohedral-to-cubic phase transition in α -AlF₃ has been studied extensively,^{13,16-20} the thermal expansion of α -AlF₃ has not been reported in detail. In 1984, Ravez *et al.* provided some information on the temperature dependence of unit cell volume but did not report expansion coefficients;²¹ they reported that both cubic and rhombohedral phases display positive thermal expansion. In 2001, Chupas *et al.* studied α -AlF₃ in the context of γ -Al₂O₃ fluorination and catalysis. They reported that some weak reflections, potentially indicative of a residual rhombohedral distortion, persisted above the phase transition at ~739 K, and their Rietveld analyses suggested that bent Al—F—Al links persisted above the phase transition temperature.¹⁶ A later total scattering study of α -AlF₃ revealed that the cubic phase contains local octahedral tilts.²⁰ The mechanism of the cubic-to-rhombohedral phase transition was studied using molecular dynamics simulations, and the authors suggested local distortions and NTE above the phase transition temperature.¹⁹ In the present paper, as part of our broader exploration of thermal expansion in ReO₃-type fluorides, we reexamine in detail the anisotropic thermal expansion of α -AlF₃ between 323 and 1177 K.

2. MATERIALS AND METHODS

2.1 Sample preparation

Anhydrous AlF₃ (American Elements, 99.99%) was ground thoroughly in an inert atmosphere and sealed in a nickel tube by welding. The Ni tube was then sealed in an evacuated fused quartz ampoule and heated at 1338 K for 72 h, after which it was quenched by removing from the furnace. The heat-treated sample was maintained in an inert atmosphere to avoid moisture exposure.

2.2 Variable temperature synchrotron powder diffraction

Variable temperature powder X-ray diffraction (PXRD) data ($\lambda \approx 0.7291 \text{ \AA}$) were collected at beamline 17-BM-B of the Advanced Photon Source (APS), Argonne National Laboratory, Illinois, USA. A PerkinElmer amorphous Si-based area detector (2048×2048 , $200 \text{ }\mu\text{m}$ pixels) was used to record diffraction images, and LaB_6 (NIST SRM 660a) was used to calibrate beam center, detector tilt angle and tilt plane rotation angle, as well as its distance to the sample. The $\alpha\text{-AlF}_3$ powder sample was packed in a fused quartz capillary under argon, and UHP nitrogen was very slowly flowed through the capillary during data collection to avoid the ingress of any moisture. Temperature was controlled with a wire-wound furnace,²² heating at a rate of $180 \text{ K}\cdot\text{h}^{-1}$ from 323 to 1177 K. No data were collected on cooling, as the sample capillary failed upon reaching the maximum temperature. Exposure times of $\sim 30 \text{ s}$ were used, with a $\sim 30 \text{ s}$ wait between exposures.

2.3 Data analysis

Two-dimensional area detector images were reduced to one-dimensional patterns with *FIT2D*.²³ A calibration curve was created from the measured and expected peak positions for a standard LaB_6 sample to correct for angular distortions in the 1D patterns that are believed to be associated with the oblique incidence of the X-ray beam on the relatively thick active layer of the detector. Rietveld analyses were accomplished in the sequential refinement mode of *GSAS*.^{24,25} A fit to data at 323 K (Supporting Information, Figure S1) with a primitive rhombohedral model (space group $R\bar{3}c$) served as the starting point for sequential refinement. An isotropic atomic displacement parameter (ADP) was refined for the Al atom, while anisotropic ADPs were used for the F atoms. Unit cell volumes per formula unit were extracted during Rietveld analyses and plotted with respect to temperature; the temperature variation of the volume CTE (α_V) was

estimated by differentiation of sixth-order polynomial fits to these data. For some of the analyses, the primitive rhombohedral lattice constant a_R and unit cell angle α_R extracted during Rietveld analyses were converted to hexagonal lattice constants a_H and c_H by the following relationships: $a_H = 2a_R \sin \frac{\alpha_R}{2}$ and $c_H = a_R \sqrt{3 + 6 \cos \alpha_R}$.

3. RESULTS AND DISCUSSION

The appearance of superlattice peaks and the splitting of other peaks at low temperatures in the variable temperature PXRD patterns (Figure 2) are evidence for the rhombohedral-to-cubic phase transition previously observed in α -AlF₃²¹ and other ReO₃-type metal trifluorides.^{11,12,14,15} The phase transition appears quite clearly just above 700 K (Figure 2). We also observe an α -Al₂O₃ phase, an impurity likely incorporated into the sample during the annealing process; the α -Al₂O₃ peaks exist over the entire temperature range but are quite small (< 1% weight fraction at 323 K). Another unidentified impurity phase appears above ~1000 K that may be a product of the reaction of AlF₃ and the quartz capillary. However, the α -AlF₃ peaks are much more intense than these impurity peaks.

Figure 2. (a) Variable temperature (323 to 1177 K) powder X-ray diffraction patterns for α -AlF₃, displayed in order of collection from bottom to top. The horizontal white lines are from frames that were lost during data collection. (b) X-ray diffraction data for α -AlF₃ at selected temperatures, showing the presence of a diffuse peak (marked by an arrow) that is incommensurate with the AlF₃ unit cell. These data are taken from the portion of (a) enclosed by a small box.

The temperature dependence of both unit cell volume per formula unit and volume CTE of α -AlF₃ are plotted in Figure 3. When heated from ambient temperature, rhombohedral α -AlF₃ exhibits strongly positive volume thermal expansion ($\alpha_V(500 \text{ K}) \sim 86 \text{ ppm}\cdot\text{K}^{-1}$) as it unfolds. Above the first-order phase transition, cubic α -AlF₃ continues to expand but with a much lower CTE ($\alpha_V(900 \text{ K}) \sim 25 \text{ ppm}\cdot\text{K}^{-1}$). The thermal expansion of rhombohedral α -AlF₃ is strongly anisotropic (Figure 4). The a -axis displays strong positive thermal expansion, while the CTE

along the c -axis is close to zero. This anisotropy occurs because the rhombohedral-to-cubic phase transition involves rotation of the AlF_6 octahedra around their three-fold axes, which are parallel to the crystallographic c -axis. Based on the temperature dependence of c/a (Figure 5a), we estimate the phase transition temperature as 713 K, which is consistent with the temperature reported in another XRD study (715 ± 10 K)²¹ but slightly lower than that measured by differential scanning calorimetry (725 K)¹⁷ and XRD (741 ± 10 K) in other studies.²⁰

Figure 3. Temperature dependence of the unit cell volume per formula unit (V/Z , red $\times$) and volume CTE (α_V , black $+$) of $\alpha\text{-AlF}_3$. Unit cell volumes were extracted from Rietveld analyses of PXRD data, and α_V were estimated from polynomial fits to the V/Z vs. T data. The dashed line indicates the estimated phase transition temperature (713 K).

Figure 4. (a) Temperature dependence of the lattice parameters of α -AlF₃. Hexagonal values a_H and c_H are reduced to their cubic equivalents by the indicated factors. A rhombohedral model was used for all temperatures, even above the phase transition, where a_H and c_H refine to the same value. (b) Temperature dependence of the linear CTEs; α_a and α_c are significantly different below the phase transition temperature but equal above it.

Figure 5. Temperature dependence of (a) the ratio of lattice constants c and a (hexagonal cell), which was used to estimate the phase transition temperature of 713 K (marked in each panel by a vertical dashed line), (b) the estimated Al—F—Al bond angle, related to the x -coordinate of F (x_F) by the equation shown, and (c) the Al—F distance. The expected value for c/a in the cubic phase is 2.449, as indicated by a horizontal dashed line in (a), and the expected value of x_F , in the absence of any disorder, in the cubic phase is 0.75, which would lead to an Al—F—Al bond angle of 180° .

As shown in Figure 2, there are some diffuse peaks at approximately the positions of the rhombohedral supercell reflections that persist to temperatures well above the phase transition, and the transition is accompanied by a significant increase in “background” scattering; it is notable that these diffuse peaks are incommensurate, in that they do not index on the unit cell. The most prominent of the diffuse peaks appears at $Q \sim 3.0 \text{ \AA}^{-1}$ (marked by an arrow in Figure

2b), which, prior to the phase transition, corresponds approximately to the rhombohedral (2 1 0) Bragg peak; its area drops significantly with increased temperature, and its width is greater than that of the Bragg peaks and increases sharply immediately above the phase transition temperature, 713 K (Supporting Information, Figure S2). In addition, the peak shifts to higher angles on heating, counter to the PTE of AlF_3 . These diffuse peaks and the jump in background due to diffuse scattering suggest the presence of short-range structural distortions in the cubic phase. Such distortions have been noted previously. Chupas *et al.* also observed weak superlattice PXRD peaks persisting past the phase transition and calculated an Al—F—Al bond angle of 175.8° at 723 K, suggesting a small degree of local rhombohedral distortion.¹⁶ Both molecular dynamics simulations¹⁹ and pair distribution function analysis²⁰ confirmed the presence of bent Al—F—Al bonds and tilted octahedra in the cubic structure.

Our attempts to fit a cubic model with a split F site to the data above the phase transition, in the manner of Chupas *et al.*,²⁰ yielded unrealistic values for the F position and atomic displacement parameters (ADP), perhaps because the Q range of our data was much smaller than that used by the previous authors ($Q_{\text{max}} \sim 6$ and $\sim 13 \text{ \AA}^{-1}$, respectively). However, by using the primitive rhombohedral model at all temperatures, where the variable x_{F} is partly accounting for disorder in the cubic phase, we estimated Al—F—Al bond angles that reasonably matched the previous observations^{16,19,20} (Figure 5b). Such an approach must be treated with caution, due to the incomplete nature of the model and possible correlations involving ADPs. The apparent Al—F—Al bond angle estimated from the rhombohedral model increases steadily with temperature to at least 1100 K, which is consistent with our observation of quite strong PTE in cubic α - AlF_3 . Furthermore, the Al—F distance does not vary greatly with temperature (300 to ~ 600 K) (Figure 5c), indicating the presence of rigid AlF_6 octahedra, with the positive thermal expansion

principally driven by coupled rotation of these octahedra. However, beginning at ~600 K, as the phase transition is approached, the Al—F distance appears to decrease with temperature. This behavior presumably reflects the presence of static/dynamic disorder rather than an actual decrease in the instantaneous Al—F distance. Zhao *et al.* reported similar, although more pronounced, behavior for the Mg—F distance in the perovskite NaMgF₃.²⁶

The strong PTE of cubic α -AlF₃ stands in contrast to the behavior of cubic ScF₃ (strong NTE) and TiF₃ (low PTE or low NTE depending upon temperature). However, there are other examples of PTE in the cubic ReO₃ family; for example, cubic NbO₂F expands on heating between 20 and 500 K.^{7,9} Based on our local structural study of TaO₂F,⁸ we proposed that the PTE in NbO₂F may arise from the presence of bent Nb—(O/F)—Nb links whose bond angles increase on heating. A similar phenomenon may be involved in the quite strong PTE of cubic AlF₃.

4. CONCLUSION

The volume thermal expansion of α -AlF₃ is strongly positive above ambient temperature, where the structure is rhombohedral. After transforming to the cubic ReO₃-type structure at 713 K, the volume CTE drops by fourfold but remains positive to at least 1177 K. The positive thermal expansion of the cubic phase may be partially due to the presence of local octahedral tilts and an associated increase in the average Al—F—Al bond angle on heating.

5. SUPPORTING INFORMATION

The following are available as supporting information: sample Rietveld fit to data collected at 323 K; temperature dependence of structural parameters for α -AlF₃; temperature dependence of

the diffuse peak at $Q \sim 3.0 \text{ \AA}^{-1}$; Rietveld refinement results at selected temperatures; primitive rhombohedral lattice constants and x -coordinate of F for α -AlF₃ between 323 and 1177 K.

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