

Probing Local and Long-Range Structure Simultaneously: An In Situ Study of the High-Temperature Phase Transition of α -AlF₃

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The physical properties of technologically important materials can often be strongly coupled to subtle local structural changes that occur during phase transitions. With this in mind, the perovskite structure is particularly noteworthy, as it is a fundamentally important archetypal structure that is adopted by a wide range of materials, including geologically important samples, catalysts, and electronic materials.^{1–7} α -AlF₃ adopts the distorted ReO₃ structure at room temperature, which is a close structural analogue to perovskite. It is an industrially important material that may be used at high temperatures as a catalyst in fluorocarbon manufacturing and as an additive to solid electrolytes in aluminum production.^{3–5} α -AlF₃ undergoes a structural phase transition to the cubic ReO₃ structure at high temperatures (Figure 1a). We have been studying the mechanism of this phase transition, with Rietveld analysis for structure analysis and molecular dynamics (MD) simulations to examine the dynamics in the material.^{5,8} Significant differences can exist between the average atomic position and instantaneous structure (i.e., a snapshot of the structure), especially in materials with mobile ions or atoms, and it is therefore essential to apply multiple analysis methods to describe the structure. We show in this Communication that the combination of Rietveld and pair distribution function (PDF) (Figure 1b) analyses allows unique insight into the nature of the phase transition, which was not available from conventional structural analysis methods alone. Image plate technology allowed structural changes to be followed in “real time” and reduced the time required to collect high-resolution PDF data from hours (with a conventional solid state detector) to seconds. This methodology produces raw data that can be analyzed simultaneously by both Rietveld and PDF analysis.⁹

Distortions in perovskite structures are conveniently described in terms of the rotations of the rigid octahedra. Glazer, and later Woodward, described the relationships between the tilting schemes and the crystallographic space group.^{1,2} Glazer’s approach used a crucial observation, that the BX₆ octahedra are relatively rigid units. More recently, the term rigid unit mode (RUM) has been coined to describe the correlated motion of polyhedra connected at their vertices, such as in tetrahedral silicate networks and perovskites.¹⁰ This concept has been applied with considerable success to the study of tetrahedral SiO₂ framework structures.¹⁰ The polyhedra, octahedra in the case of perovskites, move as rigid units in this model; as a single octahedron rotates, it causes the neighboring octahedra, joined by corner sharing vertices, to rotate, causing a correlated cascade

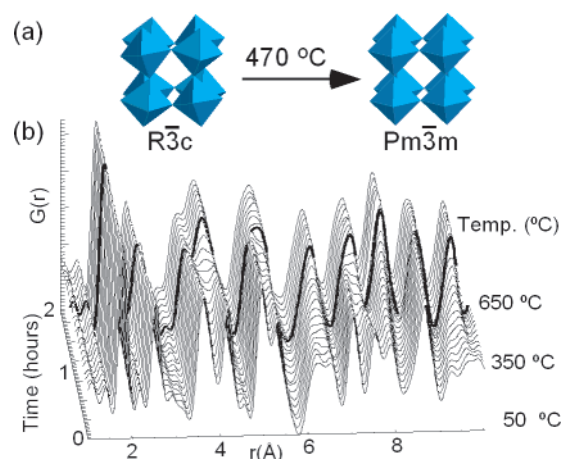


Figure 1. (a) The room-temperature rhombohedral α -AlF₃ and average cubic high-temperature structures. (b) $G(r)$ as a function of temperature (obtained from the raw diffraction data; see Supporting Information). $G(r)$, at the phase transition temperature, is shown with a darker line. $G(r) = 4\pi r[\rho(r) - \rho_0]$, where r is the radial distance, $\rho(r)$ is the instantaneous pair density, and ρ_0 is the average number density.

of rotations throughout the structure. To analyze this correlated dynamic motion fully, methods that look at both average and instantaneous structure must be applied.¹⁰

Variable-temperature data for α -AlF₃ (prepared as outlined earlier⁵) were collected from 50 to 650 °C, using a previously described apparatus⁵ and the high energy X-rays (99.6 keV, $\lambda = 0.12414$ Å) that are available at the 1-ID beamline at the APS at Argonne National Laboratory.¹¹ Fit-2D was employed to process the raw data collected from a MAR-345 image plate system.¹² Details of the determination of $G(r)$ (the PDF) from the raw diffraction data collected with image plates can be found elsewhere.⁹ Rietveld and PDF refinements were performed with GSAS and PDFfit, respectively.^{13,14}

The rhombohedral structure reported in the literature¹⁵ was used as a starting model for the 50 °C data and was subsequently refined using the Rietveld method, producing a good fit. Analysis of the high-temperature data above the transition at 468 ± 10 °C¹⁶ was performed by using the primitive cubic lattice ($Pm\bar{3}m$, $a \approx 3.55$ Å) with the fluorine located at (0.5,0,0), and an acceptable fit to the data was achieved ($R_p = 5.56\%$). However the change in Al–F bond distance determined from these two models (Figure 2a) was physically unreasonable, because the bond lengths decreased as the temperature was increased near the phase transition. Once in the cubic lattice, the Al–F bond distance began to increase as the temperature was raised, but even at 650 °C, the Al–F distance remained shorter than that observed at 50 °C. The F displacement

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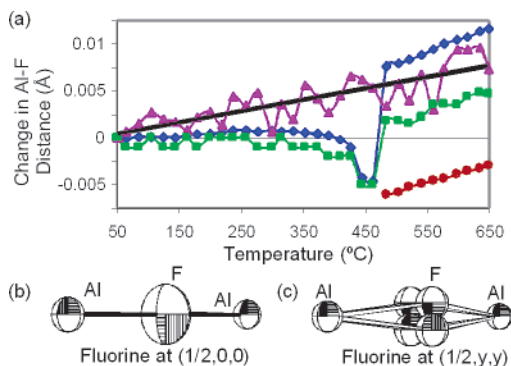


Figure 2. (a) The change in Al–F bond distance (Å) as a function of temperature from Rietveld refinements with F atoms at (0.5, y , y) (blue \blacklozenge) and at (0.5,0,0) (red \bullet), the PDF refinements (green \blacksquare), and extracted directly from the PDF plot (purple \blacktriangle). The displacement parameters obtained at 650 °C from Rietveld refinements (b) with F at (0.5,0,0) and (c) with F at the split position (0.5, y , y). The Al–F bonds are clearly longer when F occupies the split position.

parameters in the high-temperature phase were significantly larger in the direction normal to the Al–F bond direction. Thus, a second Rietveld refinement of the 650 °C data was commenced with a partially occupied (0.25) split fluorine position at (0.5, y , y) with $y = 0.0452(8)$. This produced a refinement of similar quality ($R_F^2 = 5.80\%$, see Supporting Information), but yielded longer, more physically reasonable Al–F distances at high temperatures. In the region immediately preceding the transition temperature (420–468 °C), an anomaly persists in the change in Al–F bond distance, and a region still exists where the diffraction patterns clearly index as rhombohedral, but where a smaller apparent Al–F distance is obtained in comparison to the lower-temperature data.

The Al–F bond distance was extracted directly from the PDFs (Figure 2a), by fitting a Gaussian to the peak, to clarify the details of local structure during the region preceding the phase transition. Now the Al–F bond increases as a function of temperature in a predictable fashion. Furthermore, refinements using the high-temperature PDFs (650 °C) and a split fluorine position yield a better fit ($R_{wp} = 18.5\%$; refined over the range 1–20 Å) than that obtained with F at the average position (0.5,0,0) ($R_{wp} = 21.6\%$). That the Al–F bond length increases steadily with temperature is a clear indication that the F atoms do not occupy the average position in the structure of the primitive cubic lattice at (0.5,0,0), but instead are located on positions off the Al–Al vector, resulting in bent Al–F–Al bonds (with Al–F–Al bond angles, α , of less than 180°) and tilted octahedra even in the dynamic, high-temperature structure. This is in agreement with our MD simulations of this system, which showed that the F atoms are on average located 0.54 Å away from the midpoint of the Al–Al internuclear vectors at similar temperatures (as compared to 0.20 and 0.22 Å from the PDF and Rietveld results, respectively),⁸ the tilted AlF_6 octahedra rotating between different orientations.

Both structural analysis methods indicate that the high-temperature structure is dynamic and comprises a superposition of rapidly inverting tilted octahedra. Distortions in the octahedra can be followed by monitoring the breadth of the peaks in $g(r)$ corresponding to the closest Al–F and F–F peaks. Both of these peaks remain sharp even at high temperatures, indicating that the AlF_6 octahedra move as rigid units. Again, these results are consistent with the MD simulations, which also show that the octahedra move as rigid units. It is nontrivial to determine from these experiments if the motion involves free precession of the octahedra or jumps between four (or more) different F positions. However, the discrete

peaks due to fluorine atoms, observed in the electron density Fourier difference maps (Supporting Information), suggest that jumps rather than free precession occurs. The structural models obtained from Rietveld analysis contained physically reasonable Al–F bond distances at low and high temperatures, but a significant anomaly is observed in the intermediate-temperature region. The displacement parameters of the fluorine atoms become conspicuously large in this misfit region, before decreasing again in the high-temperature region. In contrast, the local structure is captured in the PDF during the entire temperature region. Intermediate dynamic disorder has also been observed in the MD simulations of this system, motion in this regime comprising slow (on the MD time scale) interconversion between different Al–F–Al orientations (the Al–F–Al bond angles interconverting between $+\alpha$ and $-\alpha$; see Supporting Information Figure).⁸ The structure still maintains a rhombohedral distortion and an $a^-a^-a^-$ tilt scheme.

The work presented here clearly shows how the analysis of both local and long-range structural information can be advantageous in the elucidation of dynamic disorder in crystalline systems. The application of PDF analysis to this problem is made possible through the use of image plate area detectors in a technique referred to as rapid acquisition pair distribution function analysis (RA-PDF).⁹ The extension of this approach to the structural studies of a variety of other systems including catalysts, negative thermal expansion materials, and geologically important materials can be readily envisaged.

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Supporting Information Available: Details of the PDF and Rietveld refinements (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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