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High Temperature In Situ Time-Resolved Single Crystal Studies of α AlF_3

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Beamline(s): X7B

Introduction: AlF_3 prepared by flowing CF_2ClH over γ -alumina is catalytically active for the dismutation reaction of CF_2ClH [1], while AlF_3 prepared by normal synthetic methods is much less active, even when the reactivity is normalized for the much lower surface area of α - AlF_3 . The origin of this difference in catalytic activity merits further study. The structural differences between these two materials were explored by powder profile refinements of catalytic and normal AlF_3 . One explanation for the differences in properties can be found in the small but statistically different bond angles at the fluorine atoms that bridge the octagons of aluminum fluoride. The peak widths and therefore the particle size of the two forms of AlF_3 are also very different. The nature of phase transition from the rhombohedral form at room temperature to cubic at 460°C appears also to vary for the two materials. The single crystal studies performed to probe this phenomenon are reported here.

Methods and Materials: A small, partially-twinned AlF_3 crystal was wedged in a capillary and a series of single crystal data sets were collected with a Mar345 image plate detector starting below and above the phase transformation. The data for the high temperature form were integrated with the HKL suite of programs [2] and refined with SHELXTL[3].

Results: The twinned rhombohedral crystals formed a single cubic domain upon transformation. The diffraction pattern can be viewed as a doubling of the cubic axis below the transformation. The relation of this doubled cubic cell to the rhombohedral cell can be seen in Figure 1. The most unusual feature of the high temperature AlF_3 structure is the highly anisotropic motion of the bridging F atom show in Figure 2, which presumably drives the rhombohedral to cubic transition.

Conclusions: Insights into the structural distortions and the driving forces behind the phase transition can be gained from time-resolved single crystal studies of AlF_3 .

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References: [1]. P. J. Chupas, M. F. Ciruolo, J. C. Hanson and C. P. Grey, *J. Am. Chem. Soc.*, **123**, 1694 (2001)
[2] Z. Otwinowski and W. Minor, " **Processing of X-ray Diffraction Data Collected in Oscillation Mode** ", *Methods in Enzymology*, Volume **276**: Macromolecular Crystallography, part A, p.307-326, 1997, C.W. Carter, Jr. & R. M. Sweet, Eds., [Academic Press](#) (New York).
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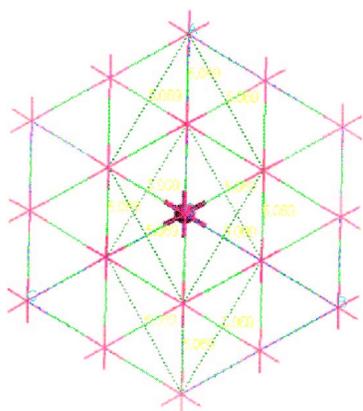


Figure 1. Double cubic cell viewed down 111 direction with rhombohedral cell inscribed on same diagram.

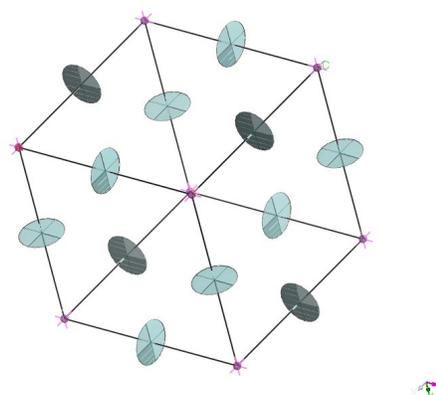


Figure 2. Thermal ellipsoids of high temperature cubic form of AlF_3 . View down the 111 direction.