Oxidation Protection of AlN/BN via $Al_{18}B_4O_{33}$

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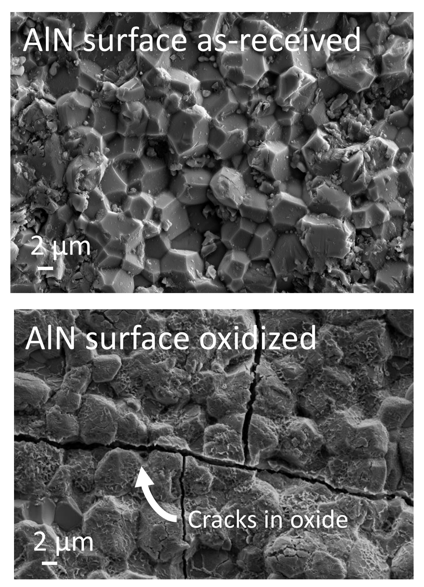
Project Scope

AlN/BN ceramic composites are materials of interest for high temperature applications because of their low elastic modulus and high thermal shock resistance. Concerns of side products that form due to BN oxidizing into reactive B_2O_3 motivate the study of the effect that B_2O_3 has on the oxidation of AlN ceramics. This study explores such effect by comparing the oxidation kinetics of AlN with that of B_2O_3-coated AlN and AlN/BN, offering insight into how liquid B_2O_3 films provide AlN with an improved protection against oxidation. Ultimately, this study provides a useful perspective on the oxidation of AlN/BN and serves as a guide to understanding why aluminum borate whiskers undergo morphological evolution in high temperature environments.

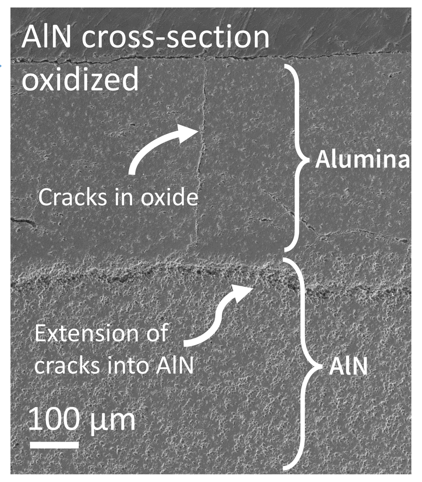
AlN Oxidation

$$4AlN + 3O_2 \rightarrow 2Al_2O_3 + 2N_2$$

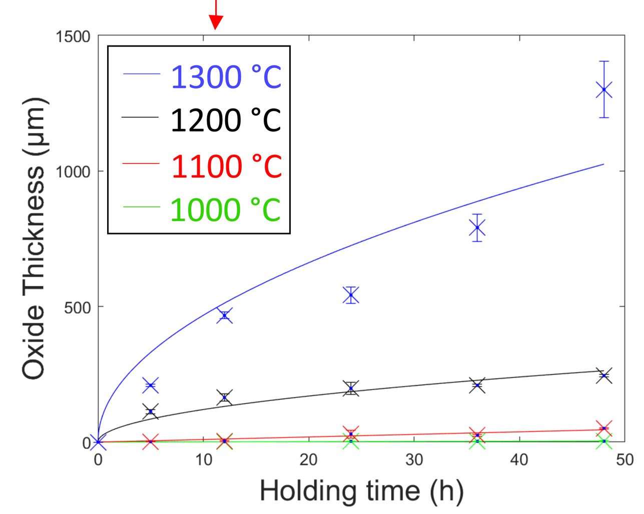
Starting at 800 °C, AlN can develop an Al_2O_3 layer that is porous from N_2 gas evolution. Differences in the coefficient of thermal expansion (CTE) between AlN (5×10^{-6} /°C) and Al_2O_3 (9×10^{-6} /°C), result in a large contraction mismatch between the layers leading to cracks forming within the oxide, facilitating O-diffusion. Oxidation kinetics of AlN are linear at T ≤ 1100 °C, and parabolic at T ≥ 1200 ° C.



Comparison of as-received AlN surface (top) and oxidized AlN surface (bottom).

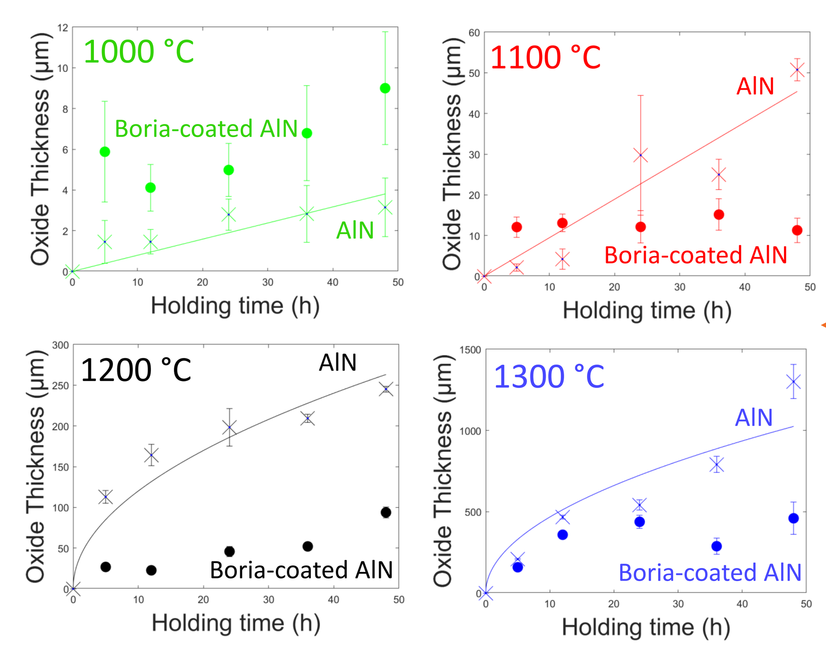


Cross-section of oxidized AlN, showing porous alumina oxide layer.



Oxidation kinetics of AlN from 1000 °C to 1300 ° C.

Boria-Coated AlN Oxidation



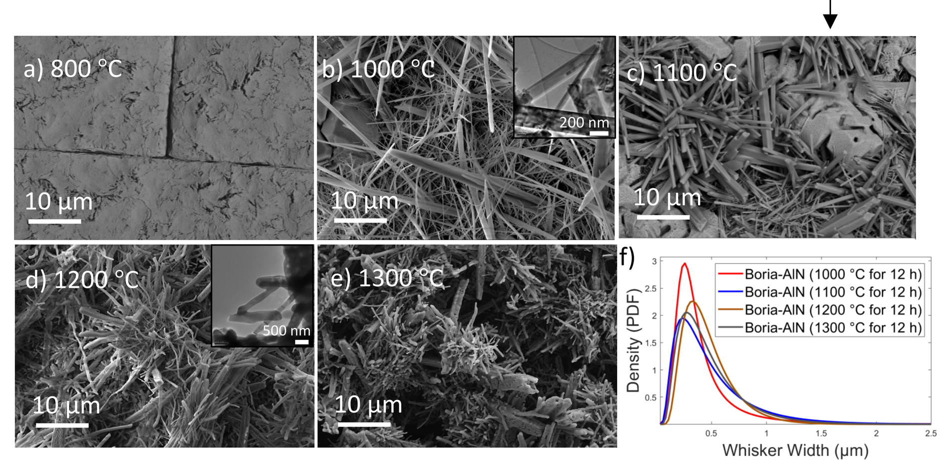
Oxidation kinetics of boria-coated AlN (●) compared to AlN (×), from 1000 °C to 1300 ° C.

Coating AlN samples with liquid boria inhibits AlN oxidation, especially at 1200 °C. Oxide layers produced on boria-coated AlN are thinner than pure AlN. This protection against oxidation is due to:

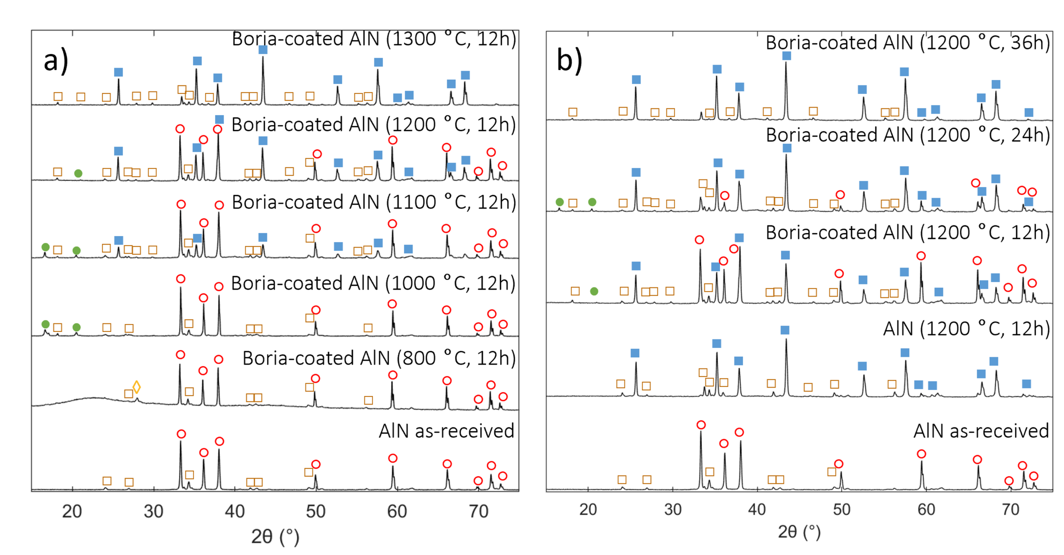
1. Boria thin films being a physical barrier to O-diffusion.
2. Boria reacting with freshly produced Al_2O_3 on the surface of AlN to form aluminum borate ($Al_{18}B_4O_{33}$) whiskers.

$$9Al_2O_3 + 2B_2O_3 \rightarrow Al_{18}B_4O_{33}$$

The whiskers are orthorhombic and can transform into Al_2O_3 starting at 1300 °C due to evaporation of boria within the crystal structure, as evidenced by X-ray diffraction.

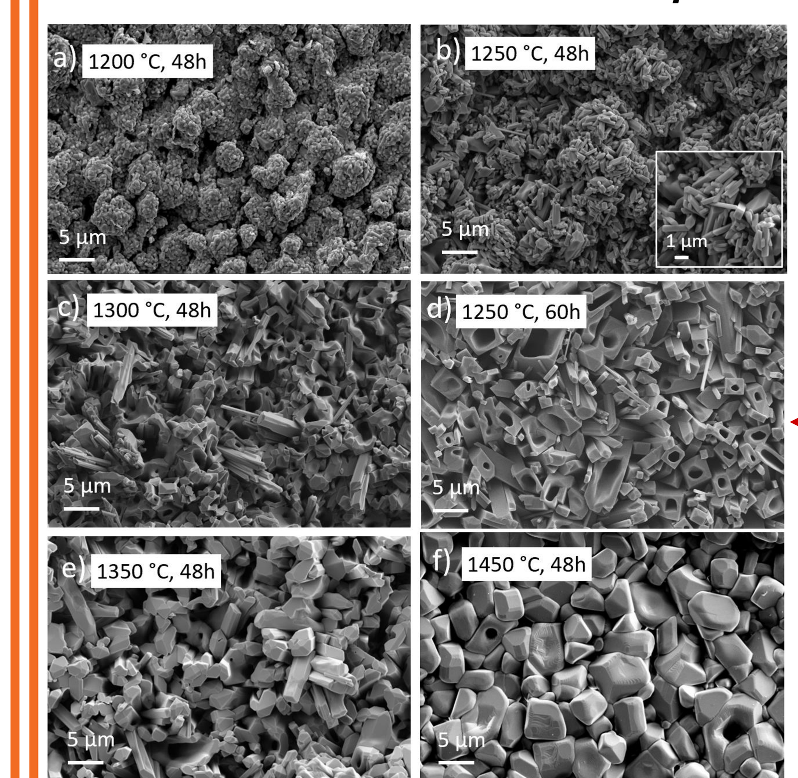


Surface microstructure of boria-coated AlN exposed to 12h of oxidation at a) 800 °C, b) 1000 °C, c) 1100 °C, d) 1200 °C, and e) 1300 °C. f) Distribution of aluminum borate whisker widths grown in the above exposures.



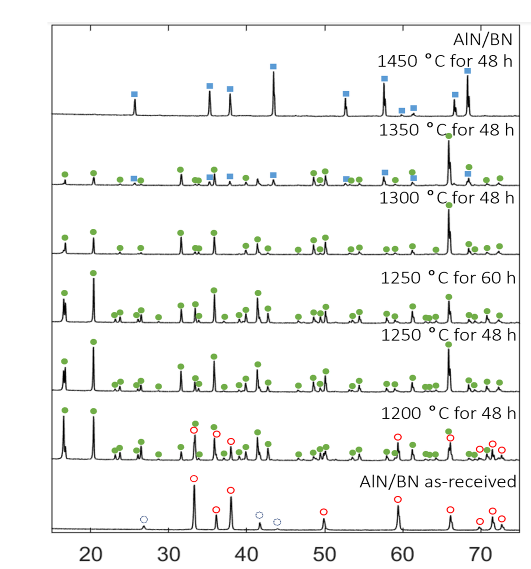
XRD spectra of boria-coated AlN at oxidation temperatures from 800°C to 1300°C in contrast to as-received AlN, b) XRD spectra of boria-coated AlN compared to AlN at oxidation temperature of 1200 °C for 12h, 24h and 36 h, where AlN (○), $Al_{18}B_4O_{33}$ (●), boria (◊), YAG/YAP (□), alumina (■).

AlN/BN Oxidation

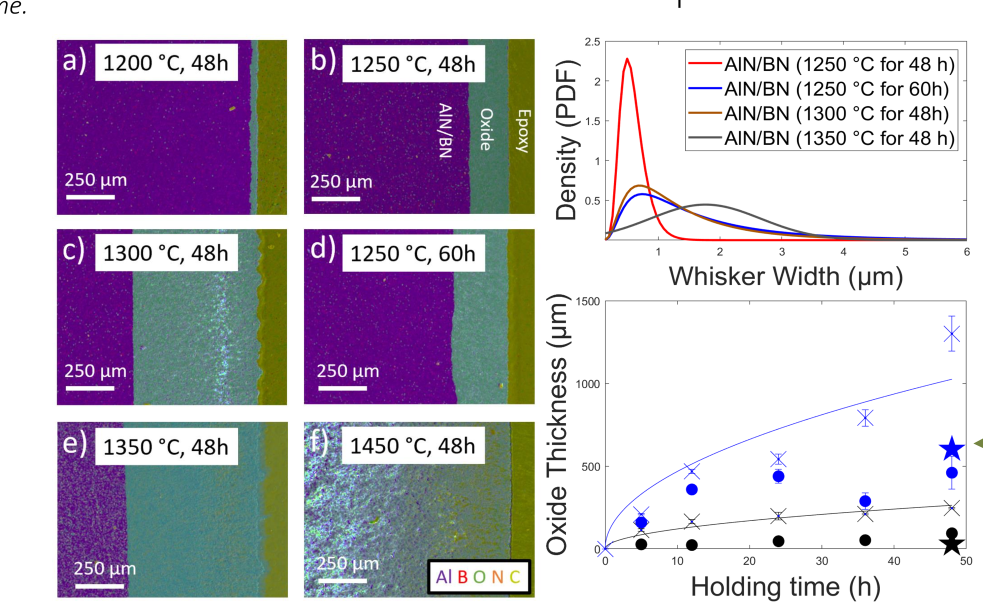


SEM images of oxidized AlN/BN composite in dry air, including oxidation temperature and exposure time.

In dry air, AlN/BN develops an oxide layer demonstrating a variety of crystal morphologies of $Al_{18}B_4O_{33}$ phases confirmed by X-ray diffraction. Oxide thicknesses are comparable to boria-coated AlN, suggesting an advanced protection against oxidation due to B_2O_3. With increased time at 1250 °C, the whisker width distribution widens as whiskers start to develop hollow cores or dimples. Hollow cores can act as pathways for O-diffusion, exposing the composite to extensive oxidation as seen in SEM-EDS maps below.

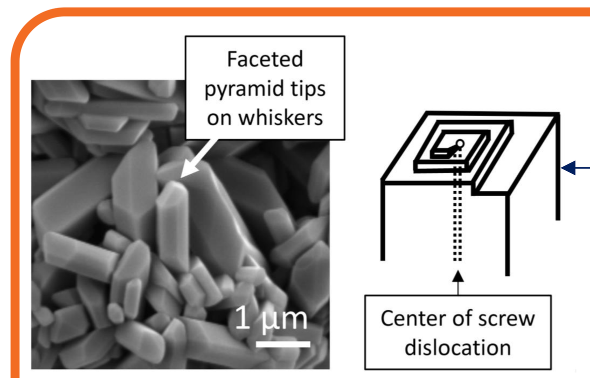


XRD spectra of oxidized AlN/BN in dry air from 1200°C to 1450°C, where AlN (○), BN (◌), $Al_{18}B_4O_{33}$ (●), alumina (■), in contrast to as-received AlN/BN.



SEM-EDS maps of oxidized AlN/BN in dry air (left). Distribution of widths of whiskers grown in described conditions (top right). Oxidation plots including data points from AlN (×), boria-coated AlN (●), and AlN/BN (★) at 1200 °C and 1300 °C (bottom right).

Aluminum Borate Whiskers and Hollow Crystals

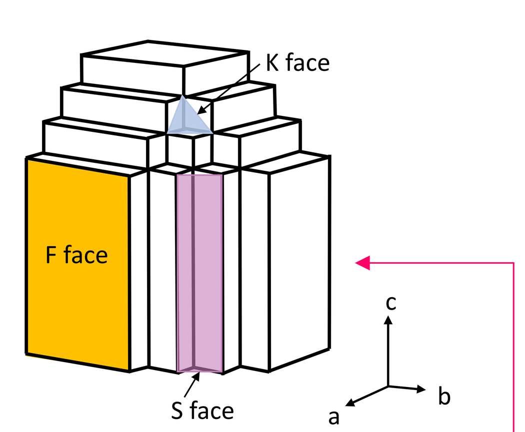


Example of whisker with pyramid tip (left), illustration of whisker growth by screw dislocation (right).

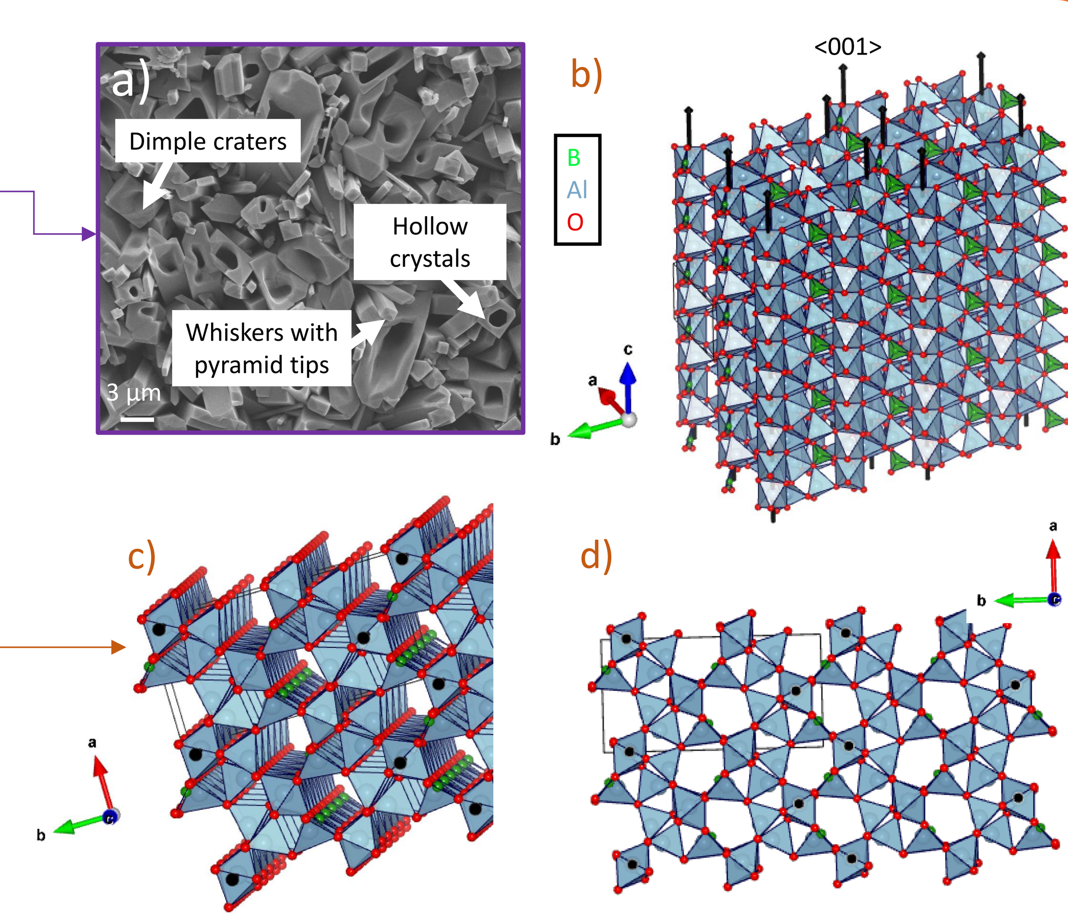
A spiral growth mechanism of $Al_{18}B_4O_{33}$ could account for its different morphologies. Nuclei of $Al_{18}B_4O_{33}$ precipitate out of a supersaturated solution of liquid boria. Anisotropic growth may then arise from screw dislocations on $Al_{18}B_4O_{33}$ surfaces, which spirally extend via a vapor-solid growth with boria vapor, and facet into pyramid-shaped tips.

Dimples and hollow cores may be explained by:

a. *Frank's theory of capillary equilibria:* strain energy mismatch between the crystal surface and the dislocation line makes it energetically favorable to create a free surface in the crystal core.
b. *Periodic Bond Chain (PBC) theory:* $Al_{18}B_4O_{33}$ is composed of strong chains of AlO_6 octahedra, AlO_4 tetrahedra, and alternating AlO_4 tetrahedra and BO_3 groups, all along <001>. High-temperature boria evaporation causes chains to break, inducing a roughening transition (S faces → K faces) that promotes growth along the edges of the crystal.



PBC theory face types, where F face represents smooth surface (// to 2 or more strong chains), S face is a step (// to 1 strong chain), and K face is a kink (// to no strong chain).



a) Close-up of AlN/BN exposed to 1250 °C for 60h, showing different morphologies of $Al_{18}B_4O_{33}$, b) Super cell (3x3x6) of $Al_{18}B_4O_{33}$, black arrows show direction of crystal growth <001>, c) shows channels through crystal along <001>, exposing BO_3 units, d) shows (001) plane. Lattice parameters a = 0.7692 nm, b = 1.4973 nm, c = 0.5682 nm.

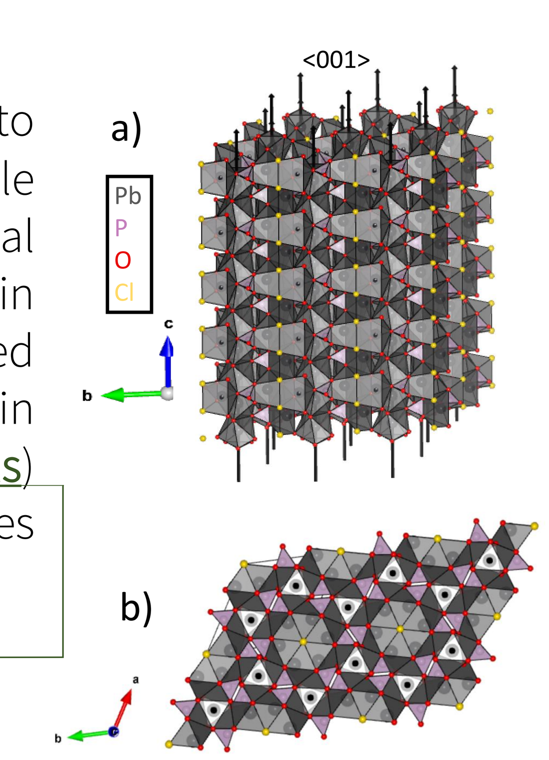
Broader Impact

The CTE of $Al_{18}B_4O_{33}$ (4×10^{-6} /°C) is comparable to AlN. Thus, $Al_{18}B_4O_{33}$ provides a more compatible protective layer for AlN than Al_2O_3, preventing thermal mismatch cracks, which leads to better performance in high-temp environments. This study has also helped shed light on how hollow cores can develop in analogous crystal systems (e.g., lead-bearing minerals) with similar growth mechanisms and crystal structures to $Al_{18}B_4O_{33}$.

Pyromorphite Pb5(PO4)3Cl

Vanadinite Pb5(VO4)3Cl

Crocoite PbCrO4



a) Super cell (2x3x5) of pyromorphite, black arrows show direction of crystal growth <001>, b) view of (001) plane.

C.S.C. and K.T.F. gratefully acknowledge support from NASA's JPL through a Research and Technology Development Grant, and for C.S.C. the Amelia Earhart Fellowship from Zonta International.