

Nano-clusters in Natural Beryllium-bearing Sapphires

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Trace amount of beryllium can sometimes be found in natural corundum crystals, often correlated with high field strength elements (HFSE). Previous studies on the submicron Ti-rich inclusions show that beryllium is concentrated in the precipitates instead of evenly distributed in the corundum crystal. [1][2] However, the beryllium concentration is not always correlated with the clouded zones, suggesting complicated trace element behavior. Two natural sapphire samples with high beryllium concentrations are studied using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) and atom probe tomography (APT) to better understand the beryllium migration and distribution in natural corundum.

The sample from Afghanistan contains extraordinarily high concentrations of W (up to 2900 ppmw), which are strongly correlated with the Be in the growth zones of the crystal. The sample from Nigeria shows high concentrations of Ta and Nb in correlation with Be. No consistent correlation between Ti and Be is observed in either sample. The Be-rich zone in the Nigerian sample is clear with no visible inclusions, whereas the Be-free zone shows banded clouds of nano-precipitates. Nano-clusters (~10 nm) of Be, separated by ~100 nm from each other, are detected in the Afghanistan sample, while all other elements, including W, are distributed evenly. Three different types of nano-clusters can be found in the Be-rich zone of the Nigerian sample, enriched in Be+Ti+Nb+Ta, Ti+Nb+Ta, and only Ta respectively, with decreasing sizes and increasing spatial density.

All the trace elements seem to be dissolved in the corundum lattice during crystallization. The nano-clusters are formed following the sequence of increasing atomic weight with decreasing mobility, with Be clustering first, followed by Ti, and finally Ta. The heavier atoms would enter pre-existing clusters before forming clusters of their own. These nano-clusters are probably precursors of the nano-precipitates or silks often observed in natural sapphires.

[1] Palke & Breeding (2017), *American Mineralogist* 102, 1451-1461

[2] Shen (2011), *GIA Lab Report*, GIA, Carlsbad, CA, USA