

The nature of the Be-Nb-Ta containing cloud in natural Madagascar blue sapphire – An FIB/HRTEM study

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Abstract

The combination of focused ion beam (FIB) sample preparation and high-resolution transmission electron microscope (HRTEM) allowed us to definitely identify the natural Be containing cloud to be nanocrystals of TiO₂ in an α -PbO₂ structure – not rutile, Anatase nor Brookite. No other separate Nb or Ta phases were seen; therefore, beryllium (Be), niobium (Nb) and tantalum (Ta) are believed to be dissolved in these nanocrystals. A separate thorium (Th) enriched phase was observed but cannot be positively identified.

Introduction

Ever since the installation of LA-ICPMS in GIA, we have analyzed thousands of blue sapphires. We were the first gem laboratory to recognize the uneven distribution of Be in some heated and unheated sapphire and the association of clouds and turbidity in the stone to higher Be concentrations (Shen et al., 2007). We concluded that these must be naturally occurring Be existing in the clouds. We were also the first to recognize the association of natural Be with Nb and Ta and in some cases other elements such as Ti or light rare earths (La, Ce etc).

It is reasonable to hypothesize that these elements are contained in these cloudy inclusions because of the close association. However, the nature of these cloudy inclusions was not clear. A few attempts were made to identify the phase (or phases) that contains these elements including fracturing the sapphire sample containing natural Be and study the fragments in SEM (with Prof. George Rossmann at Caltech) and synchrotron X-ray diffraction study (with Dr. Oliver Tschauner at UNLV). Both studies yielded no results or very little information about the phase. There is very few options left to identify these phases. One of them is to use a Focused Ion Beam (FIB) sample preparation for a High resolution transmission electron microscope (HRTEM) study. FIB preparation allows one to make a very thin sample (~50-200 nm thick) suitable for TEM study and the TEM study is the definitive identification of the nanocrystals (which includes major element chemistry and electron diffraction study).

In the global earth science community, there are quite a few HRTEM groups. However, only a very small number of groups has both FIB and HRTEM. In fact, there is no group in the US that has both instruments in the same research group. Among the groups that do have both FIB/HRTEM facilities, the group in Deutsches GeoForschungsZentrum (GFZ) at Potsdam, Germany is probably the most experienced. This group is lead by Dr. Richard Wirth, who is an electron microscopist worked on nano-inclusions in diamond and various minerals for years. Based on the availability of both instruments and the expertise of the group, I contacted Dr. Wirth in this August and explained our issues and he immediately expressed interest helping us in solving this issue. He suggested me to

work with him at Potsdam and the trip was scheduled on 11/7-11/11. This report documents the findings of this experiment.

Instrumentation

GFZ has two FIB instrument for FIB sample preparation: an FEI FIB 200TEM system and an FEI Qunata 3D DualBeam system. In this study, we used the FIB200TEM system (figure 1) to prepare the sample and an FEI Tecnai G2 F20 X-twin TEM (figure 2) for HRTEM study.

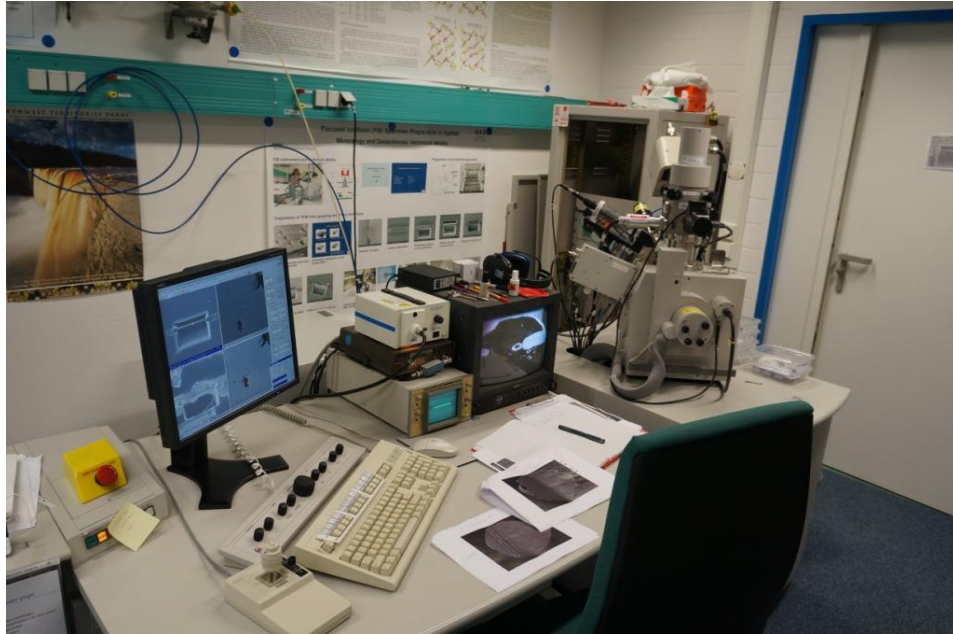


Figure 1. FEI FIB200TEM system in GFZ



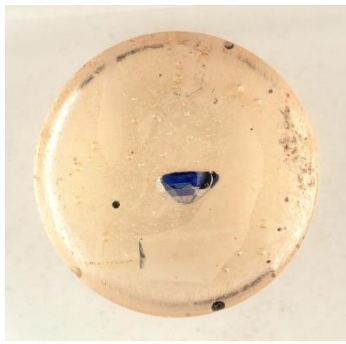
Figure 2. FEI Tecnai G2 F20 X-twin HRTEM system in GFZ

Sample description and preparation

Three stones were studied: (1) AA609 (figure 3a), 1.23 ct, unheated rough from Ilakaka, Madagascar (2) 111178 (figure 3b), 0.61 ct, faceted and heated stone from Madagascar, and (3) a 2.99 ct faceted and heated blue sapphire from unknown locality (figure 3c). All three samples have been analyzed with LA-ICPMS and all have detected natural Be presence. All three samples have obvious clouds associated with natural Be and Nb-Ta.



Figure 3a



3b



3c

AA609 has a series of ICPMS spots across the sample (figure 4) with interesting color zone and cloud distribution. The chemical data of these spots are plotted in figure 5. Clearly in this sample, the Be-Nb-Ta is directly related to the presence of the cloud (figure 5a and 5b). In the middle part of the sample, the blue area is relatively clear and very little cloud is seen.

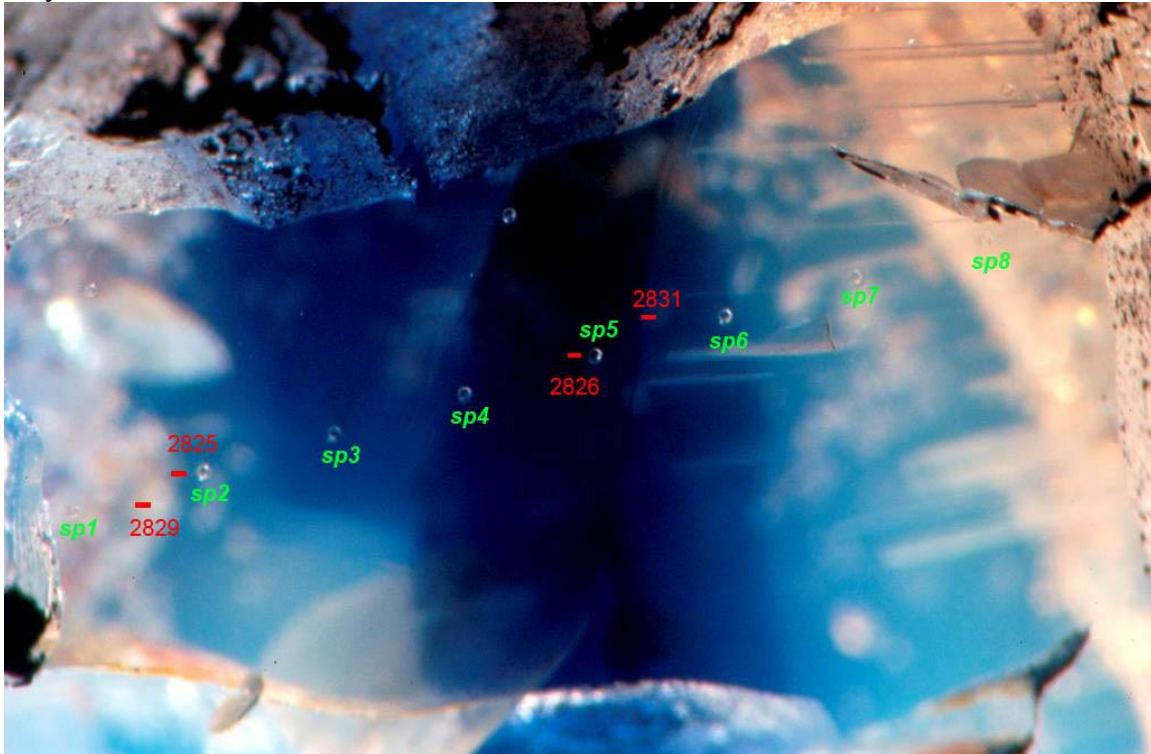


Figure 4 LA-ICPMS analysis spots and foils position in red (with their numbers shown). The green labels are the LA-ICPMS analysis spot numbers.

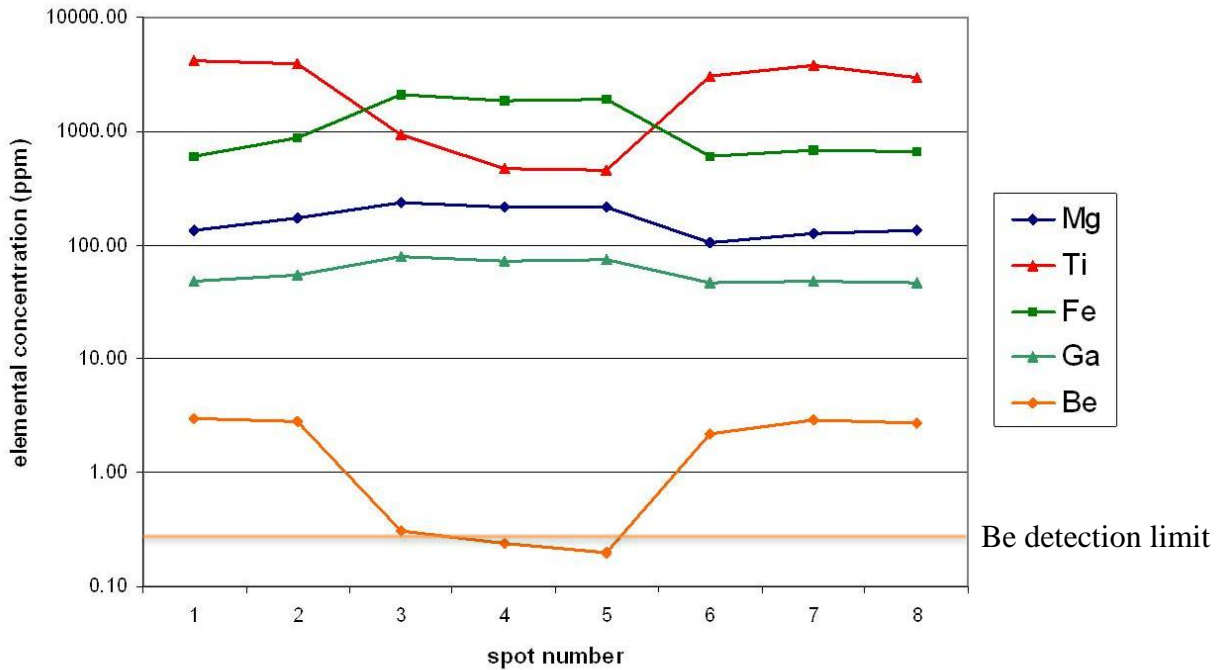


Figure 5a Chemistry of AA609 ICPMS spots – spots are labeled green in figure 4.

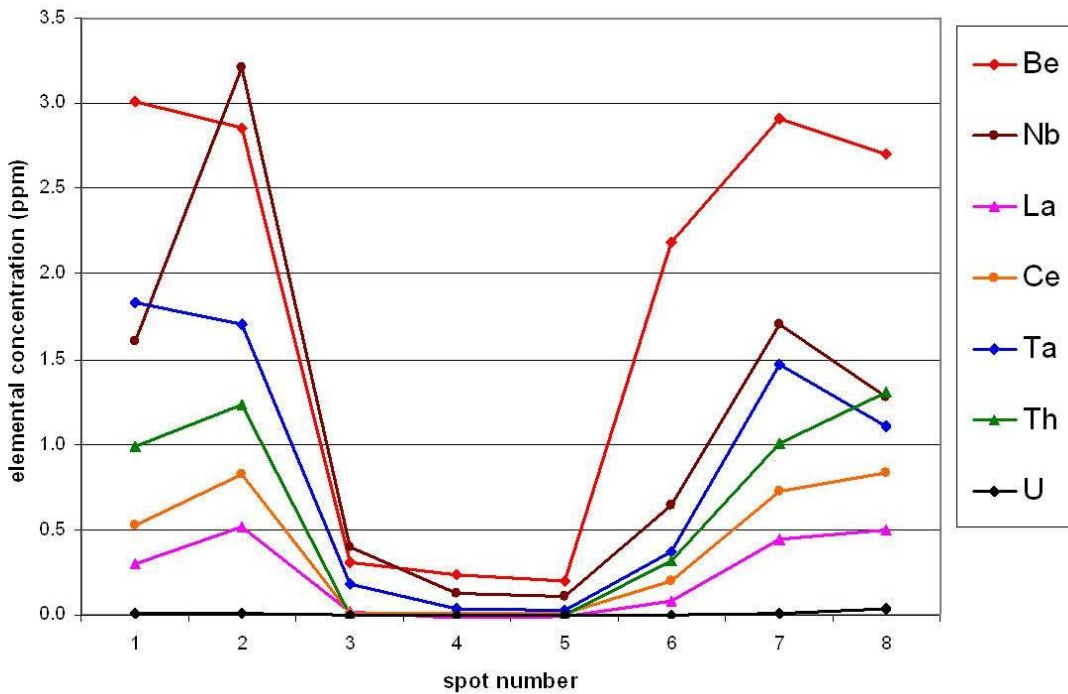


Figure 5b more chemical analysis results.

111178 was embedded in epoxy resin so that it can be polished to specific orientation. Figure 6 is a zoom-in picture of the stone. There is a cloudy area close to the girdle of the stone. It's Be concentration is ~ 3 ppmw in the cloudy area and below detection limit in

the clear area. Figure 7 is a 1000X photomicrograph taken near the laser spot on the cloudy area, it is slightly defocused into the stone and it is clearly seen the cloudy area consist of two types of inclusions – one is a milky cloud uniformly distributed in the area and the other is round bead like inclusions with much larger dimensions (~0.5 micron in diameter).



Cloudy area with a laser spot

Figure 6 Zoom-in view of 111178

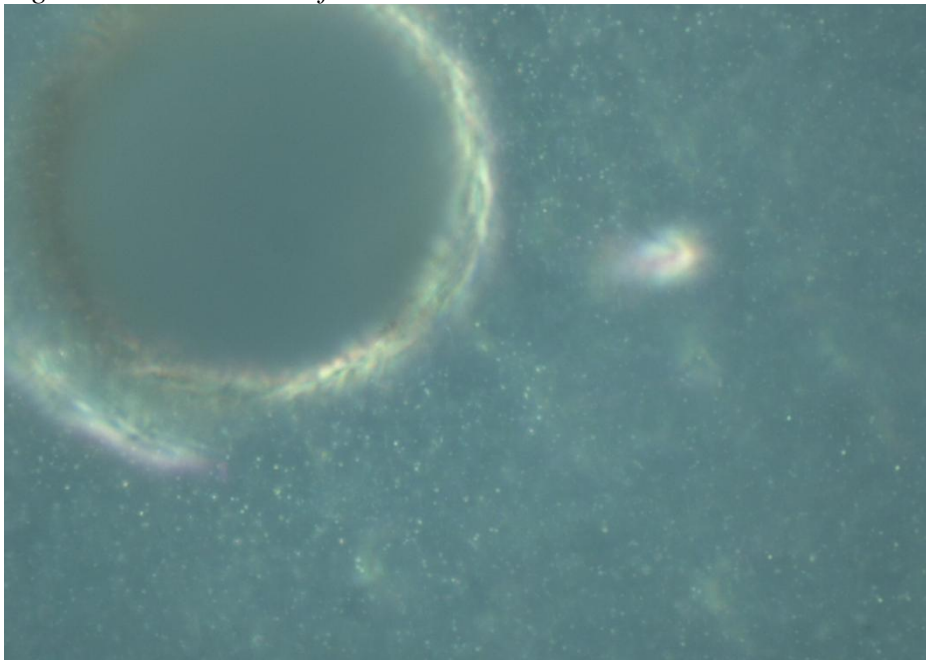


Figure 7 1000X photos of 111178 near the laser hole, two kinds of clouds are visible. The round hole is a laser spot (55 μm in diameter).

The 2.99 ct stone is a latest acquisition because of its high Be, Nb and Ta concentrations. Its Be reached 21 ppmw, but below detection limit in other area. Its Nb concentration reached 250 ppmw and Ta is even up to 350 ppmw. These are among the highest concentrations of these elements that we have seen.

Sample preparation procedure will first require the stones to be mounted and use silver paint to ensure proper conduction during the FIB preparation. After mounting, the sample needs to be coated with carbon or gold before it is placed in the FIB system.

Once the sample is placed in the FIB system, energetic Ga ions are used to mill the sample to a TEM-ready sample – it is called “foil” (Wirth, 2004). Electrons in a TEM can only penetrate a very thin sample and traditionally the sample is thinned by an argon ion mill. The FIB system allows one to mill at a location exactly a researcher wanted to study. The foils we produced for this study are around $14\ \mu\text{m} \times 7\ \mu\text{m} \times 200\ \text{nm}$ in dimension. Figure 8 is a photomicrograph of 111178 (with interference contrast) with three foils being made from this sample. There is one foil remains in the sample because it was abandoned due to insufficient depth.

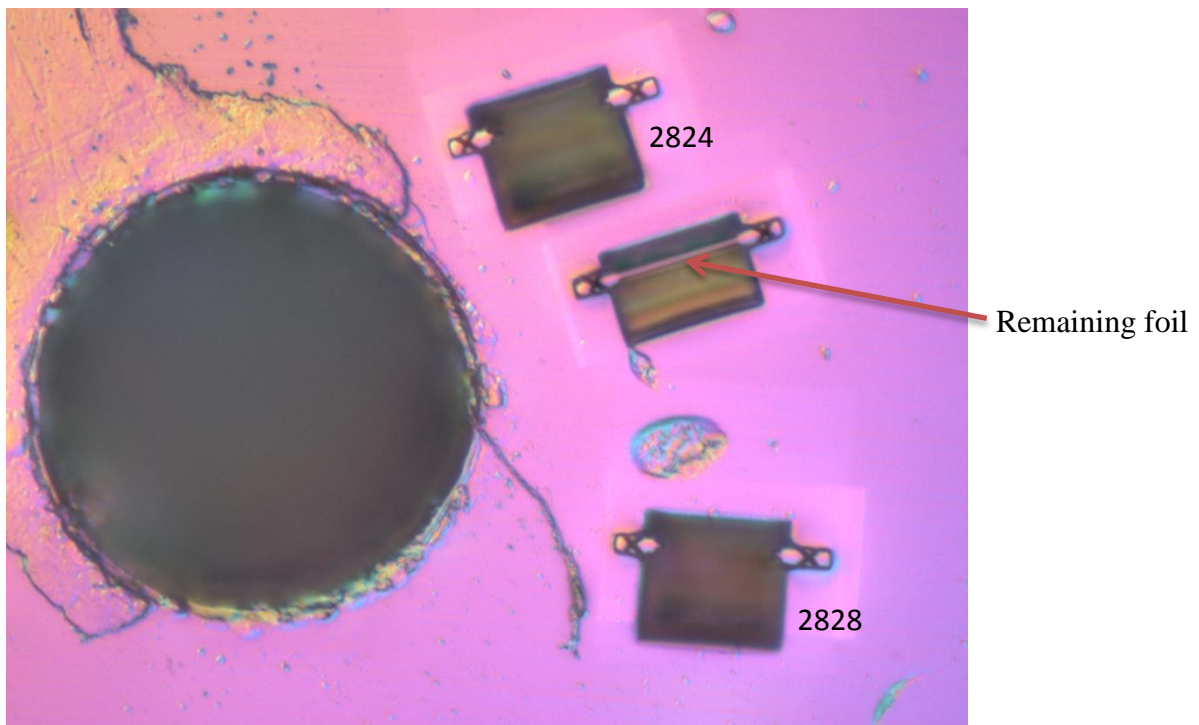


Figure 8 1000X photomicrograph of 111178 after experiment (with interference contrast). One foil is abandoned due to its shallowness and remains in the sample.

The prepared foils were transferred to a standard TEM copper sample grid – such grid is covered with a very thin layer of amorphous carbon film. The foil was first lifted from its position in the sample using a micro-sample handler together with an optical microscope (figure 9). The foil is then placed on the carbon film area of the sample grid and the atomic level attraction is very strong and it is impossible to remove the foil from the amorphous carbon film.

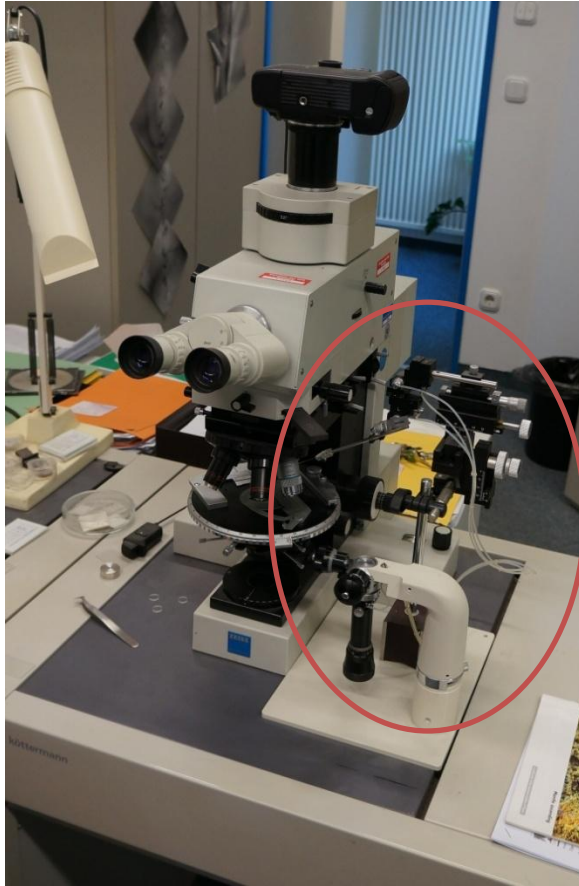


Figure 9
Mechanical micro-sample handler (circled) with an optical microscope used for removing the TEM foil from an FIB processed sample.

Total 6 useable foils were made and studied – 4 from AA609, 1 from 111178 and 1 from the 2.99 ct stone. Those four foils in the AA609 are taken at four different areas (shown in figure 4) – two of them were taken from two different milky cloud areas (#2825 and #2829), one from the blue area (#2826) and the last one was from an area close to the interface between the milky cloud and blue area (#2831).

Results and Discussions

All foils except one (#2826 from the clear blue area of AA609) showed numerous of nano-crystals (figure 10 a-e). The unheated sample has finer nano-crystals and the heated samples seem to have larger crystals.

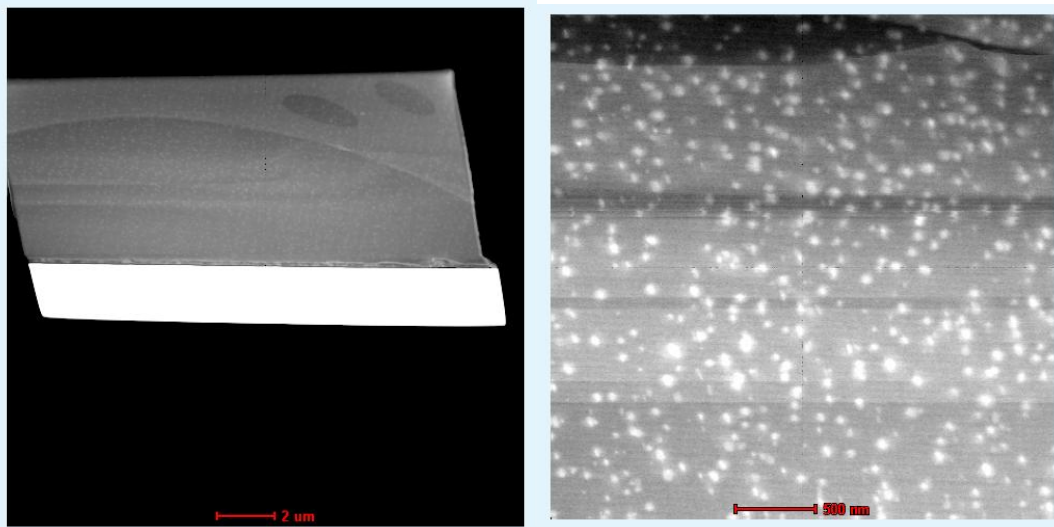


Figure 10(a) Overview #2825 (unheated AA609) Zoom in #2825

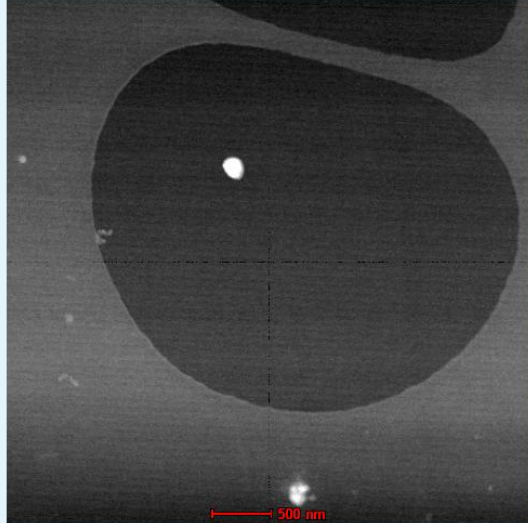
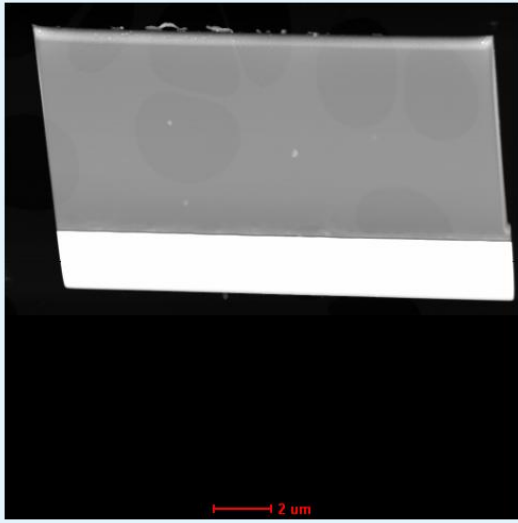


Figure 10(b) Overview #2826 (unheated AA609) Zoom in #2826

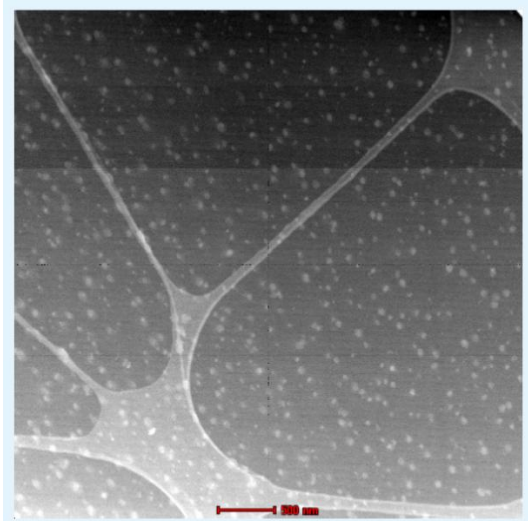
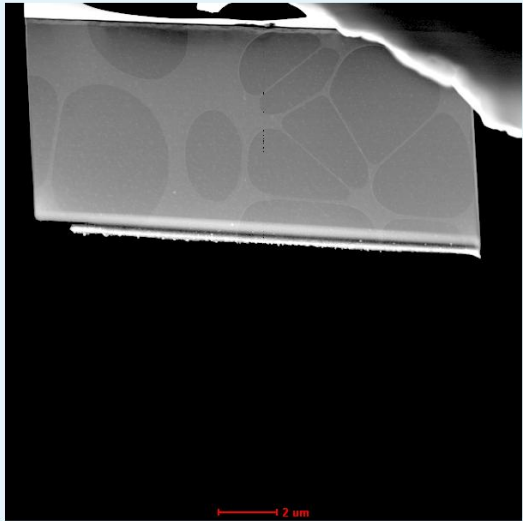


Figure 10(c) Overview #2831 (unheated AA609) Zoom-in #2831

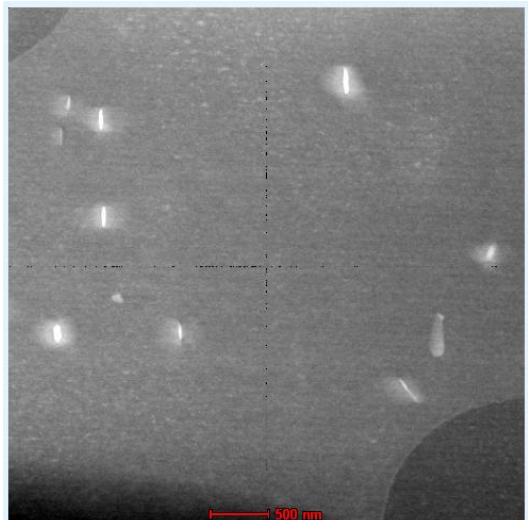
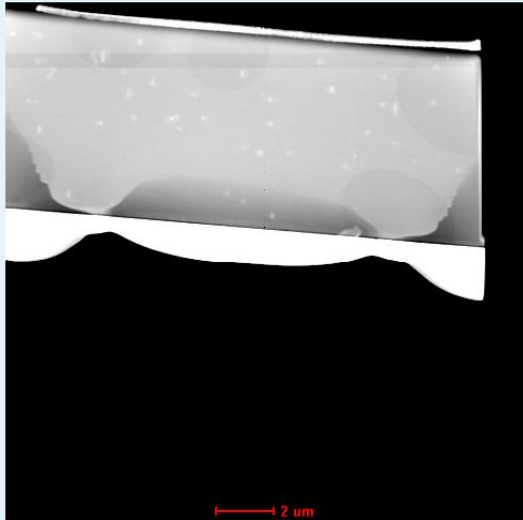


Figure 10(d) Overview #2828 (heated 111178) Zoom-in #2828

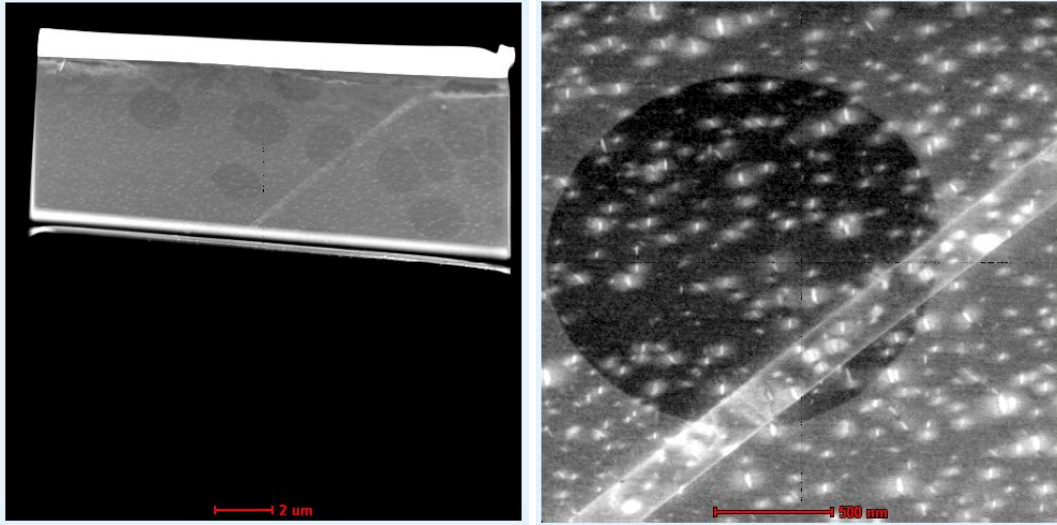


Figure 10(e) Overview #2827 (heated? 2.99 ct) Zoom-in #2827

The EDXRF unit on the Tecnac allows us to analyze the major chemistry on these nanocrystals and found they are mainly enriched in Ti. We did not see any Ta and Nb due to the high detection limit on the EDXRF unit on the TEM – estimated to be above 800 ppm for detecting Nb and Ta. The foils are machined with Ga ions and a layer of Pt deposited on each foil during sample preparation and sample holder is made of Cu; therefore, Ga, Pt and Cu are ubiquitous in these analyses.

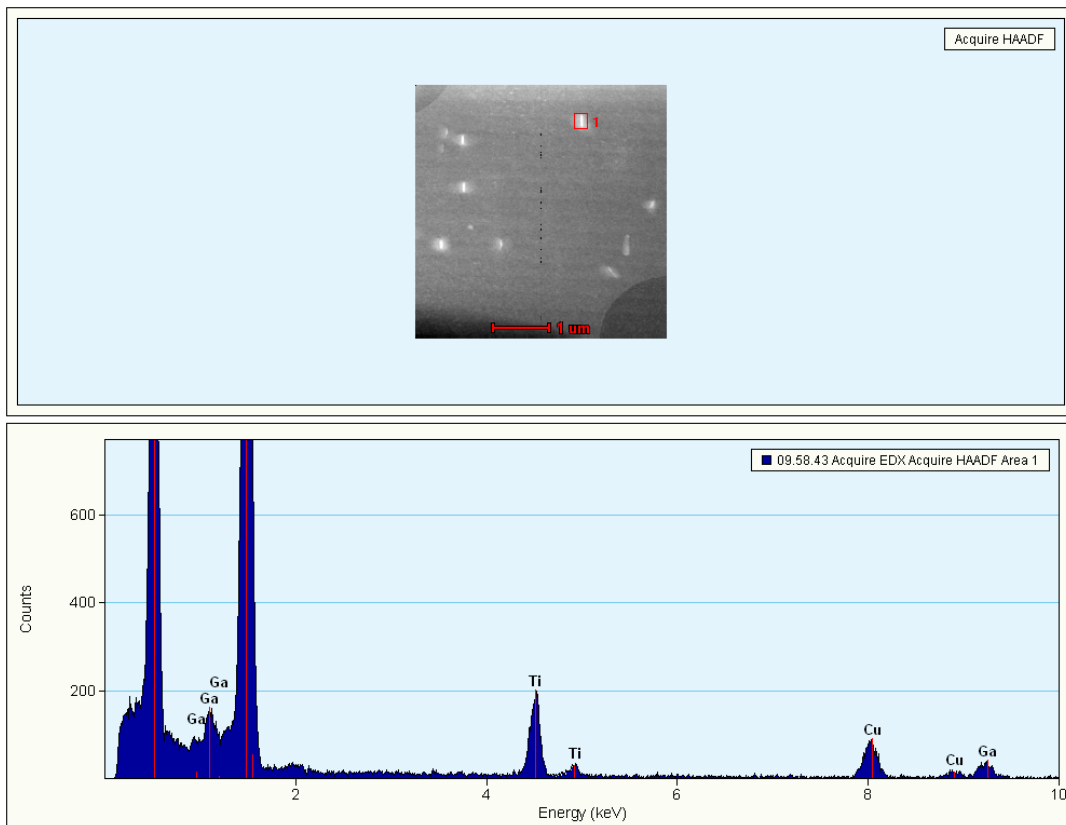


Figure 11 Chemical analysis on #2828, from red box area 1

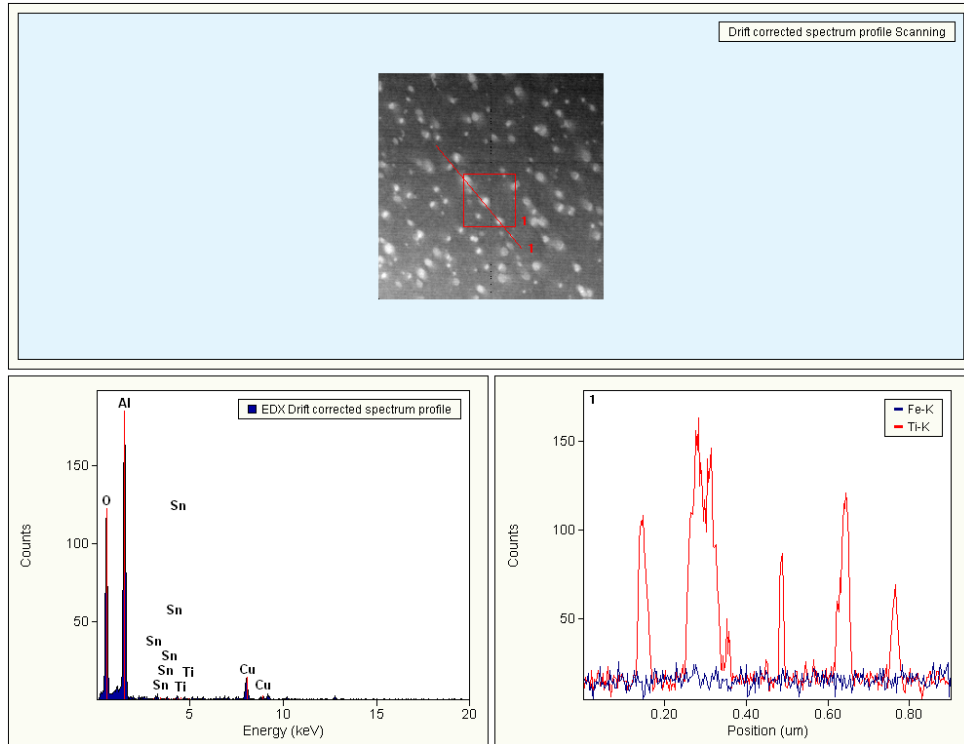


Figure 12 Chemical analysis on #2831, lower left box is analysis result from the red box area in the photo and the lower right box is scanning results from the red line

In the foils that contains these Ti-rich nanocrystals, they all show clear strain halos in bright field images – meaning these nanocrystals cause the host crystal (corundum) to strain (figure 13(a)). The Ti-rich nanocrystals are roughly 5 nm in thickness and 30 nm in width and roughly 100 nm in length. We performed diffraction studies (Figure 14 (a) and (b)) on selected few crystals from each foil and found them to be TiO_2 in $\alpha\text{-PbO}_2$ structure (for annotation purpose, we shall call it $\alpha\text{-TiO}_2$), not rutile, anatase nor brookite. This phase was first identified in some products of high pressure experiments.

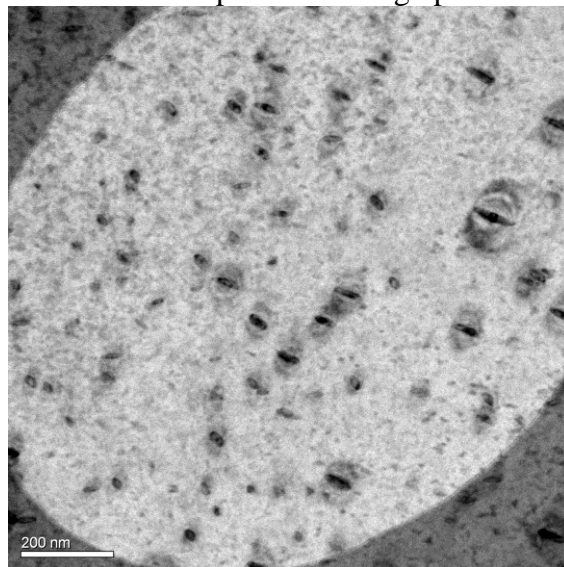


Figure 13(a) Bright Field image on #2827

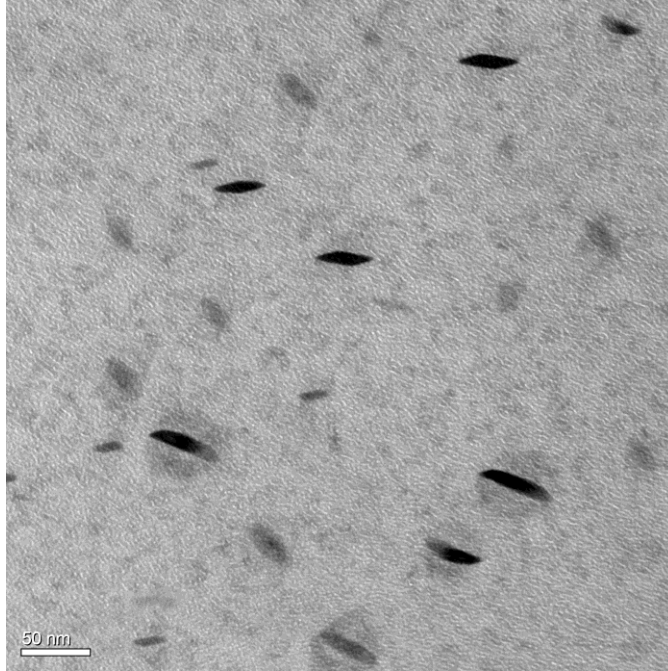


Figure 13(b) Zoomed-in BF image of #2827. Some of the crystals are twinned

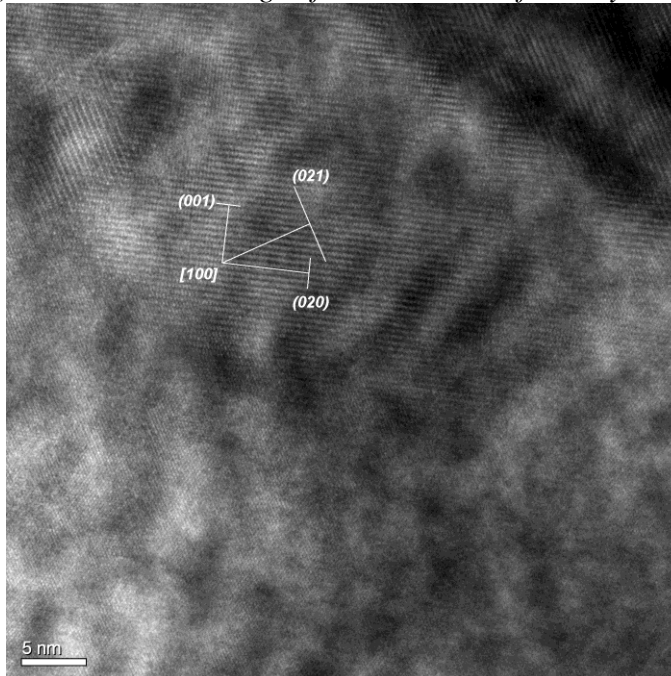


Figure 14 (a) lattice image of a couple nanocrystals on #2831

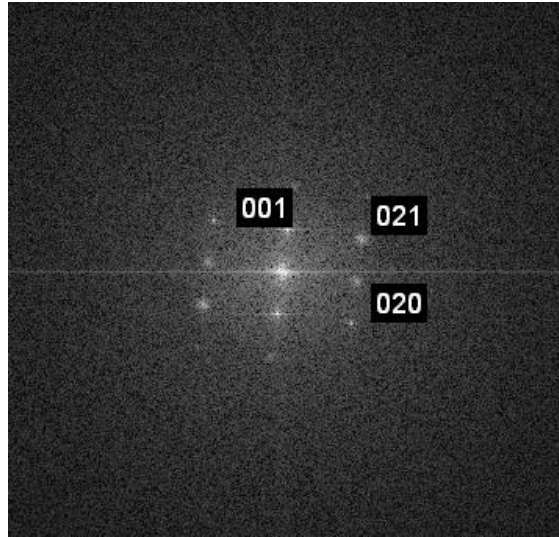


Figure 14 (b) Diffraction pattern of the previous HRTEM area

Table 1 d-spacings

$d_{(hkl)}$	Observed (Å)	Theoretical (Å)
001	4.774	4.939
020	2.778	2.748
021	2.387	2.402

Table 2 angles

	Observed (°)	Theoretical (°)
$\angle (021) \wedge (020)$	30.07	29.1
$\angle (021) \wedge (001)$	60.02	60.9

Table 1 and 2 summarize these diffraction study results, pattern in figure 14(b) was successfully indexed as labeled. The zone axis is found to be [100]. The α -TiO₂ nanocrystals were found to be aligned with the host crystal (sapphire) in a specific orientation: $(001)_{\alpha\text{-TiO}_2} // (110)_{\text{sapphire}}$ and $[100]_{\alpha\text{-TiO}_2} // [001]_{\text{sapphire}}$. That's the reason why almost all these nanocrystals seem to be aligned and all showed only the thickness and width in Figure 13. Some of the nanocrystals are apparently twinned.

The only non-TiO₂ phase we have seen in all foils is a Th-rich phase in #2824 from the heated sample 111178 (Figure 15). It showed up as a high contrast spot right next to the typical α -TiO₂ crystal. The α -TiO₂ crystal is oriented so that the full length and wide can be seen (unlike the thin skinny crystals we have seen before). Figure 16 show the chemical analysis, clearly, Th is highly enriched. There seems to be Ti and Si in this phase. We tried to fit its diffraction pattern with thorianite (ThO₂) and thorite (ThSiO₄), but we didn't get any match. The crystal seems to be in an aggregate with the α -TiO₂ crystal and the Ti signal may be coming from the α -TiO₂.

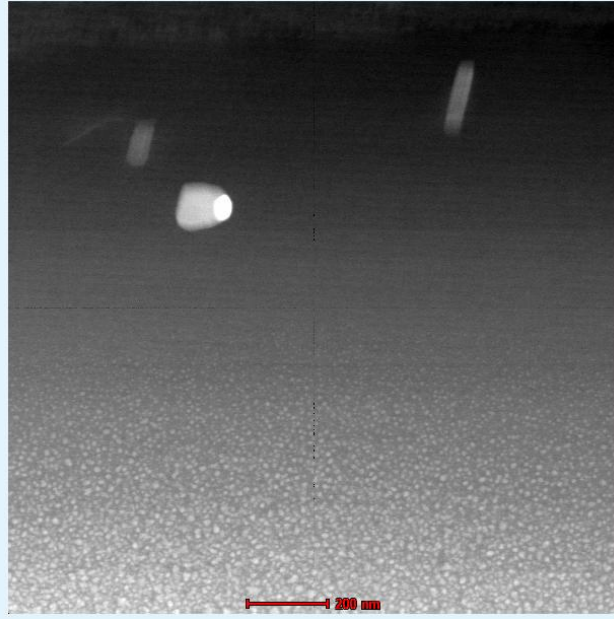


Figure 15(a) Th-rich phase in #2824 (from heated 111178). The Th-rich phase appeared as a very bright spot, which is in an aggregate with α -TiO₂ crystal. The α -TiO₂ is oriented so that the full length can be seen.

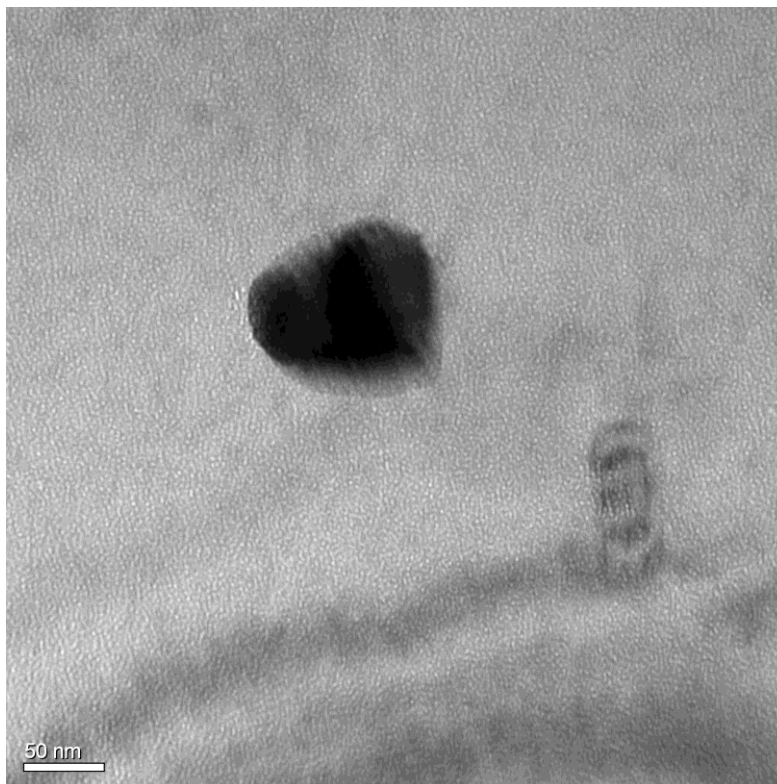


Figure 15(b) Bright field zoom-in image of the Th-rich phase and the TiO₂ phase aggregate. The Th-rich phase is to the left of the inclusion.

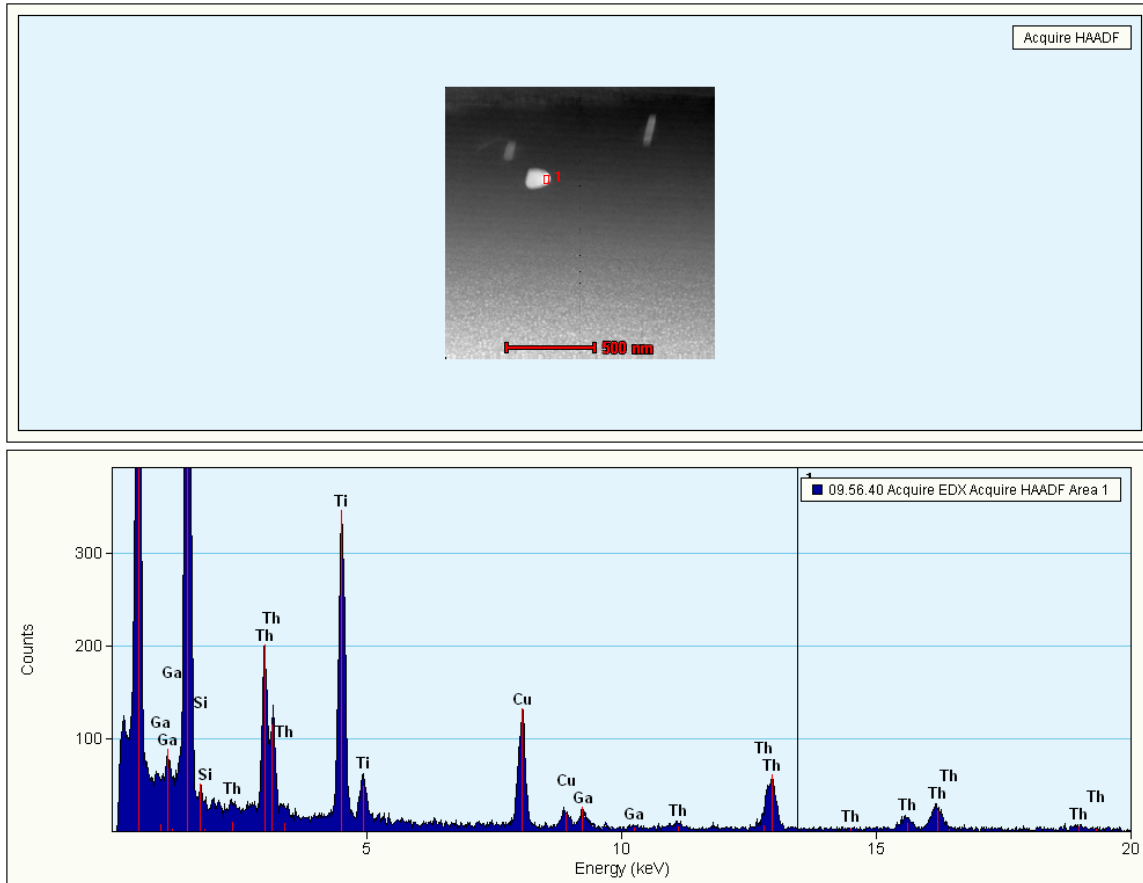


Figure 16 Chemical analysis of the Th-rich phase

The foil from the clear blue area (#2826) from the unheated sample (AA609), on the other hand, is completely free from any nanocrystals. A couple visible bright spots in the picture (Figure 10(b)) turn out to be contaminations from the air attaching to the sample surface.

From this study, we clearly did not see any other phases that is enriched in Nb or Ta. Th enrichment may be related to an unknown Th-rich phase; however, there is no direct evidence indicating Be-Nb-Ta existed as separate phases. From the close relationship between these three elements to Ti in AA609 sample (figure 4) and the HRTEM results, it is clear that these elements must be dissolved in these nano α -TiO₂ crystals.

Further Research

Current study has made solid and important progress on the issue of natural Be in sapphire. Firstly, we clearly identified the cloud is made of α -TiO₂ nanocrystals. In all gemological literatures I have found, the clouds are all identified as rutile due to this paper by Moon and Phillips (1986). Secondly, we didn't see any other phases that are enriched in either Nb or Ta. We do see one inclusion showing high concentration of Th. From the LA-ICPMS analysis we have done on the unheated sample, the results strongly

support the hypothesis that Be-Nb-Ta are dissolved in the α -TiO₂ crystals. Naturally, the extension of this study will involve using nano-SIMS to analyze these α -TiO₂ crystals.

In some material science literatures, some artificial annealing experiments have been done on Ti-rich alumina and both α -TiO₂ and rutile nanocrystals were reported, their occurrences depending on the annealing temperatures. We didn't see the rutile nanocrystals in all our samples, does that mean that natural sapphires prohibit rutile formation? How about the different localities (different chemistry)? Is Kashmir sapphire cloud also made of α -TiO₂? Some geologists have inferred high pressure metamorphic grades based on α -TiO₂ nanocrystals found, can this be a mistake? There are a lot of additional questions that are of interest to gemologists and geologists alike that can be answered by further research using the FIB/HRTEM study on cloud inclusions in sapphires.

References

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