

Distinguishing Heated Spinel from Unheated Natural Spinel and from Synthetic Spinel

A short review of on-going research

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Figure 1: Spinel rough from Tajikistan, the largest stone (upper right) weighing 242.50ct.

Abstract

Natural spinels are found in colors equal to those of fine rubies or sapphires, and since top quality spinels are one of the few 'better known' gems to have so far escaped the attention of large scale treatment processes; they are gaining a greater commercial importance. However, it would appear that at least some heat treated natural spinels are on the market and therefore it is important that criteria be established for the separation of the treated from the natural material. This paper reviews, confirms, and extends the original identification criteria developed during experiments carried out in 2005 on pink to red spinel from Tanzania and applies these criteria to a wide variety of spinels from a variety of sources.



Figure 2: Faceted Tajikistan spinels cut from the rough depicted in Figure 1.

Introduction

In 2005 some concern was expressed by the trade that certain pink and red spinels from Tanzania may have been heated to improve their appearance. In order to investigate these concerns further five samples were obtained from the trade that were stated to be unheated. These five were examined and their data recorded and then subjected to heating processes at temperatures varying from 1100 to 1700°C, in oxidizing conditions, at Crystal Chemistry. In general, and for the five samples cited, these experiments showed that the spinels did not improve in appearance but rather they became darker (Figure 3). However, the experiment was limited to a very small

sampling. Before and after inclusion observations revealed some severe alterations had taken place following heating, particularly at the higher temperatures. Given the results of these preliminary experiments, it was unclear why spinel would be heat treated. Thus a more extensive study was undertaken.



Figure 3: A 1.17ct spinel from Tanzania before heating (left) and after heating at 1400°C, in O₂, for 5 hrs (right).

Experiments

To broaden the study substantial amounts of rough spinel were obtained from the Mahenge, Morogoro, and Tunduru deposits of Tanzania, from Tajikistan, from Burma, and from the Horana, Ratnapura, Elehiyagoda, Elahera, and Okkampitiya deposits of Sri Lanka. From this rough material, several hundred polished wafers were prepared for study.

Preliminary study of these otherwise gem quality samples showed that a significant fraction (20 - 30%) contained a submicroscopic second phase as inclusions which scatters light. This second phase produces a slightly sleepy to quite cloudy appearance in faceted gems, depending on its optical density. Thus the removal of this second phase might well be the motivation for the heat treatment of spinel.

To study this possibility a variety of spinel wafers exhibiting the second phase were heat treated in air at successively higher temperatures starting at 250°C and working up to 1200°C. Each temperature was held for 24 hours. Before heating, and after each heat treatment step, the wafers were photographed on a special high intensity dark field illuminator to accentuate the visibility of the second phase. Typical results are shown in Figures 4 – 8 for a sample of Mahenge, Tanzania spinel. It is clear that the second phase and thus the light scatter are little changed until the 1200°C step. At that point the sample is completely clarified. The bright spots and streaks seen in Figure 8 are not in the bulk of the wafer, but are the result of thermal damage to the poorly polished surface at 1200°C.



Figure 4 Natural Mahenge, Tanzania spinel

Figure 5: Sample heated at 600°C



Figure 6: Sample heated at 800°C.

Figure 7: Sample heated at 950°C.

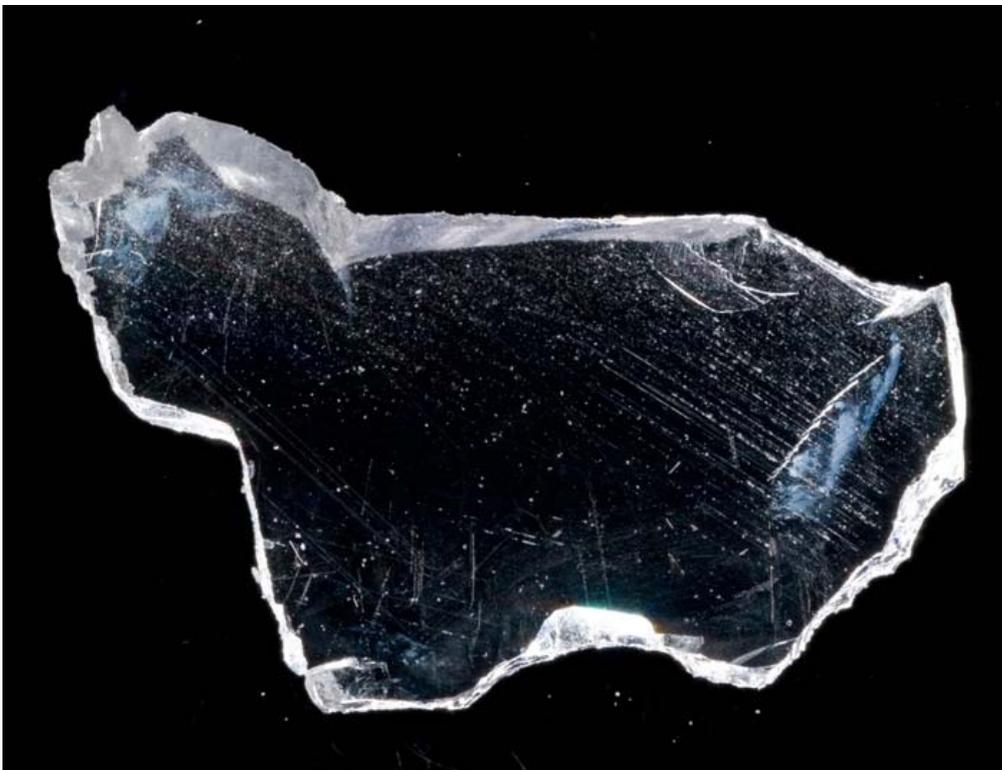


Figure 8: Sample heated at 1200°C. The bright spots and streaks are not in the bulk of the sample, but are thermal damage to the poorly polished surfaces.

Examining many such samples we find that a large percentage is clarified at temperatures between 950°C and 1150°C. Often at these low temperatures there is little alteration of the inclusion scene or of the color. These facts, when combined with the fact that natural spinel is often free of inclusions, requires us to develop new criteria to determine if beneficial heat treatment has taken place.

Spinel is a term used to describe a wide variety of compounds with the same crystal structure. “Normal” spinel is usually represented by the formula AB_2O_4 , where the A ions are on tetrahedrally coordinated sites and the B ions are on octahedrally coordinated sites. “Invert” spinel is also known which can be described as $B(AB)O_4$. In this case the B ions are on both sites and the A ions are on the octahedral site. Any intermediate combination of normal and invert spinel is usually described as “disordered”. Most gem spinels are primarily the normal spinel $MgAl_2O_4$. The “ordered” spinels can often be disordered by heating, and thus disorder might be used as criteria to determine if the stone has been heated.

What are the effects of disorder? Since disorder rearranges some of the cations in the unit cell, we can expect changes in the Raman spectra of the crystal, and we can expect changes in both the fluorescent emission and absorption spectra of impurity ions in the crystal such as Cr^{3+} , which is known to fluoresce strongly in spinel.

The Raman spectrum of a spinel from Sri Lanka is shown in Figures 9 – 11. The most prominent feature is the narrow line at about 405 cm^{-1} . The FWHM (full width at half maximum) of this line is 7.43 cm^{-1} . Heating to 650°C does not alter the width or shape of this line. However, heating to 800°C dramatically increases the width of the line to 33.66 cm^{-1} FWHM, as well as spreading it to the low energy side. This is the signature of disorder in magnesium aluminate spinel. In natural unheated gem spinels we have found that FWHM width of the 405 cm^{-1} line ranges from about 6.8 to 10.6 cm^{-1} depending on origin.

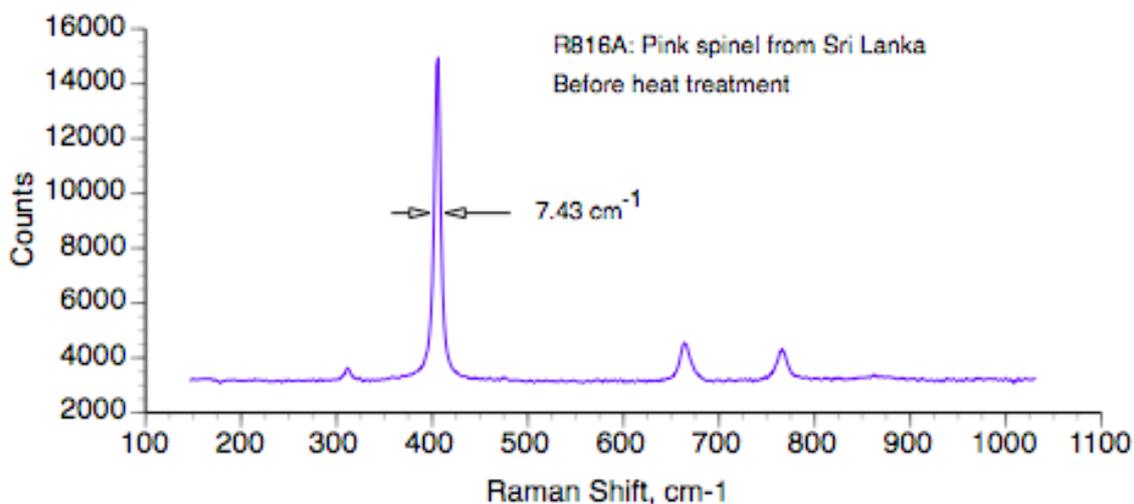


Figure 9

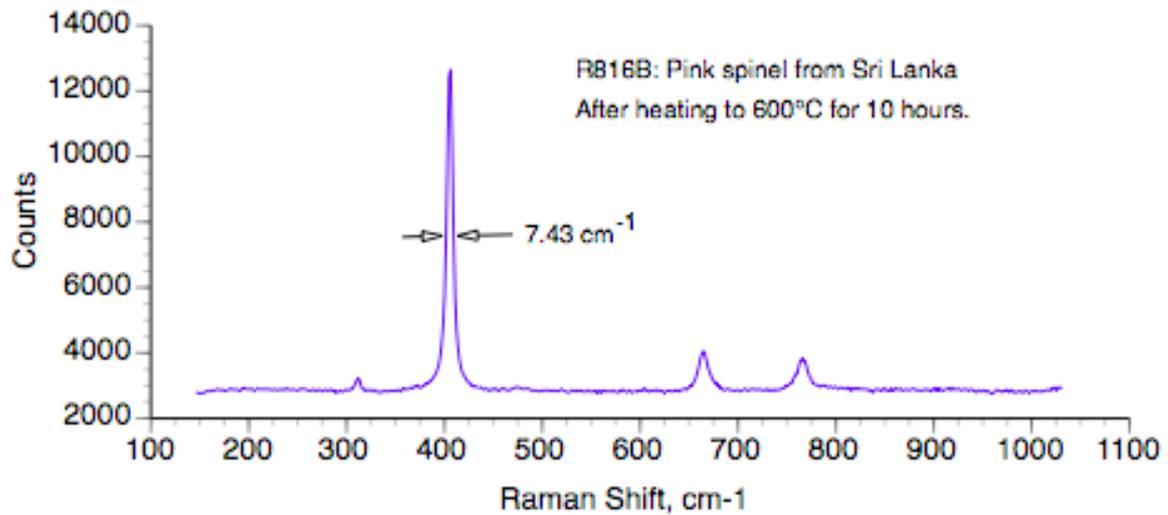


Figure 10

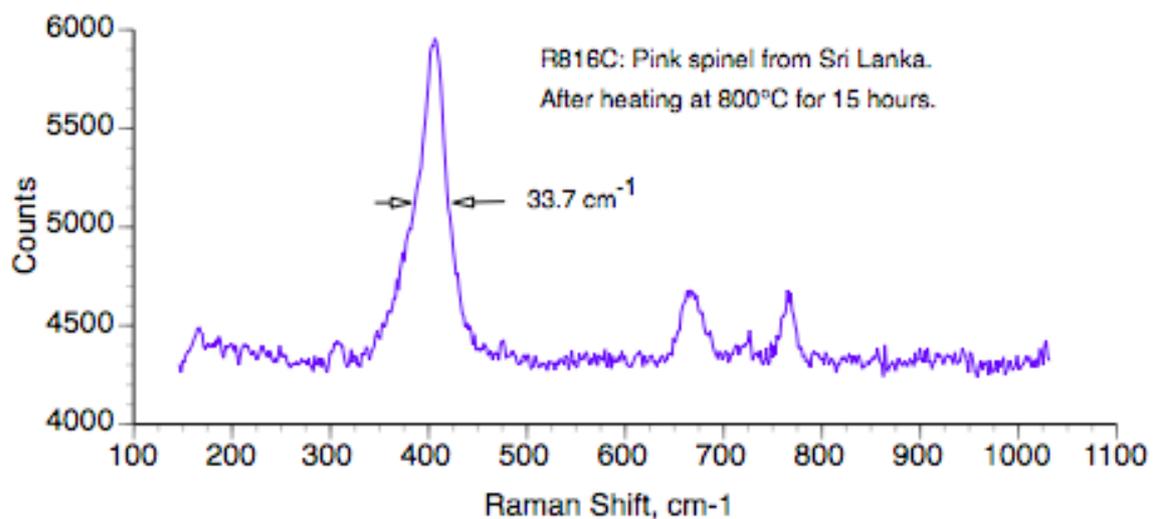


Figure 11

Studying these phenomena a little more closely, we find that the disorder temperature is close to 750°C. All stones we have studied from all the locations mentioned above disorder dramatically at the same temperature. Thus we have simple criteria to determine if magnesium aluminate gem spinel has been heated above 750°C. Since we have previously shown that clarifying these stones requires temperatures well above 750°C, we have a solid criterion to determine if a gem has undergone beneficial heat treatment. This criterion is independent of the color or trace element composition of the spinel and is thus applicable to all natural gem spinels with the possible exception of high refractive index gahno-spinels, which we have not yet studied.

Since disorder occurs at a temperature below beneficial heat treatment of spinel, we have also examined its effect on the photoluminescent (PL) emission spectra and the

absorption spectra of Cr^{3+} . The PL spectra were recorded using both 488 and 532 nm lasers, but any source within the chromium absorption bands will work as well. The PL spectrum of Cr^{3+} in spinel is complex as it is comprised of a strong zero phonon line near 685 nm as well as vibronic sidebands of that line, and other lines associated with Cr^{3+} pairs. Focusing only on the zero phonon line which is the strongest, we find that it also broadens greatly at the disorder temperature. Figures 12 – 14 show this effect dramatically for a pink spinel from Horana, Sri Lanka. The Cr^{3+} zero phonon line broadens from 0.82 nm in the natural stone to 5.82 nm after heat treating at 800°C. Thus far we have recorded a range of 0.82 to 1.12 nm FWHM for the unheated line width in natural spinels which appears origin dependent.

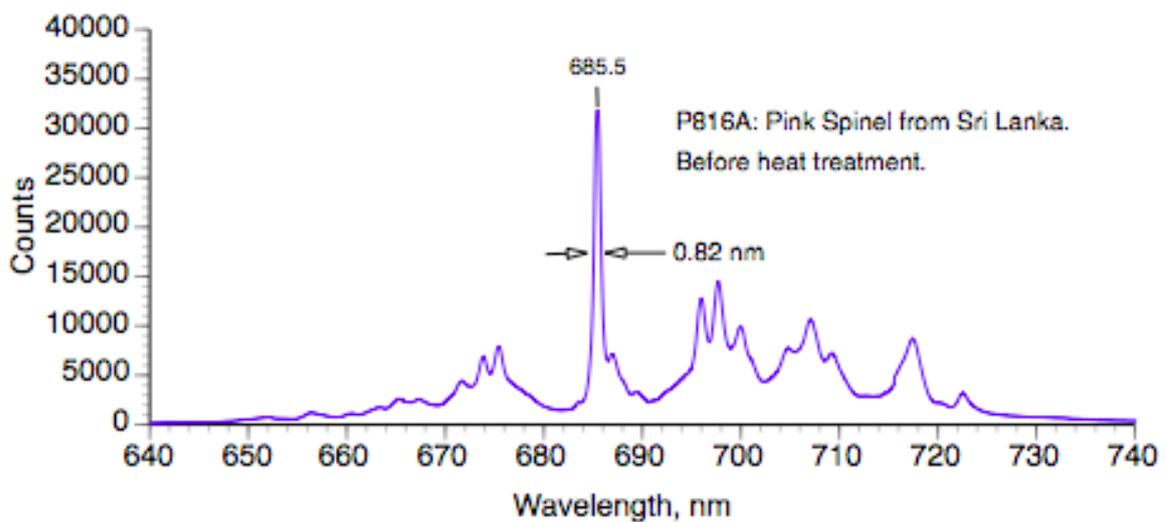


Figure 12

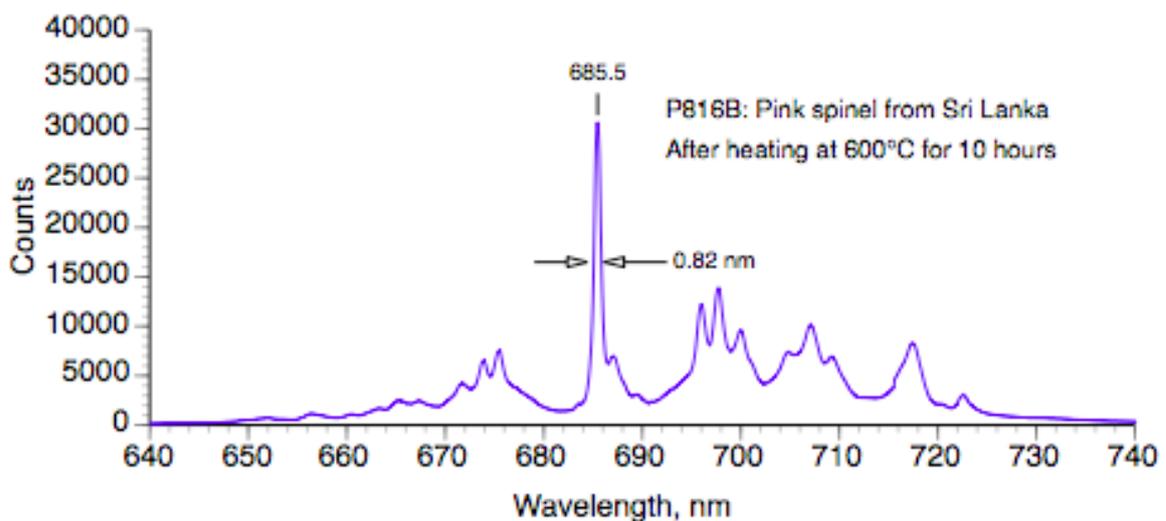


Figure 13

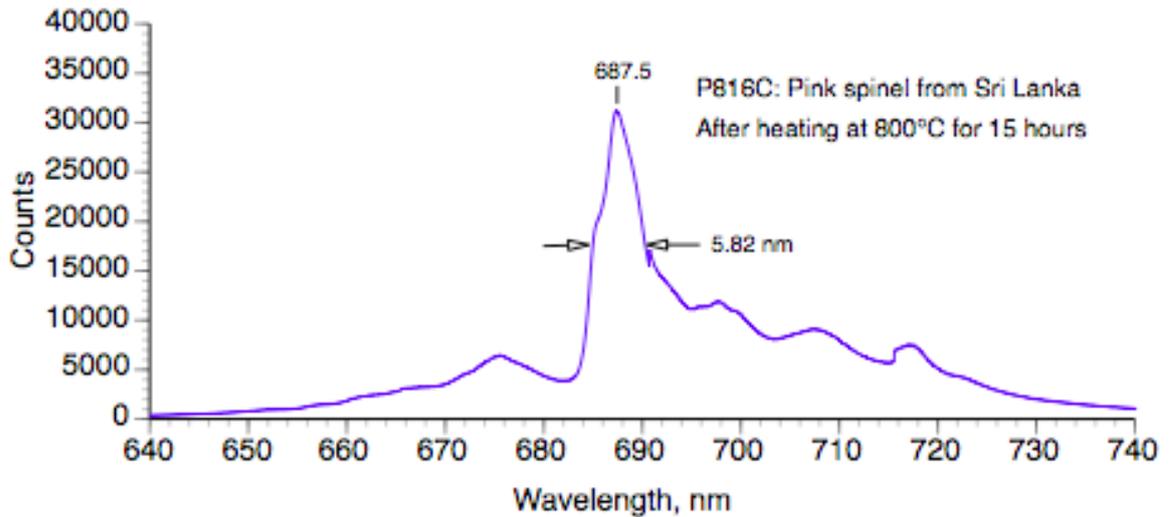


Figure 14

The PL spectra for 108 natural unheated Burmese spinels from the Gübelin Collection were examined. For the natural pink to red spinels, the typically sharp zero phonon line was recorded for all stones. Thus PL spectroscopy seems to be as effective as Raman spectroscopy for separating heated from unheated natural pink to red spinel.



Figure 15: A selection of the Burmese origin spinels from The Gübelin Collection examined to confirm the original PL identification criteria for heated spinel.

Given the great sensitivity of today's Raman instruments when used in the PL mode, we have found that the majority of all colors of spinel tested (except black) show sufficiently strong Cr^{3+} PL to make this measurement. Thus it is as nearly a universal criterion as the width of the 405 cm^{-1} Raman line.

Finally, it is worth noting that the disorder from heat treatment can also be observed in the absorption spectra of natural pink to red spinels, although not with such great sensitivity. Figure 16 shows the absorption spectrum of a natural red spinel from Burma before and after heating to 800°C. The peak of the green centered absorption band shifts from 537 to 544 nm. In examining a number of pink and red spinels of different origins we find that the natural band peak ranges from 536 to 539 nm, while after heating to 800°C it shifts to 544 to 547 nm. Note that there is some broadening of this band also.

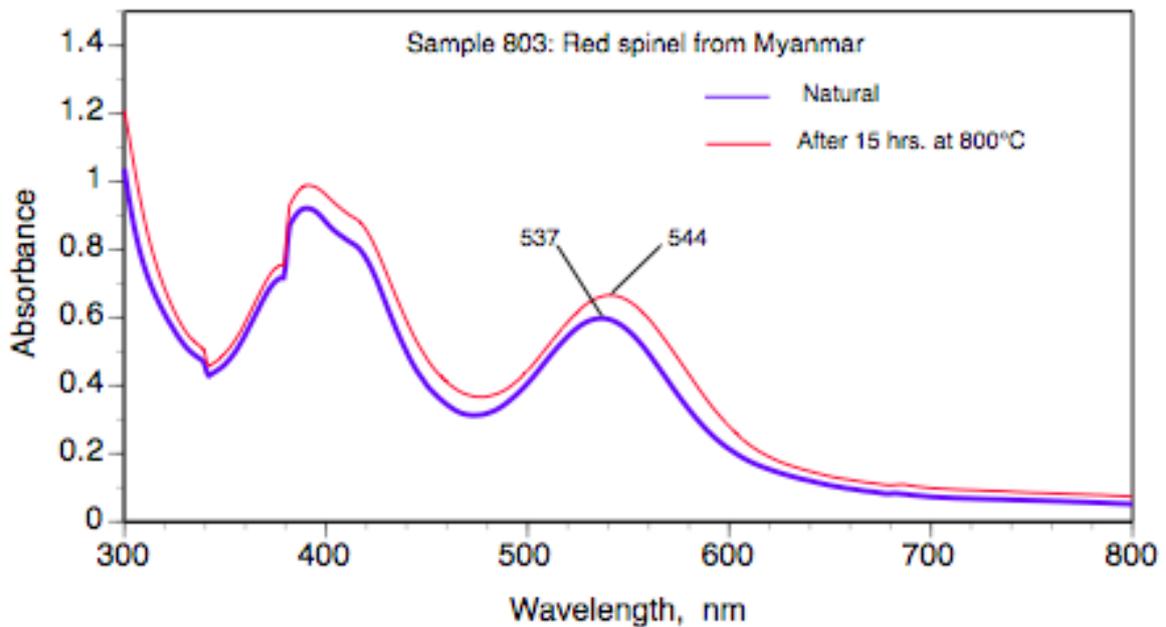


Figure 16

At this point it is worth asking the question as to whether the disorder in heat treated spinel can be annealed out by heating at a temperature well below 750°C where the ordered state is the energetically preferred state. While we do not have a definitive answer at this time, we have test annealed a few pink spinels that were previously disordered by heating at 800°C. These samples were held at 500- 600°C in excess of 1700 hours with no reduction in Raman linewidths

It should also be noted that similar broad, rather than sharp, PL spectra are observed in synthetic pink to red spinels, and broad Raman lines are observed in all synthetic gem spinels. There are two factors involved in these observations. First, all synthetic magnesium aluminate spinel is grown well above the 750°C disorder temperature. Flux growth is usually done in the 1200° – 900°C range, while Czochralski and Verneuil growth is usually done in the 2150° – 2250°C range. Thus synthetic spinel is grown disordered. Second, the stoichiometry of synthetic spinel can vary widely. If we look at spinel as being made up of MgO and Al₂O₃ we can write natural spinel as MgO•nAl₂O₃ where n = 1. However if we examine the MgO - Al₂O₃ phase diagram, we note that at high temperatures of Czochralski or Verneuil growth spinel can form over a broad composition range corresponding to approximately 0.8 ≤ n < 4.3. They are all spinel and they are all cubic crystals. In fact only at temperatures below about 1000°C does spinel have a single well defined composition with n = 1. Thus

the flux grown spinel in the gem marketplace is usually close to $n = 1$, whereas Verneuil and Czochralski material is typically grown in the range of $2.5 \leq n \leq 3.5$ for reasons having to do with strain in the crystals. This can be simply observed by measuring the index of refraction. Synthetic spinel with $n = 1$ has an index of refraction of 1.717, whereas at $n \approx 3.3$ the refractive index is ≈ 1.734 . The larger fraction of aluminum on cation sites is accommodated by magnesium and oxygen vacancies which further broadens the 405 cm^{-1} Raman line and introduces some new lines to the spectrum, while also further broadening the Cr^{3+} PL spectrum.

Distinguishing natural unheated inclusion free spinel from $n = 1$ synthetic spinel is simply a matter of looking at the linewidth of the 405 cm^{-1} Raman line, or at the linewidth of the Cr^{3+} zero phonon line in the PL spectrum. However, distinguishing heat treated inclusion free natural spinel from synthetic spinel requires additional techniques.

Chemical analysis by EDXRF and LA-ICP-MS can provide the additional information to distinguish these possibilities. Energy Dispersive X-Ray Fluorescence (EDXRF) trace element analysis is an excellent tool for this purpose. In flux-grown synthetic spinels, EDXRF showed that chromium (Cr) and iron (Fe) are found to be major trace elements and nickel (Ni), vanadium (V), zinc (Zn), and gallium (Ga) are all found to be minor trace elements. In contrast, all natural spinels analyzed thus far, have had higher levels of Zn than the flux-grown synthetics, and Ti is present as a minor trace element. LA-ICP-MS analysis revealed significant amounts of Li, Be, Zn, and Ga in all of the natural spinels (over 100 samples) tested. These elements are usually absent or extremely low in concentration in synthetic spinels. No overlap in concentration was observed between natural and synthetic spinels (Figures 17 – 18).

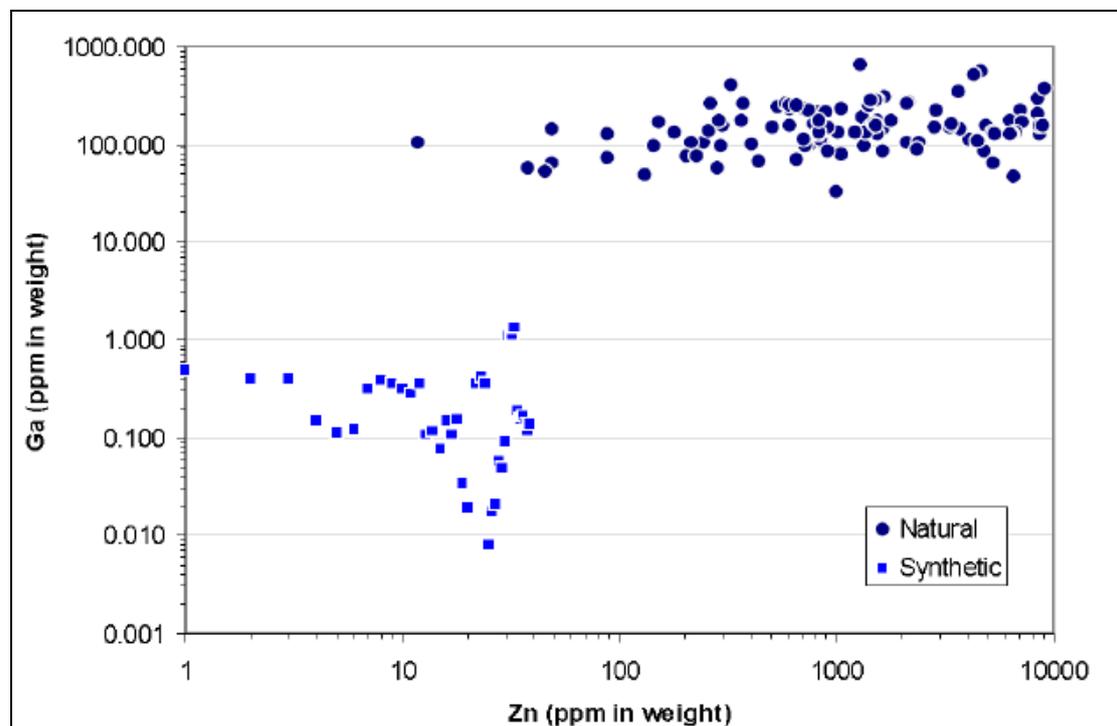


Figure 17: Trace element population fields (Ga and Zn) for natural and synthetic spinel showing a clear separation between the two.

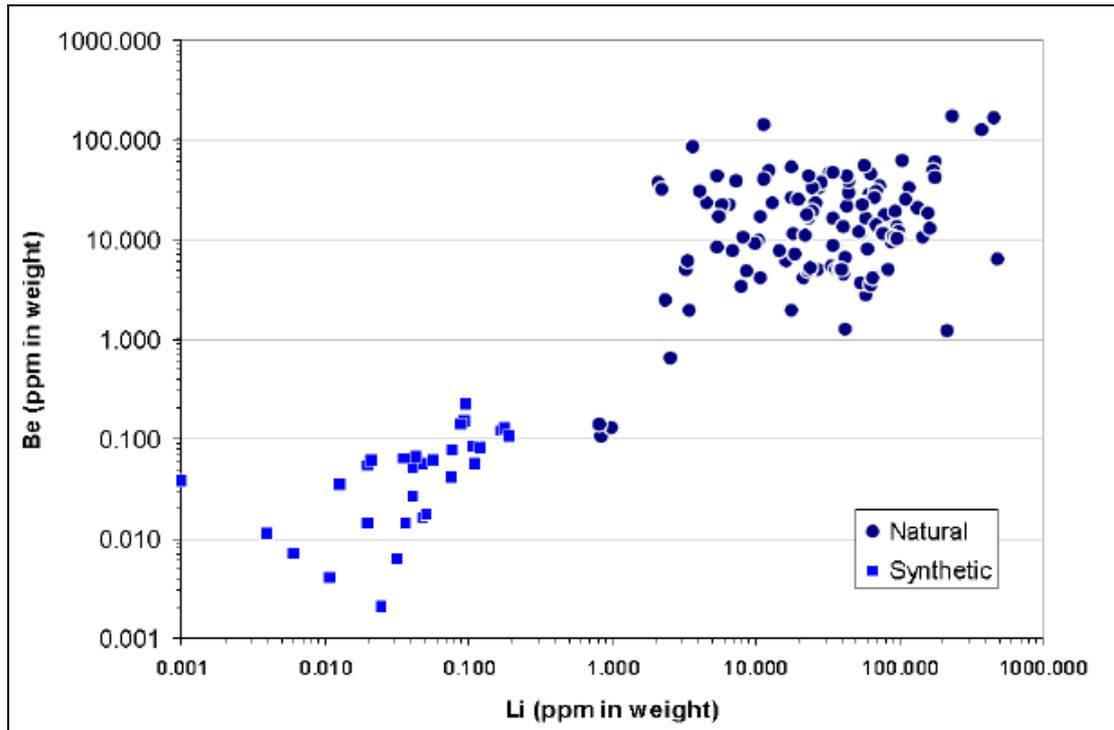


Figure 18: Trace element population fields (Be and Li) for natural and synthetic spinel showing a clear separation between the two

Conclusions

Unheated natural spinel is easily separated from heated natural spinel or synthetic spinel by examining the width of the 405 cm^{-1} Raman line, or by examining the width of the zero phonon line of the Cr^{3+} PL spectrum in stones containing sufficient chromium. Separating inclusion free heated natural spinel from some synthetic spinels requires examining the trace element chemistry with EDXRF and LA-ICP-MS where the differences become quite clear. These techniques have been in routine use in GIA's laboratories for well over a year. Further and more comprehensive data will be published as research continues.

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