Comments on:
“A Question Concerning Heat–Treated Blue Sapphires,” by John I. Kovula and Alethea Inns

John L. Emmett
Crystal Chemistry
Brush Prairie, WA

The patterns noted by Koivula and Inns are indeed interesting observations. Offered here is a partial elucidation of these observations, and suggestions for additional data collection that should allow a more complete understanding.

Their major observations can be summarized as follows:

1) Heat-treated blue sapphires, which contained a fine rutile exsolution distribution pattern along the three crystallographic directions parallel to the basal plane that has become blue following heat treatment, do not show either SWUV excited fluorescence or a 3309 cm^{-1} absorption line (Koivula and Inns, figure 1).

2) Other heat-treated blue sapphires, which do not show the particular rutile exsolution pattern mentioned above but yet contain rutile, may or may not exhibit the SWUV excited fluorescence and/or the 3309 cm^{-1} absorption line. (Koivula and Inns, figures 2 and 3)

In what follows, I will provide some background information and present a framework for understanding such observations. First I address the matter of the 3309 cm^{-1} absorption line and then follow with a discussion of fluorescence.

3309 cm^{-1} Absorption Line

It has been shown (Moon and Phillips, 1991 and 1994) that the 3309 cm^{-1} line arises specifically from the presence of hydrogen (as OH^{-}) that is associated with titanium in solution in the corundum crystal. Hydrogen is a common trace element in natural corundum, although present only at very low concentrations (Beran and Rossman, 2006).

To understand the presence or absence of hydrogen (and thus the 3309 cm^{-1}) line in heat-treated corundum requires a discussion of heat treatment objectives and techniques. Natural corundum contains Fe, and Ti as trace elements at some level of concentration. Often in nearly colorless or pale blue corundum the iron is in solution as Fe^{3+}, and much of the titanium is exsolved as rutile. To make the sapphire blue what must happen is for the titanium to go back into solution as Ti^{4+}, for some of the Fe^{3+} to be reduced to Fe^{2+}, and for the Fe^{2+} and Ti^{4+} ions to locate on adjacent Al^{3+} sites in the lattice. This forms the Fe^{2+} - Ti^{4+} ion pairs which exhibit a strong and wide absorption band centered at about 580 nm. This

J. L. Emmett. Comments on: "A question concerning heat-treated blue sapphires," by John Koivula and Alethea Inns. News from Research, August 7, 2009. http://www.gia.edu/research-resources/news-from-research

band absorbs much of the green, yellow, and red light leaving the transmitted light blue to the eye, thus ‘turning the sapphire blue’.

To accomplish this transformation, the heat treater heats the corundum to a high enough temperature (1500–1800°C) to fairly rapidly dissolve the rutile back into the crystal, introduces some hydrogen into the furnace atmosphere (referred to as a reducing atmosphere) to reduce some of the Fe^{3+} to Fe^{2+}, holds the temperature long enough for the Fe^{2+} and Ti^{4+} ions to diffuse together, and then cools the corundum rapidly (compared to geologic time scales) to freeze the ions in the new configuration, producing a blue sapphire.

[The actual physics of this process is substantially more complex and must take into account other trace elements present, trace-element solubilities, and ion diffusion rates. However, the above simplistic description will suffice for our purposes here. Note also that there are a variety of other heat treatment processes with different objectives and different recipes.]

During the process described, hydrogen diffuses into the corundum crystal and dissociates into a proton and an electron. The electron reduces the Fe^{3+} to Fe^{2+}, while the proton associates with an O^{2-}, making it an OH^{-}. It is the OH^{-} that absorbs at 3309 cm^{-1}. This is the common heat treatment process which is usually used on the type of material shown in Koivula and Inns, figures 2 and 3. Thus such stones will generally show the 3309 cm^{-1} line.

[It is probably worth an aside here to comment on the atmosphere in a heat-treatment furnace. There are two general types of furnaces used for heat treatment: electrically heated and combustion heated. In the former case hydrogen is injected into the furnace from gas cylinders usually as some mixture such as H_2 and N_2, H_2 and H_2O, or H_2 and CO_2. In a combustion furnace burning hydrocarbons and air or oxygen, the situation is quite different. In a combustion furnace, a reducing atmosphere is achieved by running fuel rich, which is well known to produce some soot and also carbon monoxide. What is less commonly recognized is that running fuel rich produces about the same amount of free hydrogen as carbon monoxide (Emmett and Douthit, 1993).]

While the process for producing blue sapphires in a reducing atmosphere described above is very well known, what is far less well known is that some sapphires in a given parcel of stones will turn blue when heat treated in an oxidizing atmosphere, and that these often exhibit the best blue coloration of the lot. Thus for equal weight and clarity, they have a higher value and are more likely to be seen by gem labs. During heat-treatment in an oxidizing atmosphere, any naturally occurring hydrogen will diffuse out of the stone eliminating any trace of the 3309 cm^{-1} absorption line after heat treatment. The production of blue sapphires by heat treatment in an oxidizing atmosphere (air or oxygen) is often noted for sapphire from Sri Lanka and from Southern Madagascar, although a few such pieces are found in parcels from many other mining locations. Thus many heat treaters run a parcel in an oxidizing atmosphere first and pick out good blue stones before doing the normal reduction process. The stones of this type that we have seen tend to look a lot like Figure 1 of Koivula and Inns. That is, they are characterized by a moderate density of exceedingly fine crystallographically aligned rutile needles. What process is at work here?

When rutile dissolves into corundum the valence state of the titanium ion, which occupies an aluminum site, is +4. Since aluminum has a valence of +3, some sort of charge compensation is required to maintain electrical neutrality in the crystal. In high purity sapphire, charge compensation is provided by the formation of aluminum vacancies as shown by the following equation in Kröger-Vink notation (see note at the end of this paper):

$$TiO_2 \xrightarrow{Al_2O_3} Ti^{\bullet}_{Al} + 2O^{x}_{o} + \tfrac{1}{3} V'''_{Al} \qquad (1)$$

What this equation says is that each of the three titanium ions that enter the lattice will force the creation of an aluminum vacancy to charge compensate them. (If you don’t like fractions, multiply all terms by 3.) In natural sapphire which contains a variety of trace elements, there are more options for charge compensation of titanium. One which is particularly interesting to us is as follows:

$$TiO_2 + Fe^{x}_{Al} \longrightarrow Ti^{\bullet}_{Al} + Fe'_{Al} + \tfrac{3}{2} O^{x}_{O} + \tfrac{1}{4} O_2(g) \qquad (2)$$

What this equation says is that titanium ions entering the lattice can reduce Fe^{3+} to Fe^{2+} while expelling oxygen from the lattice. This process creates our Fe^{2+} - Ti^{4+} pairs without a reducing atmosphere in the furnace. But then, why does this process not work all the time when rutile is present? I suspect that it depends on the relative (or absolute) concentrations of iron and titanium in the stone, and perhaps on the concentration of other trace elements like Mg and/or Si as well.

To sort out this question we need to collect a lot more data. When these stones are seen in the labs it would be helpful if LA-ICP-MS data could be taken on the composition. XRF data is not adequate as we need to know the Mg concentration also. Comparing the trace element chemistry of a group of these stones with that of the more usual heat-treated sapphires exhibiting the 3309 cm^{-1} line, might give us the clues we need to unravel the process.

Finally, it is worth noting that sapphires are often heat treated many times in an attempt to increase their value. For example, a stone might be heated in an oxidizing atmosphere and remain an uninteresting color. It might then be put through a reduction process with the result that the stone might be too dark blue. It might then be heated in a neutral or oxidizing atmosphere in an attempt to lighten the color. In that way the hydrogen in the stone would be lost in the last process and the 3309 cm^{-1} line would disappear. Thus in the final analysis, the absence of the 3309 cm^{-1} line means only that during the last heat treatment process hydrogen was not present in the furnace atmosphere, and thus any hydrogen that may have been in the stone naturally or from a previous process, diffused out.

J. L. Emmett. Comments on: "A question concerning heat-treated blue sapphires," by John Koivula and Alethea Inns. News from Research, August 7, 2009. http://www.gia.edu/research-resources/news-from-research

Fluorescence

Fluorescence in minerals is a complex and subtle subject. Yet in a age when gemology has moved into highly sophisticated measuring devices such as FTIR spectrophotometers and LA-ICP-MS machines, its study of fluorescence in colored stones remains stuck with only the bluntest of instruments—the mineral light. One wonders why.

Is the observation that some of the heat-treated stones fluoresce with SWUV and others do not, fundamental, or is it just a difference in brightness of the fluorescence? As discussed elsewhere (Emmett, 2005), the bluish white, sometimes chalky fluorescence observed in heated sapphire originates from Ti^{4+} ions in the sapphire lattice. The excitation spectrum of the fluorescence is a band which peaks at 230 nm and is about 40 nm wide. This charge transfer absorption corresponds to exciting an electron from the valence band to the Ti^{4+} ion, temporarily making it Ti^{3+}, which then relaxes back to the Ti^{4+} state with the emission of the fluorescence. Two excellent papers on this subject are Wong, McClure, et al. (1995a and 1995b).

What is known about this fluorescence is that it is sensitive to the local environment of Ti^{4+} in the lattice. In high purity sapphire the charge compensation is by aluminum vacancies. At low concentrations of Ti^{4+}, the vacancy can be local, that is, on a nearest neighbor lattice site, or nonlocal which means many lattice sites away. The fluorescence band peaks at about 420 nm for nonlocal compensation and about 480 nm for local compensation. In natural stones Mg^{2+} and Fe^{2+} can also provide charge compensation. The peak emission wavelength for Mg^{2+} locally compensated Ti^{4+} is about 510 nm. All three of these bands are very broad so the visual color impression is bluish to whitish. [Note that these bands were measured with a time resolved spectrometer, an instrument not available in gem labs.] Now what about Ti^{4+} compensated by Fe^{2+}? Currently there is no data, but it is my conjecture that it does not fluoresce, or if it does, it is exceedingly weak. This conjecture is based on the fact that iron is a very effective quencher of fluorescence in many other systems and thus will probably quench the Ti^{4+} fluorescence also.

The “chalky” visual appearance often ascribed to this fluorescence is simply the result of the fact that in most cases the emission is only from regions quite close to the surface of the stone. This results from the fact that the oxygen-iron charge transfer absorption is exceedingly strong in the region of the 253.7 nm mercury emission line. For a sapphire with 200 ppma iron, the 253.7 mercury line illumination is attenuated to 2% of its initial intensity at a depth of only 80 microns.

So what conditions in heat-treated sapphire lead to the absence of fluorescence? First let’s discuss rutile dissolution. If a rutile needle is very fine it will dissolve rapidly becoming an expanding cylinder of Ti^{4+}, expanding at the diffusion rate. As it expands radially, the average Ti^{4+} concentration will drop inversely with the square of the radius. During heat treatment, high Ti^{4+} density regions will be primarily charge compensated by aluminum vacancies, but as the density drops charge compensation will become dominated by Fe^{2+} and Mg^{2+}. If the rutile crystals are significantly larger, or clustered at high density, the Ti^{4+} concentration will not fall far enough during heat treatment to meet this requirement. Thus the conditions for the absence of fluorescence are: 1) that the initial rutile distribution be comprised of a relatively low to moderate average density of very fine needles, or other crystal shapes, that will dissolve rapidly with the Ti^{4+} concentration dropping below the necessity for aluminum vacancy charge compensation during the heat treatment time interval, 2) an iron concentration high enough to charge compensate all of the titanium, and 3) a low magnesium concentration so that very little of the titanium is charge compensated by Mg^{2+}. This latter condition can probably be relaxed if the iron concentration is high enough to effectively quench the fluorescence from the Ti^{4+} - Mg^{2+} pairs. The conditions for strong fluorescence are, of course, just the reverse of these.

To develop a much more quantitative understanding of the fluorescence of heat-treated sapphire, we need to have good trace element analyses, including magnesium, for a large number of heat-treated sapphires that both do and do not fluoresce. We also need to be cognizant of the fact that our current system for stimulating and observing fluorescence is inadequate in the extreme. The DiamondView instrument developed for the observation of fluorescence in diamond is much more effective than a mineral light for observing sapphire fluorescence. While the transmission filter in the DiamondView is not optimal for sapphire, it is adequate. We have used the DiamondView to observe fluorescence in sapphire that does not appear to fluoresce with a mineral light. But what is needed is an instrument that is more optimized for colored stones.

Fluorescence can be a very valuable tool in the study of corundum, particularly in detecting new enhancement processes. It was an unusual fluorescence, after all, that raised Crowningshield’s curiosity (Crowningshield, 1966) about certain sapphires. Subsequently, it was learned that the fluorescence he observed was a signature of heat-treated geuda. However, to really take advantage of this tool we need to be able to record both excitation and emission spectra, measure fluorescent decay times, and time resolve emission spectra. Existing commercial instruments can be modified to meet most of these requirements, and one or two special instruments can be developed to meet special needs.

Note: The notation used to write the chemical reactions shown in equation 1 and 2 was developed (Kröger and Vink, 1956) specifically to address chemical reactions of dilute impurities in solid media. It turns out to be an excellent formalism for understanding trace element interactions in corundum. The advantage of this approach is that the rules for writing these chemical reactions equations lead you to figuring out what types of reactions are possible and what types of charge compensation are possible. I strongly recommend that people interested in the physical chemistry of corundum learn this formalism as there is an extensive literature on trace elements in corundum, nearly all of which uses it. The single best reference that I have found to learn from is Smyth (2000). The next best is Kingery, Bowen, et al. (1976), which also contains a great deal of information on the whole array of physical processes encountered in the heat treatment of corundum.

References

Beran, A. and G. R. Rossman (2006) OH in naturally occurring corundum. *European Journal of Mineralogy* 18: 441–447.

Crowningshield, R. (1966) Unusual items encountered. *Gems and Gemology* 12(3): 73, 95.

Emmett, J. L. (2005) The blue fluorescence of synthetic sapphire, the “chalky white fluorescence” of heat treated sapphire, the lack of fluorescence of natural blue sapphire, etc. Memo to Dick Hughes and the Corundum Group

Emmett, J. L. and T. R. Douthit (1993) Heat treating the sapphires of Rock Creek, Montana. *Gems & Gemology* 29(4): 250–272.

Kingery, W. D., H. K. Bowen, et al. (1976) *Introduction to Ceramics*. New York, John Wiley & Sons.

Kröger, F. A. and H. J. Vink (1956) Relations between concentrations of imperfections in crystalline solids. In *Solid State Physics; Advances and Applications*. F. Seitz and D. Turnbull. New York, Academic Press. 3: 307–435.

Moon, A. R. and M. R. Phillips (1991) Defect clustering in H,Ti: α-Al_2O_3. *Journal of Physics and Chemistry of Solids* 52(9): 1087–1099.

Moon, A. R. and M. R. Phillips (1994) Defect clustering and color in Fe,Ti: a-Al_2O_3. *Journal of The American Ceramic Society* 77(2): 356–357.

Smyth, D. M. (2000) *The Defect Chemistry of Metal Oxides*. New York, Oxford University Press.

Wong, W. C., D. C. McClure, et al. (1995a) Charge-exchange processes in titanium-doped sapphire crystals. I. Charge-exchange energies and titanium-bound exitons. *Physical Review B*, 51(9): 5682–5692.

Wong, W. C., D. C. McClure, et al. (1995b) Charge-exchange processes in titanium-doped sapphire crystals. II. Charge-transfer transition states, carrier trapping, and detrapping. *Physical Review B*, 61(9): 5693–5698.