COATED TANZANITE

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Examination of 23 tanzanites coated by an apparently new technique revealed that the smaller stones (4–5 mm) could be identified as coated based on a combination of the unusually intense color and microscopic examination, which revealed surface iridescence as well as wear on facet junctions (small areas where the coating was abraded away). The two larger (3+ ct) stones did not show iridescence or wear, only small clues with high magnification, and therefore were much more difficult to identify. EDXRF and LA-ICP-MS analyses showed the presence of Co, Zn, Sn, and Pb in the coating.

The practice of coating gemstones to improve their color has existed for thousands of years (see, e.g., Ball, 1950; Nassau, 1984). None of these coatings is permanent, but they range in durability from being difficult to scratch with a metal point to being easily wiped off with a cleaning cloth. As a result, the treatment is impractical at best and fraudulent at worst (Overton, 2004). Last year, GIA researchers reported on the emergence of a new generation of coatings—created using technology from other industries—that are much more durable than those studied previously (Shen et al., 2007). Although we are aware that a number of companies are using this treatment on diamonds, the *Gems & Gemology* report focused on colored coatings on diamonds by a company called Serenity Technologies.

While we were studying the diamond coatings, we learned that some of these same companies were also applying coatings to colored stones and pearls, as well as to various gem simulants. In many cases, the treaters maintained that the coatings were diamond-like carbon (DLC) and were being applied to improve durability (see, e.g., Serenity Technologies, 2008; Zolastar, 2008). There appeared to be some basis for these claims, since for some gem materials the addition of color either was undesirable (e.g., white pearls) or unnecessary because the stone already had plenty of color (e.g., garnet).

During our investigation of these new coating operations in 2006, we also examined a tanzanite that purportedly was coated to enhance its durability. We noted some coating material on the surface of the stone, but it covered only a very small portion of the pavilion near the girdle and could be removed with a mere cleaning cloth. Chemical analysis of the coating revealed a large concentration of cobalt (together with Zn, Sn, Ta, Ag, Au, and Pb). The client also supplied an uncoated control sample of tanzanite that was similar to the one he had coated, and there was no significant difference between the colors of the two face-up. The nonpermanence and ineffectiveness of this coating did not distinguish it from most of the coatings that have been reported in the past. (For reviews of coatings in the marketplace since the 1980s, see Kammerling et al., 1990; McClure and Smith, 2000; Overton and Shigley, 2008.)

In April of this year, however, Los Angeles colored stone dealer Evan Caplan of Omi Gems contacted us about a parcel of tanzanite his company had just received from New York. Mr. Caplan said the color did not look right, and when his company had one stone repolished, the color became significantly lighter (figure 1). This indicated the material might

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be coated, so we asked Mr. Caplan if we could examine some of the stones. Initially, his company sent two 3+ ct octagonal step cuts and four 4–5 mm rounds (figure 2). Examination of the step cuts at about 10× magnification did not reveal anything obvious. Coatings are usually visible in reflected light or by looking through the table of the stone toward the pavilion in transmitted light. The features we typically look for—surface iridescence in reflected light, or gaps or worn-off areas in the coating—were not immediately evident. In fact, polishing lines were plainly visible on most of the facets.

On closer inspection at higher magnification, however, clues began to appear. Subsequently, at our request, Omi Gems sent us 18 more samples of 4–5 mm round brilliant cuts. All these samples had a depth of color that would be considered very unusual for tanzanite in such small sizes (again, see figure 2). Similar samples were supplied to the American Gem Trade Association Gem Testing Center (AGTA GTC) and American Gemological Laboratories; their observations were outlined in a press release issued on May 23 (see, e.g., "AGTA GTC. . .," 2008). Many of their findings parallel our own, but we discovered some additional identification features (McClure, 2008) and were able to more thoroughly characterize the coating material through laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS).

MATERIALS AND METHODS

As indicated above, we examined a total of 23 coated tanzanites. Two weighed 3.01 and 3.21 ct, respectively, while the remainder were between 0.27 and 0.62 ct (4–5 mm; again, see figure 2).

Figure 1. These two 5 mm stones were originally the same color. Repolishing of the one on the right resulted in a significant loss of color. Photo by C. D. Mengason.

All stones were examined with a gemological microscope at various magnifications and with several lighting conditions. A polarizing filter was employed to check the pleochroism of 10 stones. To test the durability of the coatings, we used a standard steel straight pin on three samples and a hardened chrome-steel knife blade on one of them.

Qualitative chemical analysis was conducted on 20 stones, table and pavilion, using a Thermo-Noran Spectrace QuanX energy-dispersive X-ray fluorescence (EDXRF) spectrometer. Quantitative chemical analysis using a Thermo X Series II ICP-MS, combined with a New Wave UP-213 laser-ablation system, was performed on three of the smaller samples: (1) one set of three spots on the girdle and a second

Figure 2. Omi Gems brought these tanzanites to the lab's attention because they suspected some form of treatment. Even the 4–5 mm stones were strongly colored. All proved to be coated, but it was very difficult to detect the coatings on the two larger tanzanites (3.01 and 3.21 ct). Photo by C. D. Mengason.

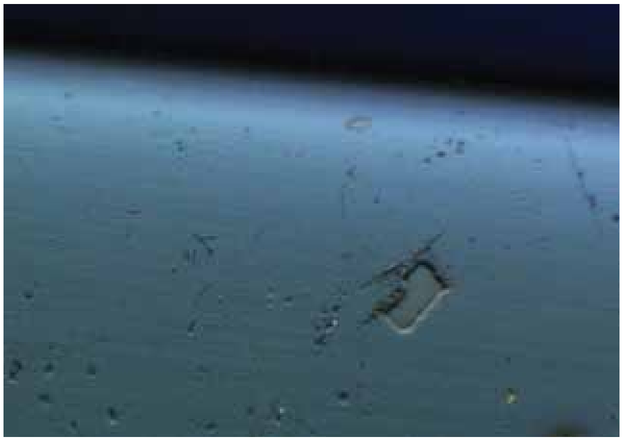
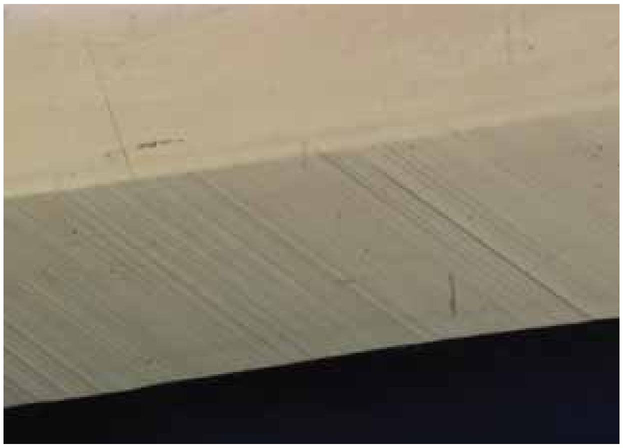


Figure 3. Examination with magnification as high as 60× and reflected light revealed numerous tiny holes in the coatings on the two 3+ ct tanzanites. Photomicrograph by S. F. McClure; image width 0.64 mm.

set on the pavilion, (2) one set of three spots on the girdle, and (3) three spots on the girdle and one spot on the table. The laser setting was 40 µm spot diameter, 10 J/cm^2 fluence, and a 7 Hz repetition rate using National Institute of Standards and Technology (NIST) 610 and 612 glasses for calibration. The laser-ablation time for each spot was 40 seconds; as the laser was ablating into the surface over this period, the signal recorded by the ICP-MS was in fact a depth profile of the material being analyzed. A chemically homogeneous material will yield a smooth and consistent signal throughout the analysis, but a thin layer of foreign material will show up in the time trace as a spike or peak in one or more of the elements being analyzed. The relative position in the time trace is a good indication of the relative position of this foreign chemical layer. If the spike in the element signal is at the beginning of the laser ablation, it is clear the layer is at the surface of the material.

Figure 4. Some facets on the larger step-cut coated tanzanites did not show any holes or breaks in the coating. They also did not show any iridescence. Photomicrograph by S. F. McClure; image width 2.48 mm.



RESULTS AND DISCUSSION

Appearance. Face-up, with the unaided eye, the color of these stones—violetish blue to bluish violet—did not appear unusual for tanzanite. The one exception was the depth of color in the 4–5 mm stones (again, see figure 2). It is very uncommon to see such intense color in tanzanites this small.

Microscopic Examination. We examined the two large step cuts first. The coating on these stones was not obvious at 10× magnification. As noted above, there was no surface iridescence in reflected light and no easily visible gaps in the coating or abraded areas on the surface of the crown or pavilion. With reflected light at higher magnification (up to 60×), however, we saw numerous tiny holes in the coating on some of the facets (figure 3). These holes seemed relatively

Figure 5. Numerous whitish marks that resembled dirt (but could not be wiped off) were visible on most of the coated tanzanites with fiber-optic illumination, which also revealed orange iridescent lines crossing facet junctions on some stones (see inset). Photomicrographs by S. F. McClure; image widths 4.04 mm and (inset) 0.56 mm.

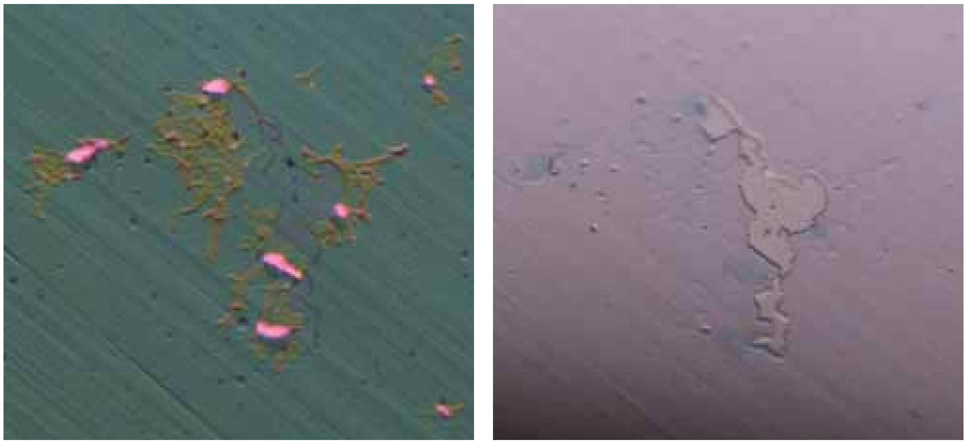


Figure 6. Tiny bright pink to orange flashes were visible on some of the coated tanzanites with fiber-optic illumination (left). These flashes are related to minute areas of damage to the coating that could be seen with transmitted light (right). Photomicrographs by S. F. McClure; image widths 0.52 mm (left) and 0.44 mm (right).

sharp-edged, and the coating looked thicker than we typically see. However, several of the facets showed no holes or other evidence of a coating (figure 4).

Fiber-optic illumination revealed whitish marks on the surface that looked like dirt but could not be wiped off (figure 5). It also revealed several orange iridescent lines that crossed facet junctions; these were similar in appearance to lines that might be left by a liquid drying on the surface (again, see figure 5). In addition, there were tiny bright pink to orange flashes of light that turned out to be related to minute areas of damage on the coating (figure 6). Although sometimes difficult to see on our coated samples, none of these surface features would be observed on an uncoated tanzanite.

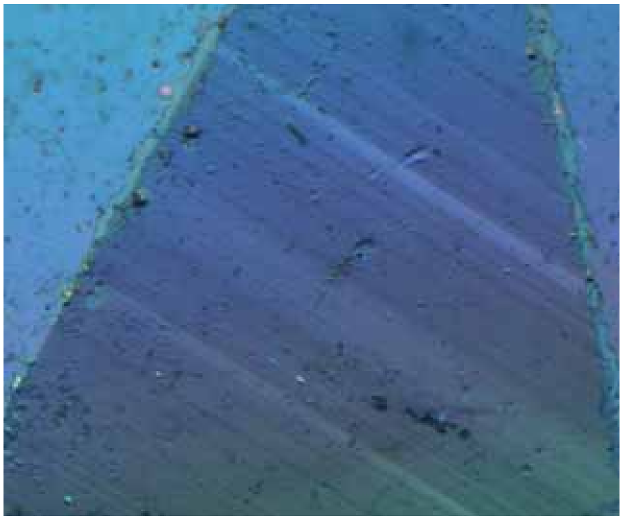
The color coating Shen et al. (2007) described was present only on the pavilion of the diamonds, and a difference in luster between the coated pavilion and the uncoated crown was readily apparent. No such easily distinguishable difference was visible in these two larger coated tanzanites. Immersion in water also showed very little evidence of a coating. Tiny areas of lighter color could be seen, but they were not obvious. In general, these two larger tanzanites lacked many of the features we expect to see in coated stones, and the treatment would be particularly difficult to detect on them.

However, all the smaller samples showed some characteristics that would be associated with a coating. Examination with magnification and reflected light revealed a pale iridescence on the surface of all the smaller coated tanzanites (figure 7). In addition, the coating was worn off along some facet junctions or at the culet on all of those stones; such abrasion is typical of the “paper wear” often present on gems that are stored in stone papers as lots instead of individually (again, see figure 7). The worn facet junctions and culets were readily apparent when the tanzanites were examined with immersion in water, since they appeared lighter in color than the rest of the stone (figure 8). These features made the smaller stones easier to detect.

The 10 samples we examined using a polarizing filter showed the typical strong pleochroism that one would expect for tanzanite. This clearly indicates that these stones have some intrinsic color, if not the depth of color seen with the coating (again, see figure 1).

We were unable to scratch the coating with a pin, which is consistent with the Serenity coatings we examined earlier. However, we did scratch it without difficulty using the hardened chrome-steel knife blade.

Figure 7. All the smaller tanzanites examined for this study showed a weak iridescence in reflected light and areas along facet junctions or the culet where the coating had worn off. Photomicrograph by S. F. McClure; image width 0.66 mm.



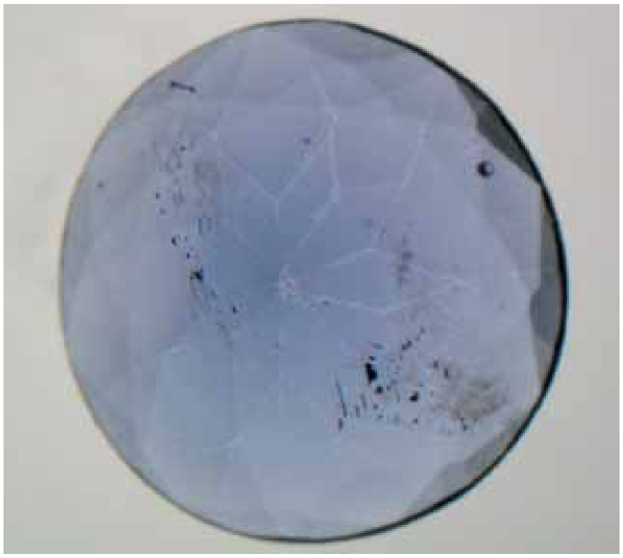


Figure 8. Abrasion of the coating at facet junctions was plainly visible when the smaller tanzanites were immersed in water over diffused transmitted light. Photomicrograph by S. F. McClure; image width 4.93 mm.

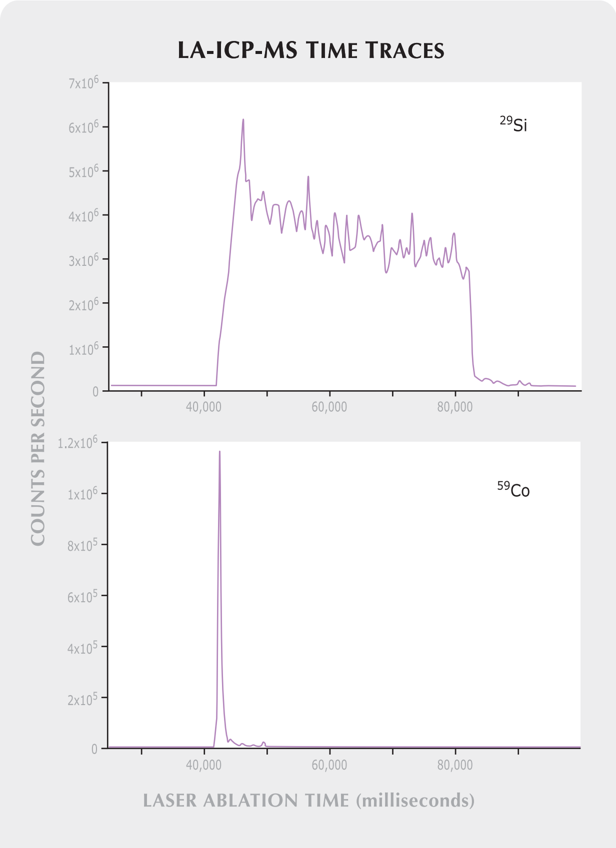
Chemical Analysis. EDXRF analysis showed cobalt as a major constituent of the coatings on all the samples we examined. This is consistent with the composition of the coating on tanzanite we documented in the laboratory in 2006 and very different from the Serenity diamond coatings we examined (i.e., no silver or gold; again, see Shen et al., 2007). In all 20 samples tested, significant amounts of cobalt were found only on the pavilion and girdle facets. The crown facets typically showed only minute amounts of cobalt, a small fraction of that recorded on the pavilion.

The LA-ICP-MS results on the girdle and pavilion were very consistent: In the time traces of Co, Zn, Sn, and Pb, all spots showed spikes in the element signals at the surface that were not seen deeper in the stone (see, e.g., figure 9 for Co; the analyses for Zn, Sn, and Pb are available in the *G&G* Data Depository at www.gia.edu/gemsandgemology). This is a clear indication that there is a surface layer on these tanzanite samples. The spot on the table showed only minute (sometimes below the detection limit of the instrument) but nearly constant concentrations of Co, Zn, Sn, and Pb (i.e., no spikes), which confirms that the coating was only on the girdle and pavilion facets of the stone. These ICP-MS results are somewhat similar to those for the tanzanite sample we examined in 2006 that was allegedly coated to improve its durability. In that sample, sharp surface spikes of Co, Zn, Sn, Ta, Ag, Au, and Pb were seen on both pavilion and girdle facets. No analysis was done on the table facet.

CONCLUSION

To summarize, the 4–5 mm tanzanites were immediately suspect because of their great depth of color, which is very uncommon for uncoated tanzanites in

Figure 9. The relative positions of peaks in these LA-ICP-MS time traces (taken from a spot on the pavilion facet) provide a good indication of a surface layer with a foreign chemical composition on this tanzanite. The horizontal axis indicates the time (in milliseconds, which translates to depth within the stone) and the vertical axis is the count rate. During the first 40 seconds, the laser is not firing and the system background level is evaluated. Because silicon (^{29}Si, the top trace) is in the chemical formula for tanzanite, it is present throughout the time period when the laser is firing. Cobalt, on the other hand (here ^{59}Co, the bottom trace), appears only as a spike at the surface of the stone and then disappears; it is not intrinsic to tanzanite and clearly is present in a very thin layer on the surface of the stone.



these sizes. These smaller stones also exhibited a weak iridescence as well as abrasion of the coating on the facet junctions and/or culet, probably from paper wear, which makes the coating somewhat easier to detect (provided the gems are stored in this fashion). However, larger stones that are likely to be stored individually may not show these features, and we know that at least some do not show iridescence in reflected light. Detection of a coating on these larger stones requires careful observation with a gemological microscope or, where available, chemical analysis. One might think the pleochroism, which is so strong in tanzanite, would give a useful clue to the coated nature of these stones. In this case, though, because the starting material already possessed some color, pleochroism was not helpful.

It is important to emphasize that these coated tanzanites were sold undisclosed on the market in New York. We do not know at this time how far down the pipeline they passed from the treater, or who originally decided to sell them without disclosing the treatment, but unfortunately it is inevitable that this will happen at some level. As with all treatments that have a substantial effect on value, this coating must be disclosed when present. In addition, sales of gems with nonpermanent treatments such as coatings must include instructions on any special care necessary to prevent damage; failure to do so in the United States is a violation of the guidelines set out by the Federal Trade Commission.

It is also clear that we are witnessing a new era of coatings on gemstones, which are both much more durable and much more difficult to detect. It is very possible—no, likely—that this treatment will be applied commercially to other gem materials. Gemologists must be more vigilant in their search for coatings than ever before. In the case of tanzanites in particular, every stone—regardless of size—should be checked carefully (keeping in mind that the coating may appear on only part of the stone) with a gemological microscope or sent to a well-equipped laboratory for advanced testing.

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