Gem Market News

Glass Filled Rubies-Part II
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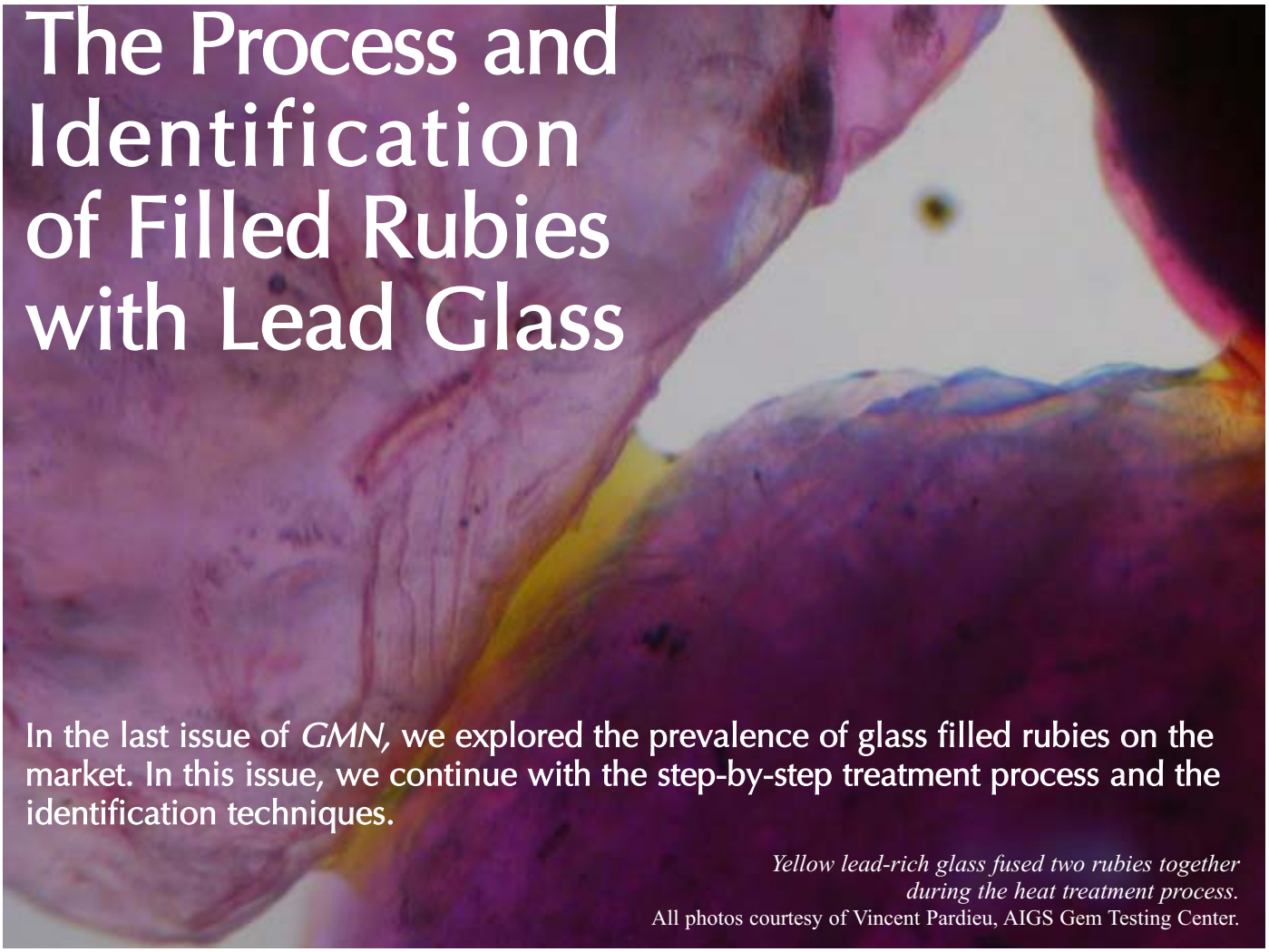
The Process and Identification of Filled Rubies with Lead Glass



In the last issue of *GMN,* we explored the prevalence of glass filled rubies on the market. In this issue, we continue with the step-by-step treatment process and the identification techniques.

Yellow lead-rich glass fused two rubies together during the heat treatment process.
All photos courtesy of Vincent Pardieu, AIGS Gem Testing Center.

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The following is a presentation of the treatment performed in Chanthaburi, Thailand by Master Burner Mahiton Thondisuk. It is a multi-step treatment involving simple heating and the use of different lead rich compounds to fill the fissures and cavities of the stones. Most of the "repaired" stones are large but small stones less than 1.0 carat have also been treated this way. In this study, the rough material presented is low quality material from the Andilamena area in Madagascar. In June and September of 2005, the author visited this area to further study its material.

Step-by-Step

Step One: The stones are preformed to eliminate the matrix and other impurities that could disturb the treatment.

Step Two: The stones are heat treated to remove any impurities possibly present in the fissures that could create problems when the glass is added. The heat treatment may also by itself improve the stone color.

This "warming" can be conducted at different temperatures from 900ºC to 1400ºC depending on the ruby type. As 900ºC is not hot enough to melt inclusions such as rutile, many stones can still have an unheated

aspect. But all stones are heated.

Step Three: The stones are then mixed with oxide powders and heated. The composition of the powder is mainly a mixture of silica and lead, but sodium, potassium, calcium and metallic oxides like vanadium or bismuth also enter in some glass composition. It could be interesting to compare the glasses used here with those used for diamonds, but this would need further investigation. There are two main types of glass compositions used in this process but experimentations about new glasses are in process.

The basic formula is a simple lead rich transparent glass. This formula is used for most of the best quality larger stones. This orange powder will turn into a yellowish to orange glass after heating as you can see in the

Mixing the chemicals before the burn.

Used crucible showing yellowish to orange glass after heating.

accompanying photo of the used crucible. In this case, the heat treatment temperature is believed to be around 900ºC in Chanthaburi. But the treatment temperature can be higher or lower for other burners as other components are used in the composition of the glass and this can affect the melting point of the oxides used.

The second formula also incorporates some other metallic oxides to produce glass, optimizing the color and aspect of rubies. This formula was known in the market as the "popular" formula and was used on iron stain rich commercial quality stones. This formula is actually a mix of many oxide powders that turns to a light pink glass, after melting. With this formula, the treatment temperature is believed to be slightly higher than in the basic case, nearing 1000ºC.

The powders are added to the stones with care along with some oil to cover them. The stones are then placed in crucibles and brought to the furnace. The powders will fuse during the heating process and turn into glass. A well-balanced glass composition is the key to achieving good transparency and fluidity so the glass will fill the entire fissure. The glass stability is also an important concern to create a durable product. New improved fillers will probably soon be tested and used to get better results.

Rubies covered by colorless lead rich glass after heat treatment in Chanthaburi.

These stones are then heat treated with the glass powder under a controlled atmosphere using electric furnaces. Special precautions have to be used at this step due to the use of lead compounds involving high temperatures. Gas masks, gloves and special compounds are used to clean the clothes and the treatment area. Heat treatment using chemicals of this kind is very technical and requires special knowledge and security precautions as lead vapors are very toxic.

Then, the stones are preformed and heated again using lead glass mixture to get a better result. Some stones can be heated several times with several types of oxides up to

the desired result achieved. The stones are finally cut and polished. Sometimes the resulting stones have their surface treated again using several chemicals to improve their surface luster. This last surface treatment may explain why it is easy to detect lead on the stone using EDXRF technology.

Identification and Analysis of the Repaired Rubies

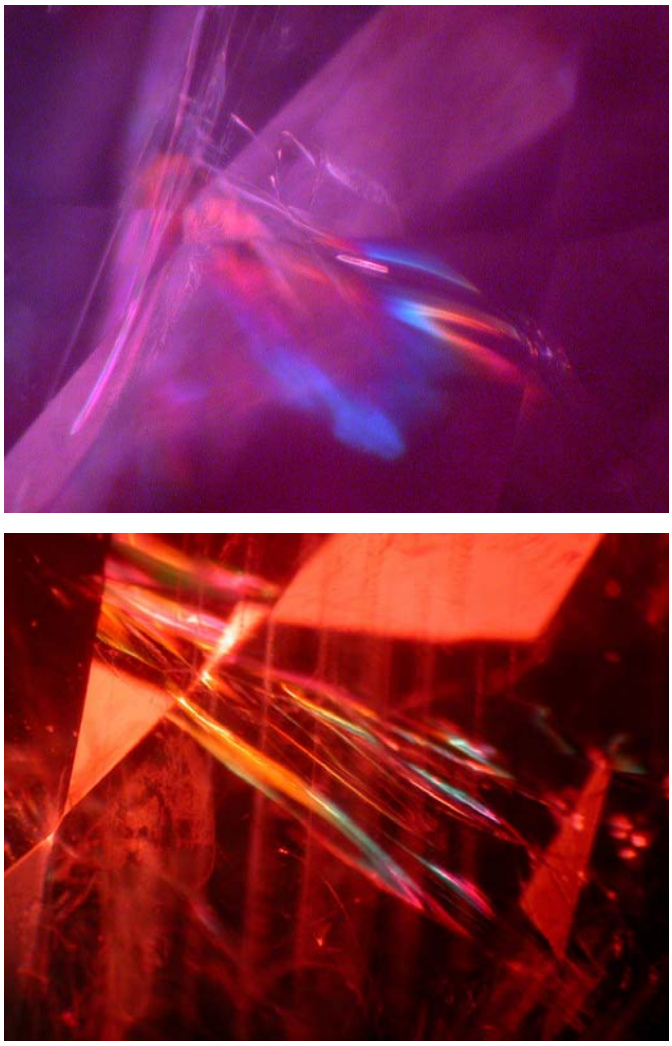
Identification of the lead glass repaired rubies is very easy for any laboratory that owns an EDXRF (Energy Dispersive X-Ray Fluorescence), but microscopic observation is in most cases enough for the experienced gemologist. Using EDXRF the AIGS laboratory found lead and in a few cases, bismuth. It is the ideal instrument to provide a rapid diagnostic result.

EDXRF: This instrument's main use is to provide qualitative and quantitative information on the chemical composition of a given stone. EDXRF can detect any element heavier than fluorine and it is especially efficient for heavy elements such as lead. This instrument provides a very fast and reliable diagnostic analysis. The AIGS laboratory utilizes this instrument on all rubies presented for identification.

Because lead and bismuth are very heavy elements, we are here in the exact opposite situation compared to the beryllium issue. Beryllium is a very light element. Its detection is not possible using EDXRF, which makes their detection more complicated.

Ultra Violet: Examination of the stones using a standard SW and LW (short wave and long wave) fluorescent box did not give any diagnostic result.

Microscope: An experienced gemologist using a microscope and dark field illumination can identify correctly the repaired rubies without any difficulty. Using darkfield illumination, most lead-rich glass filled fissures will display blue/orange flashes as seen in the accompanying photos. This observation can be easier using fiber optic illumination looking near parallel to the fissure. This is a very typical diagnostic feature that is similar to the opticon flash effect in emeralds or in lead glass filled diamonds. However, occasionally a stone may not have this obvious feature.



In darkfield illumination, multiple flashes of color are easy to see.

With careful close-up examination of the fissures, an observer may also find gas bubbles or "platelets." Gas bubbles were found in many rubies filled with the simple lead glass. Some platelets may be found in the repaired rubies using the popular formula from Bangkok. These platelets could be remnants of former iron stains formerly present in many rough stones from alluvial mining areas. Orange or yellowish before heat treatment, they turn whitish or blackish after treatment.

The platelets present in many stones do not present the typical shape of flattened glass bubbles but could be in fact the result of the mixing of the glass with some iron rich natural powders. "The number of such platelets can be reduced with careful temperature control," said master burner Mahiton Thondisuk. Careful observation of these platelets shows that they were transparent when observed from most directions, but they can also act as small mirrors inside the gem. In this case they often appear reddish. Color concentrations in the fissures were not found in any stone from Chanthaburi using the immersion technique, but some platelets did seem to have subtle coloration. In rubies enhanced in Bangkok by the Orange Sapphire Company, some yellow to orange color concentration appears in large fissures and in cavities. The fact that lead glass used in most Chanthaburi treatment is pink explains why it is most of the time not visible inside the gem.

An attempt to explain the reason why the stones repaired using the popular formula present a stronger col-

After heating, the chemicals form a glass coating as seen in this dish of ruby rough.

oration than the stones using the lead-only formula could be in the fact that the transparent platelets could act as mirrors inside the gem. They are normally present in a random orientation inside the gem, following the former fissure planes. They do not block the light path as orientated rutile silk can do. The light passes through some of them and is reflected by others. These reflections could increase the length of the travel of the light inside the gem. As we know, the longer the length of the light passing inside the gem, the more saturated the stone color will be. But this attempt to explain the improvement of the color should be confirmed by more in-depth studies.

Some inexperienced observers could be disturbed by the fact that the heat treatment temperature is not high compared with the temperature at which many stones are heated today using gas furnaces. Many inclusions may still appear as unheated.

Heat treatment temperature can vary from as low as possibly 800ºC to more than 1300ºC. As rutile needles begin to resorbe at over 1000ºC, it is possible to find perfectly shaped needles in lead glass repaired rubies. Burmese star rubies are also known to have been repaired by burners in Mae Sot. It is important to bear in mind that because of the glass composition, the treatment parameters and the ruby material used differs in Chanthaburi, Bangkok, Mae Sot and in the other places this treatment is or will be performed. Therefore, different features are possible.

Origin of Color

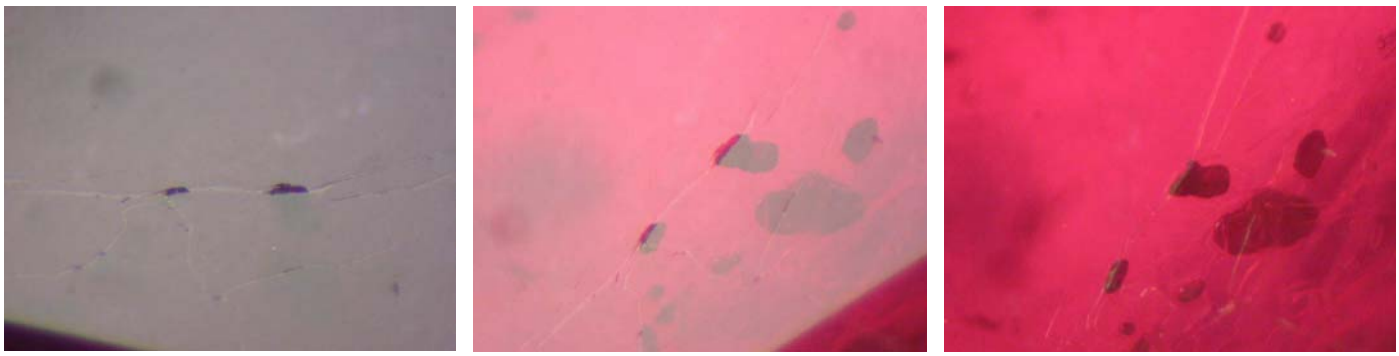
The gemstone color improvement seems to result from the fact that the fissures that were formerly filled with air or liquid are then filled with a transparent glass. As lead glass and ruby refractive index are very close, the light can then travel more easily inside the gem, and as a result, the overall color looks dramatically improved. The same phenomenon is encountered with emeralds before and after oiling them. Some questions were raised about the fact that some pink colored glass is used in Chanthaburi, and a more yellow one in Bangkok:

Some question if the stones can be described as dyed. Although we have observed some light color in some wide fissures and cavities in rubies from Bangkok ovens, it was never enough to honestly say that the stone was dyed. Color concentration in fissures was not detected in Chanthaburi stones.

Some red or orange color can be seen in some stones using daylight tubes like those in common use in Chanthaburi's buying offices. But these red looking inclusions described as copper platelets by Mahiton Thondisuk, present similarities with the glassy areas showing similar red coloration found in many Mong Hsu rubies heated with flux under the same illumination.

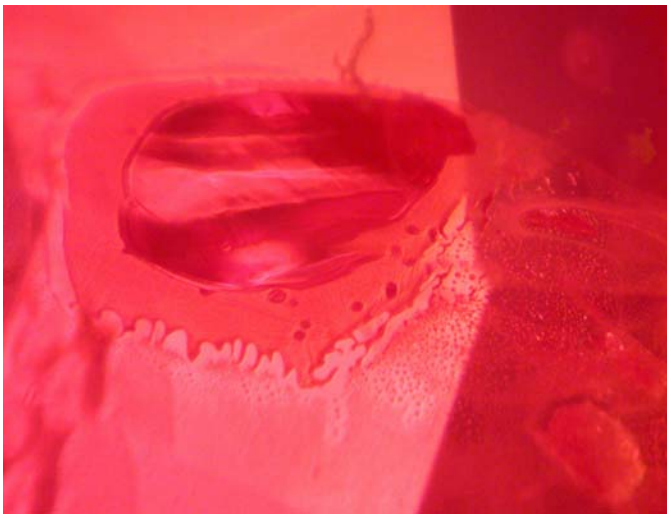
The lead glass present in this new treatment or the flux residue glass present in Mong Hsu act as a mirror, reflecting the color of the stone to finally give the illusion that the glass is colored. The same phenomenon can also be observed when twinning is present. Twinning planes can appear colored under some orientations. Twinning planes cannot be described as colored.

Dyed rubies exhibit some very clear color concentrations in fissures that are in strong contrast with the light



A wide fissure filled with lead glass from a Bangkok repaired ruby presents a noticeable orange color. Left to right: overhead, transmitted and dark field illumination.

colored to colorless body color regardless of the direction we observe them. The presence of a light pink or yellowish glass visible in wide fissures or cavities in repaired rubies is very different in intensity compared to dyed rubies in which fissures are filled with intensely colored red dying agent. In fact, this light colored glass found in some important fissures can be compared to iron stain in natural stones. The coloration of the glass is not the origin of the color, but massively filling important fissures, it can modify the stone color if the stone color is weak.



Twinning planes seen in Mong Hsu rubies heated with borax presenting some pinkish to reddish coloration.

Durability and Care

To answer the durability question, the AIGS laboratory has performed several tests. Other tests have been performed by the GIA and the results were presented in an article published in *Gems & Gemology,* Spring 2006. Based on the various studies conducted internationally, these stones are durable but should still be handled with care.

However, the study was done during a one year span and none of the treated stones were more than a year old, so time will tell if the durability holds up long-term. If we compare this glass filling method to the glass filling used in diamonds, the treatment looks to be suitable for normal wear.

Compared to emerald oiling or impregnation using resins, this current ruby treatment is probably more durable. Glass is more stable than resin and its presence in a fissure will probably lower the probability that the fissure will expand. The fact that the fissures are closed with a lead rich glass is also probably improving the durability of the repaired gemstone, but not as much as those fissures filled by flux additives. In this case the fissures are closed by the re-crystallization of corundum during the process. Because of this re-crystallization, the fissure is no longer a danger for increasing.

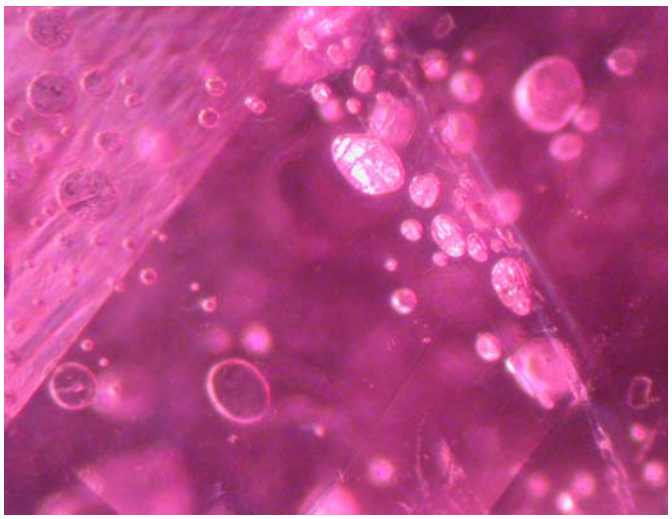
Assuming these stones are more durable than an impregnated emerald, but less than a ruby heated with flux, is a reasonable assumption. However, we must also consider that many companies are trying to perform this treatment. If they succeed, new technical problems may occur. Since the glass composition might vary considerably in the future, some surprises are probably still to come.

In our tests we observed the following.

1. One stone was exposed to a jeweler's torch for a few seconds. Glass began leaving the fissure producing glassy bubbles on the surface. This stone would then need to be polished again at a minimum to enhance its appearance.

2. Some stones were also boiled for several hours, immersed in detergents and exposed for short periods to ultrasonic cleaning without any apparent damage.

3. Several stones were submitted to light and heat fade tests to study the color stability after long exposition to light. No color modification was observed.



Platelets found in Chanthaburi rubies. They are either transparent or acting as mirrors depending on the light orientation.

4. Re-cutting or re-polishing should be performed with care as the glass used is very soft and could be damaged during the process. Many stones studied presented damaged or incomplete fillings.

5. The most important threat to the stone's durability and beauty is contact with powerful acids, such as hydrofluoric acid (also known as HF). AIGS exposed several stones to hydrofluoric acid for 12 hours and 48 hours. In all cases the acid dissolved the glass and the fissures in the stones were much more visible. The color and the clarity of the gemstones were then seriously damaged in three cases out of four. The attractive transparent purplish red stones had lost some saturation after immersion in HF and

were then presenting unpleasant shiny whitish fissures.

Sizes Encountered

Large and small stones are heated together in quantity. The most suitable material is corundum exhibiting multiple fissures. But small stones and clean materials are submitted to the treatment in large parcels along with fissured stones. After cutting, these stones will not present filled fissures, so finding diagnostic blue/orange flashes will not be possible. Lead detection using EDXRF can also become a problem. When dealing with small stones, getting diagnostic results is more difficult as we have less material to investigate. Small stone testing presents some identification challenges and several EDXRF tests on different parts of a given stone are recommended. The AIGS laboratory has studied several stones less than 1.0 carat presenting lead reactions using EDXRF only when studied on the pavilion as no filled fissures were reaching the stone surface on the crown.

An assortment of sizes and shapes may be found in the market.

Country of Origin

Although most stones are from Madagascar, we encountered several Burmese rubies presenting lead glass, especially star rubies and recently some Indian star rubies. In fact this treatment is likely to be seen in any stone presenting fissures that can be heated at temperatures up to 1000ºC.

Note: This treatment is likely to spread to other corundums and even other gemstones with fissures that can support temperatures around 1000ºC.

Conclusions

Different type of lead glass filled rubies are present in the market as several companies and individuals have invested in this process and are using stones from different origins and slightly different techniques and parameters. Lead glass can be found today in some facet cut rubies but also in star rubies.

The detection of these repaired rubies should not be a problem for any experienced gemologist with darkfield illumination microscope or using EDXRF technology. But the fact that the treatment can be performed at low temperature, allowing many inclusions to remain in their unheated appearance, we recommend all ruby buyers check their purchases with care. Most experienced gemological laboratories can provide rapid identification if needed at affordable costs, which is not the case with beryllium treatment.

As long as these stones are properly disclosed and priced, AIGS feels that these stones should find their place in the gem trade where large size and low prices are of prime importance.

The stone durability under normal wear should not be a problem, but it is important to notify that these stones have to be kept away from excess of heat or chemicals. If some repairs are required special attention similar to that used for glass filled diamonds and epoxy filled emeralds, should be observed. Jewelers wishing to use these stones in jewelry should be cautious, but if handled correctly, this product can be used in jewelry without problem. ◆

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AIGS Laboratory Reports Comments

For proper disclosure to a customer, the AIGS Gem Testing Laboratory currently uses the following terminology.

Full Reports:
Result–Found to be a Natural Ruby
Comments–This stone has been clarity enhanced. Lead rich foreign substance found in fissures and cavities.

Mini Reports:
Identification–Natural Ruby. This stone has been clarity enhanced. Lead rich foreign substance found in fissures and cavities.