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离子束弹性背散射光谱分析经离子注入改性的玻璃填充红宝石

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摘 要: 宝石业是泰国的重要产业之一, 但大多数宝石并不完美且带有缺陷, 常采用玻璃填充的方法来处理。但该方法填充的宝石含有有毒重金属, 因此急需开发新的宝石改性技术。离子束是近来发展起来的新技术, 可以用来处理玻璃填充的宝石并可以去除其含有的有毒金属。文中采用泰国本地的玻璃填充红宝石样品先经 80 kV 加速的氮离子束注入至 10^{17} ions/cm² 剂量, 然后分别在泰国清迈和中国武汉用 2 MeV 和 1.7 MeV 的质子束做弹性背散射光谱分析。研究了离子束处理前后, 玻璃填充宝石的金属杂质、含量及其分布。两地的分析结果互相印证、共同揭示了宝石中主要的有毒金属是铅, 铅的浓度经离子束处理后约为 0.15%, 比离子束处理前降低了 20 倍, 且铅在宝石中的分布是均匀的。结果表明: 离子束是一种有效的处理玻璃填充宝石的方法。

关键词: 离子束分析; 弹性背散射; 离子注入; 红宝石; 玻璃填充; 铅

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Ion Beam Elastic Backscattering Spectrometric Analysis of Ion Implantation Modified Glass Filled Ruby

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Abstract: Gemstone industry is one of the important Thailand local businesses. However, the majority of the stones are not perfect but with defects or flaws. Glass-filling treatment has been a traditional method to rescue the poor stones. Since the glass-filled stones may contain toxic heavy metals, development of new gemstone modification techniques is necessitated. Ion beams have been developed as a novel technique of modifying gemstones for gemological improvements and the technique is also being applied on the glass-filled gemstones to remove the toxic metals. Therefore, the glass-filled gemstones before and after ion beam modifications should be clarified for their metal impurity concentration and distribution. In this work, gemstone samples of local glass filled ruby were firstly by irradiated with 80 kV accelerated nitrogen ions to 10^{17} ions/cm² and then analyzed using elastic backscattering spectrometry techniques with 2 MeV and 1.7 MeV proton beams in Chiang Mai (Thailand) and Wuhan (China), respectively. Both elemental concentration and distribution in the materials were analyzed

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before and after ion implantation. The results reveal that the dominating toxic heavy metal in the stone is confirmed to be lead. The atomic concentration of lead in the ion beam treated ruby is about 0.15% in a uniform distribution, decreased by near 20 times compared with that of the as-glass-filled stone, demonstrating the effectiveness of ion beam treatment of the glass filled gemstones.

Keywords: ion beam analysis; elastic backscattering spectrometry; ion implantation; ruby; glass filled; lead (Pb)

0 Introduction

Gemstone business is very important for Thailand local economics. Locally, raw gemstones would go through traditional heat treatment and turn into vivid colored gems which are then contributed to the market. However, nowadays, raw materials in the local area are diminishing and cannot respond to high demands of the gemstone market as it used to be. Local gem traders have been seeking and stocking raw gemstones from other regions to feed the industry. The problem derives from the arrival of foreign traders who purchased good quality gems, leaving low quality raw gemstones or those with poor textures that cannot be enhanced even with heat treatments. To solve the problem of the majority of the stones being not perfect but with defects or flaws, modified heat treatment methods were developed. Chemical compounds including heavy metals were introduced into gemstones during the heat treatment. Those compounds would fill the fissures and cavities of gemstones and give the same result as the traditional heat treatment does; the gems would then be brilliance, vivid and can be cut. The industry calls this innovation as the “glass filling” process^[1].

But, since the glass filled stones may contain toxic heavy metals, like lead, bismuth and tantalum, costumers are concerned about their safety. The problem is further that recipes of the glass filling have usually been undisclosed due to commercial secret issues and hence physical information of some heavy metals introduced in the gemstones is not clear. Nevertheless, lead has been suspected to be involved in the glass filling in dominance.

Some methods have been developed to extract the toxic metals from the glass-filled gemstones while still maintaining the brilliance and endurance to the equivalence of traditionally heat treated stones^[2]. Recently, ion beams have been explored as a novel method to modify gemstones^[3], including the glass filled gemstone, for improving their gemological qualities while also removing the toxic metals. Therefore, the glass-filled gemstones before and after heavy metal extractions must be clarified for their metal impurity

types, concentrations and distributions to ensure the costumers the safety level of the gemstones.

Ion beam analysis is the unique nondestructive technique to obtain information on the element type and concentration in the sample materials. Particularly, elastic backscattering spectrometry techniques including Rutherford backscattering spectrometry (RBS) and non Rutherford backscattering spectrometry (non-RBS) can effectively and easily analyze materials for the information as well as the elemental concentration distribution which however can hardly be obtained using other ion beam analysis methods. From the RBS spectrum, the positions of the frontiers of peaks and plateaus are correlated with the elements; the heights of the peaks or plateaus are correlated with the atomic concentrations of the elements; and the shape of the spectrum is correlated with the elemental depth distribution. RBS analysis conventionally applies proton beam or heavier ion beams of such as helium and lithium, the former giving information in longer depths owing to light ions penetrating deeper, while the latter being more sensitive owing to heavier ions having larger scattering cross sections.

In order to provide the gemstone industry and costumers with convincing and authoritative evidence on the heavy metal impurity level in the ion beam treated glass filled gemstone, a small scale round robin test was performed. This test included two ion beam analyses carried out in two laboratories of two countries respectively and one X-ray fluorescence measurement in the third laboratory. In this report, the work on ion beam analyses which used MeV-proton beams for confirming the lead presence and determining its concentration level and depth distribution of the glass filled ruby before and after the ion implantation treatment is described. The ion beam analysis results were compared with the previously obtained X-ray fluorescence measured results to confirm the final results.

1 Experimental Section

Glass filled cut ruby which had the basic composition of Al_2O_3 and a minute quantity of Cr came from Thailand

local gemstone dealers. The gemstone size was about 1.5 cm long and 1 cm wide. The front side of the stone was cut in a convex shape with multi cut facets, many of which had flat areas smaller than 1 mm², while the back side was majorly flat. The color of the ruby was dark red. Optical microscopic observation revealed the stone filled with other materials due to nonuniform reflectivity. Some ruby samples were treated by mixed N+N₂ ion beam which was accelerated by 80 kV to a fluence in an order of 10¹⁷ ions/cm² with a beam current of 1 mA using a commercial 100 kV non-mass analyzing ion implanter (Fig.1) (Chengdu Tongchuang, Tongchuang Applied Plasma Technology Center, Chengdu, China). Applying tens-keV nitrogen ion beam to treat gemstones was based on our previous experience and successes in ion beam gemological modification^[3-7] and also certainly on the technical availabilities of our ion implanters.

General considerations on using N-ion beams were that N-ion was a relatively heavy and active ion species which could produce better effects on materials modification and tens-keV N-ions could be easily and

economically generated by normal low energy ion implanters. During ion implantation, the sample stage was continuously rotated and water-cooled. N-ion implanted and unimplanted gemstone samples were analyzed using ion beam elastic backscattering spectrometry at the flat back side which could give an ideal backscattering angle. One analysis was carried out at Chiang Mai University (CMU), Thailand, applying 2.018 MeV proton (H⁺) beam (2 MeV from the accelerator acceleration plus 18 keV from the ion source extraction) which had a beam current of tens of nA at the target and a beam spot size of 1 mm in diameter controlled by an aperture. The backscattering angle was 166°. The other backscattering spectrometry analysis was operated at Wuhan University (WHU), China, using a normal incident 1.705 MeV proton beam with a backscattering angle of 170°. The ion-energy and channel number relationship for the ion beam analysis at CMU was experimentally calibrated in-situ using two backscattering spectra from the ruby (mainly Al₂O₃) sample itself (Fig.2) and another auxiliary thin film Ti-on-Si sample which was placed in the close neighborhood of the target ruby sample (Fig.3(a)) in combination. Table 1 lists the known and suspected elements with their front-edge channel numbers involved in the samples.

The relationship was assumed to be linear, i.e. $E = ai + b$, with E the energy, I the channel number, and a and b two coefficients to be determined. A linear fitting of the backscattered energy E_1 which was calculated from the kinematic factor K as a function of the front-edge channel

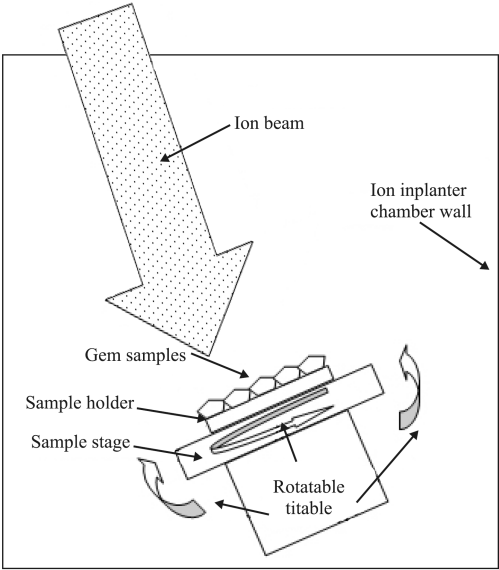


图1 武汉大学 100 kV 无质量分析离子注入机靶室侧面示意图(红宝石样品固定在直径 6 厘米的样品盘上, 置于一个可旋转、可倾斜、水冷却的样品台上, 箭头表示离子束注入方向)

Fig.1 Schematic diagram of side view of the 100 kV non-mass-analyzing ion implanter chamber which is installed in Wuhan University(the ruby samples were fixed on a sample holder (Φ 6 cm), placed on the sample stage which is rotatable, tiltable and water-coolable; the arrow indicates the incident implanting ion beam direction)

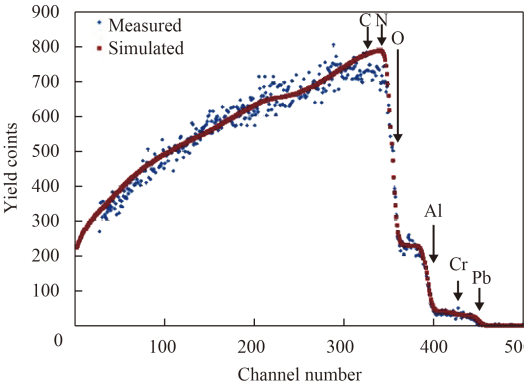


图2 离子注入的玻璃填充红宝石样品上获得的 2.018 MeV 质子束的 RBS 谱及拟合的 SIMNRA 模拟谱。对测量谱和模拟谱进行最佳拟合得到铅原子数分数为 0.13%。

Fig.2 2.018 MeV proton beam RBS spectrum from the N-ion-implanted glass-filled ruby sample, together with the fitted SIMNRA simulated spectrum. The best fitting between the simulated and measured spectra yields 0.13 at%.

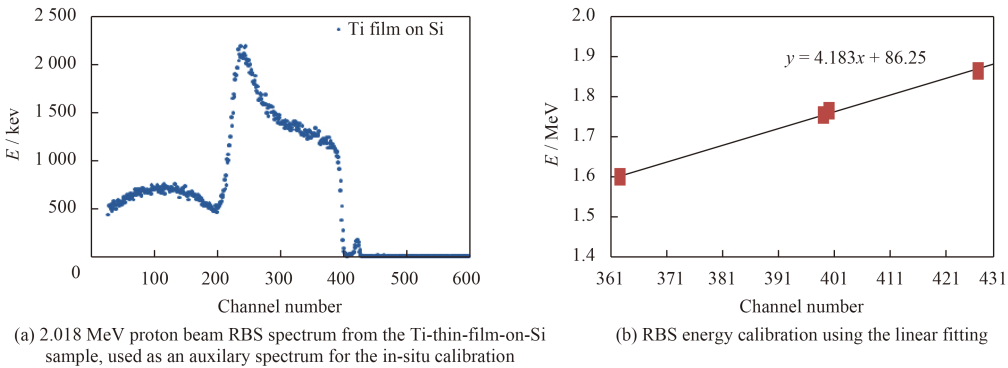


图3 RBS 离子能量-通道数校准

Fig.3 Calibration of RBS energy-channel number

表 1 已知和可能的元素在 RBS 谱中的信号峰前道数计算值、原子质量数、动力学因子数，及能量为 2 018 keV 的质子对它们背散射后的能量计算值

Table 1 Relevant known and suspected elements with their front-edge channel numbers in the RBS spectra, atomic masses M_2 , kinematic factor K and the backscattered ion energy E_1 of incident $E_0 = 2\,018\text{ keV}$ protons from them

Parameters	Values				
Target element	O	Al	Si	Ti	Pb
Channel number	361	399	400	427	454
M_2	16	27	28	48	207
K	0.791	0.870	0.875	0.925	0.982
Backscattered ion energy, E_1/MeV	1.596	1.756	1.765	1.866	1.982

number of four elements, i.e. O, Al, Si and Ti, gave the calibrated channel number - energy relationship to be $E = 4.18i + 86.25$ (keV) (Fig.3(b)). As the heavy metal was the target element to be detected, the ion beam analysis and spectral simulation at CMU were focused on RBS. In the ion beam analysis carried out at WHU, the relationship between the ion energy (E) and channel number (i) was calibrated using the quadratic formula $E = a + bi + ci^2$ with coefficients $a = 0$, $b = 7.93$ and $c = 2.15 \times 10^{-3}$ for the sample of unimplanted ruby and $a = 10$ (keV), $b = 7.88$ and $c = 2.15 \times 10^{-3}$ for the sample of ion-implanted ruby.

The simulation of the backscattering spectra using the SIMNRA program^[8] was focused on non-RBS for better fitting to the spectrum from the light elements of the sample. In the simulation, the multiple scattering process was adopted with the accurate pile-up model using the data of stopping power data from Ziegler/Biersack^[9], carbon nuclear reaction from Mazzoni^[10] with $E_{\min} = 343\text{ keV}$ and $E_{\max} = 3\,000\text{ keV}$ for unimplanted ruby and from Amirikas^[11] with $E_{\min} = 1\,000\text{ keV}$ and $E_{\max} = 3\,500\text{ keV}$

for implanted ruby, respectively, oxygen nuclear reaction from Gurbich^[12] with $E_{\min} = 701.62\text{ keV}$ and $E_{\max} = 4\,030.77\text{ keV}$, and aluminium nuclear reaction from Rauhala^[13] with $E_{\min} = 1\,000\text{ keV}$ and $E_{\max} = 2\,450\text{ keV}$ for unimplanted ruby and from Chiari^[14] with $E_{\min} = 783\text{ keV}$ and $E_{\max} = 3\,031\text{ keV}$ for implanted ruby, respectively. As a round robin test, both ion beam analyses analyzed the same ion-implanted glass-filled ruby sample, while the X-ray fluorescence measurement in the third laboratory measured more than one sample, including the ion-beam-analyzed sample.

2 Results and Discussion

The original ion backscattering spectrum from the ion-implanted ruby sample analyzed at CMU is shown in Fig.2. Three plateaus are clearly seen at channel numbers 454, 399 and 361 for the front edges. Some unclear noises are also present at high channel numbers. With using the calibrated relationship between the channel number and the ion energy, the backscattered ion energy at channel number 454 for the suspected Pb was calculated to be $E = 4.18 \times 454 + 86.25 = 1\,984\text{ keV}$. Comparing this energy with the energies listed in Table 1, we could find the closest one, 1 982 keV, which is of Pb, while all others were far away from 1 984 keV. Actually, since one channel number corresponded to about 4 keV energy, the difference between 1 982 keV and 1 984 keV meant that the error in estimating the plateau front edge channel number was only within half a channel number. Therefore, the suspected element was confirmed to be truly Pb. Furthermore, the plateau but not a peak shape of the Pb signals in the spectrum indicated the Pb atoms uniformly distributed in the gemstone ruby. From the calibration it was known that for the highest backscattered ion energy which was the incident ion energy

2 018 keV, the channel number should be $i = 462$. This meant that all signals at channel numbers more than 462 were noises, not from any target elements.

For determining the Pb concentration by iterating simulations to fit the spectra, a starting value of the concentration was first worth estimating. In a previous RBS analysis of implanted Pb in single crystal Al, as shown in Fig.4^[15], the Pb peak yield was seen at about 720 counts (Fig.4(a)). The Pb peak atomic concentration was about 3.7%, determined by a conversion from the spectral peak of Pb to the Pb depth profile (Fig. 4(b)). In the present measured RBS spectrum, the Pb yield was about 30 counts. Therefore,

the present Pb concentration should be about $(30/720) \times 3.7\% = 0.15\%$. Then, with this starting value of the Pb concentration, the ion backscattering spectrum was simulated using SIMNRA^[3] focused on Rutherford backscattering. The simulation was based on an assumption of uniformly distributed four main elements in the bulk of ruby, namely dominant Al_2O_3 , and very low quantities of Cr which was originally in ruby, and Pb, and a top layer including both bulk elements and implanted nitrogen and surface carbon contaminant. The best fitting between the measured and simulated spectra finally yielded the Pb concentration to be 0.13at%, as shown in Fig.2.

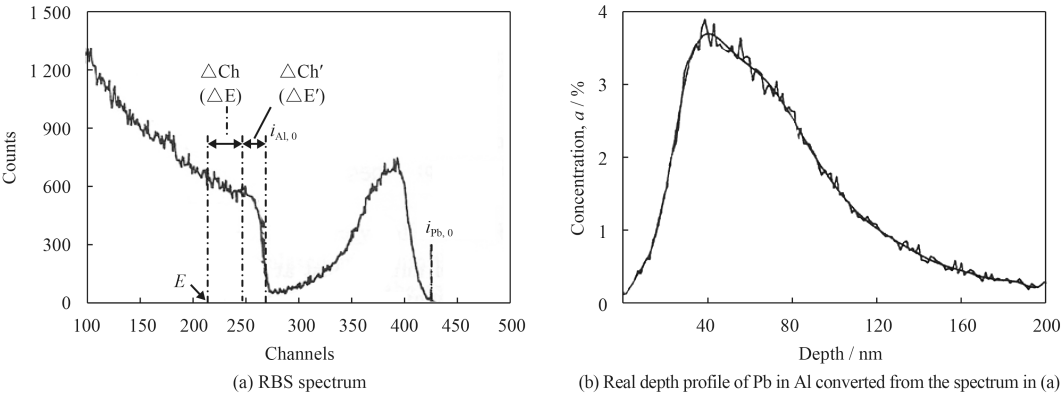


图 4 RBS 分析 Al 单晶中注入 Pb 的浓度深度分布^[15]

Fig.4 RBS analysis of implanted-Pb concentration depth distribution in Al^[15]

The elastic backscattering spectrometry analysis operated at WHU, as shown in Fig.5, provided precise results and confirmed the RBS focused analysis result obtained at CMU. As seen in the figure, both measured and non-RBS focused simulated spectra are fitted fairly well. There are three main signal plateaus, the same as those of RBS spectrum. The plateau at the higher channel number or energy was identified to be of Cr and Pb, the plateau in the medium channel number or energy was of Al, and the one in the lower channel number or energy was of O. The Pb concentrations were measured to be 0.17at% from the N-ion implanted ruby (Fig.5(b)), fairly close to that from the RBS-focused analysis, but 2.7at% from the unimplanted ruby (Fig.5(a)). This concentration difference indicated a considerable decrease in the Pb concentration by about 16 times owing to the N-ion implantation treatment. In the heavy metal plateau of the spectrum, a minute quantity of Cr was detected, as the fact is that the Cr concentration is normally 0.01at%–0.02at% (0.03wt%–0.05wt%) present in ruby^[16]. The impurity Cr was responsible for red color seen

from ruby. In the O plateau, a peak of carbon was identified. Since the C signals were in a peak shape, it indicated that the carbon was present on the top surface of the stone, supposed to be due to C contamination from sample fixing on the holder with carbon tape.

Both ion-beam backscattering spectrometry analyses obtained Pb concentration around 0.15at% (between 13at% and 17at%), corresponding to about 0.3wt% Pb (converted based on the commonly known mass density of 4 g/cm^3 of ruby with the dominant composition of Al_2O_3), was in a good agreement with the energy-dispersive X-ray fluorescence (EDXRF) measured data, 0.35wt% PbO_2 ^[17], remaining in the ion-implantation de-lead ruby. This low Pb concentration level ruby has been given a trade name as “Organic Ruby” to imply a lead-free product for customers^[17]. The range of 80 keV N-ions in Al_2O_3 (which is the dominant composition of ruby) was about 250 nm^[5] and that of 2 MeV protons was more than 50 μm ^[5]. The proton beams detected the lead reduced in a fairly deep region of the stone, indicating that the tens-keV N-ion beam

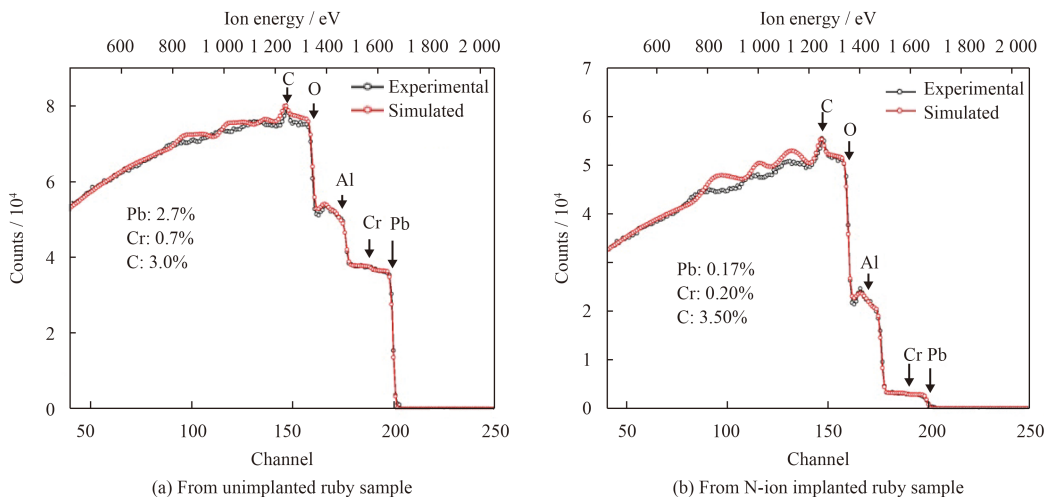


图5 非卢瑟福背散射分析谱及模拟拟合

Fig.5 Non-Rutherford backscattering analysis spectra and fitting with simulated spectra

treatment could induce effect on lead reduction in a depth considerably greater than its penetration range. This puzzle might be interpreted as following. Ion implantation induced removal of Pb from gemstone was due to the high fluence and high current ion implantation induced heat driven diffusion. The diffusion was further accelerated by ion implantation created structural micro defects which formed diffusing channels.

It has been shown that ion implantation is not only able to remove lead from glass filled gemstone but also can directly improve gemological qualities of gemstones^[3,6] and this is unique compared with other de-leading methods. It should be noted that removal of lead by ion implantation should certainly depend on the ion beam conditions such as ion energy and fluence. It is supposed that the higher the ion energy and the fluence, the more the lead can be removed. The current ion implantation modification of glass-filled ruby only provided an evidence of the potential of ion beam in effectively removing lead. Further investigations on the ion beam condition dependence of more effective lead removal and the critical ion beam condition able to result in a real safety level of lead in glass-filled ruby are still needed.

3 Conclusion

Ion implantation modified glass-filled ruby for reducing potential toxic heavy metal impurities such as lead. The ion implantation treated glass filled ruby was analyzed using proton RBS at Chiang Mai University and non-Rutherford backscattering spectrometry at Wuhan

University. The toxic heavy metal impurity in the glass filled ruby was confirmed to be Pb, which was uniformly distributed in the gemstone with a concentration determined to be around 0.15at% for the N-ion implanted sample, decreased by about 20 times compared with that of the unimplanted sample. The result well agreed with that obtained from the EDXRF measurement. The analysis result indicated that the N-ion beam modification of glass-filled ruby had a pronounced effect on reducing toxic heavy metals introduced by glass filling treatment of the gemstones to a safe level.

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