Influence of metamictization on the gemological properties of natural zircon: A Raman spectroscopic study of zircons in the gemological collection of Abraham Gottlob Werner

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**Abstract**

Raman spectroscopy is a convenient, efficient, and non-destructive technique that could estimate the metamictization degree of zircon, particularly for gem-class or historical samples. The full width at half maximum value of the $\nu_3$(SiO$_4$) band around 1000 cm$^{-1}$ can classify the structural state of zircon as crystallized (the full width at half maximum value is less than 5 cm$^{-1}$), intermediate (the full width at half maximum value ranges from 5 to 15 cm$^{-1}$), and metamict (the full width at half maximum value is more than 15 cm$^{-1}$). This study focuses on the zircon samples from Sri Lanka in the gemological collection of Abraham Gottlob Werner. These samples show red to green, according to the Munsell color system and the CIEL*$C^*h^*$ color system, and their density is from 4.07 to 4.87 g/cm$^3$. Comparing the color and metamictization degree data of zircon samples, crystallized zircon displays a more red tone with yellow. The green tone in zircon occurs with metamictization. The density of zircon could be an indicator of the metamictization degree as crystallized zircon is 4.57 to 4.70 g/cm$^3$ in a 95% confidence interval, which matches the theoretical density (4.61–4.76 g/cm$^3$) better, whereas metamict zircons present a density of 4.37–4.59 g/cm$^3$, and the density of zircon decreases with metamictization. The metamictization has a significant influence on the gemological properties of zircon, whereas the typical color tone and low density can be a sign of the metamictization.

**KEYWORDS**
color, density, metamictization, Raman spectroscopy, zircon

**1 | INTRODUCTION**

Zircon, a zirconium silicate (ZrSiO$_4$), generally occurs as an accessory mineral in the igneous rocks, particularly in granites and syenites. It can also be found in metamorphic rocks and sedimentary rocks.$^{[1,2]}$ Zircon has a widespread geological significance as the best available geochronometer for the absolute ages of magmatic or metamorphic events, the age of source rocks, and the timing of alteration events.$^{[3–9]}$ Although pure ZrSiO$_4$ is colorless, one reason that zircon is an attractive gemstone is its wide variety of color, commonly, brown, orange,
red, purple, yellow, green, and blue. This variety is related to zircon containing trace amounts of Mn, Ca, Fe, Mg, Al, P, and Hf and radioactive trace elements U, Th, and so forth.\[1,10–13\] The polished surface of gem-class zircon presents an adamantine luster to glass luster, and the fracture is greasy luster. It has a strong dispersion with 0.038. The refractive index can range from 1.810 to 1.925. Zircon’s Mohs hardness is 6–7.5. Owing to its high quality of optical properties and chemical durability, it has been used as a gemstone for a long time. Zircon is widely distributed, and gem-class zircon is mainly produced in Sri Lanka, Myanmar, France, Norway, the United Kingdom, Russia, Tanzania, and China.\[2,14–24\]

The structure of zircon can be heavily damaged by the radioactive decay of naturally occurring radionuclides and their daughter products in the $^{238}$U, $^{235}$U, and $^{232}$Th decay series. Natural zircon is commonly found to be “metamict,” an amorphized state, resulting from the loss of medium-range ordering.\[25–30\] The physical properties, such as color, transparency, and density, also change as a result of this process.\[10,31–44\] Zircon with low radioactivity displays color series from colorless to pink to red depending on age, remaining translucent and refringent. The color of zircon with high radioactivity changes from colorless to yellowish brown, orange, even to black, and opaque with time. The relationships between zircon coloration, radioactivity, and structural order (or degree of metamictization) are still needed to be studied.

Raman spectroscopy has been used to study the radiation effects and annealing processes of zircon in recent years.\[4,30,34,45–50\] As a non-destructive measurement, Raman spectroscopy is a good way to characterize the metamictization of gem-quality or historical zircon. Raman data demonstrate that systematic shifts in peak wavenumber and line broadening occur, which are related to metamictization. The most intense Raman bands of zircon lie in the ranges between 350–450 cm$^{-1}$ and around 1000 cm$^{-1}$. These bands correspond to the internal vibrations of the SiO$_4$ tetrahedron.\[10,51\] For both modes, internal and external, changes in their associated bands can be observed due to the accumulation of radiation damage. These changes are decreased band intensity, shifts in band position, and band broadening. With a decreasing degree of lattice order, the bands of internal (intra-tetrahedral) as well as external (inter-tetrahedral) vibrations become less intense and less sharp. Besides, as zircons become increasingly metamict, the vibrational frequencies are lowered. The increase in band half-widths and the accompanying decrease in intensity can be interpreted in such a way that, during metamictization, the distribution of bond lengths and bond angles within and between SiO$_4$ tetrahedra becomes increasingly irregular. Wavenumber shift and band broadening rely on the degree of metamictization. The degree of lattice decay can be estimated using the full width at half maximum (FWHM) of the $\nu_2$ (SiO$_4$) Raman band at about 1000 cm$^{-1}$, even in a highly metamict zircon with an extremely disordered lattice. The FWHM values of about 3 cm$^{-1}$ or less characterize a sample as well crystallized. Metamict zircons show the values of more than 15 cm$^{-1}$, and highly metamict has values equal to or greater than 30 cm$^{-1}$.\[4,30,31,33,34,45–49,52–56\]

Color systems show color effectively by graphically organizing all possible color precepts and notating the relationships of those colors in a quantitative way. The American painter Albert Henry Munsell (1858–1918) developed the first successful and widely accepted color system in the early 20th century. The Munsell color system describes the color as three variables: hue (the color name: red, blue, green, etc.), value (lightness or darkness), and chroma (purity, or difference from neutral gray). Every color is alphanumerically labeled with a letter for the hue, a number for the value, and a number for the chroma, which notates the relationships of the colors in a quantitative way effectively.\[57–62\] Except for Munsell color books and naked eyes, no other instruments are needed. The Munsell color system provides a color standard that is the closest to the human visual experience. Nevertheless, the data determined according to the Munsell system cannot be used for further analysis because these data of the cylindrical coordinates make its application for statistical calculations difficult. The CIE L*a*b* system was elaborated in 1976 by the International Commission on Illumination. It expresses color as three values: L* for the lightness from black (0) to white (100), a* from green (−) to red (+), and b* from blue (−) to yellow (+).\[63–66\] Instead of Cartesian coordinates a*, b*, the cylindrical coordinates C* (chroma, relative saturation) and h° (hue angle, the angle of the hue of the CIE L*a*b* color wheel) specify in the CIEL*C*h* color space. The CIE L*a*b* lightness L* remains unchanged. The conversion of color data from the Munsell color system to the CIEL*C*h* not only satisfies the efficiency and simplicity of data collection but also facilitates the subsequent statistical analysis.\[65–71\]

The theoretical density of zircon can be calculated by its unit cell volume ranging from 255.59 to 264.16 Å$^3$.\[17,19–21,23,25,72–82\] The effect of nuclear radiation from the decay of uranium, thorium, and their daughter elements on the density and unit cell dimensions has been studied. During the course of the irradiation, the density of zircon drops by 16%. Damage is dominated by the accumulation of isolated point defects, which cause unit cell expansion and distortion that account for most of the decrease in density.\[26,27,37,39,42–44,48,50,75,77\] The degree of metamictization can reflect these damages well.
Abraham Gottlob Werner (1749–1817) was one of the first scientists to systematize geology to be a science subject. He left a large number of geological and mineralogical samples in his collections, and he numbered these samples in different groups from their classification based on his knowledge. According to the catalog in 1823 by Werner. No. 039-173 samples are classified as zircon. Most of them are grain (46.7%) and crystal (39.3%), 10 groups of zircon samples were cut in different forms; 6 crystals with mother rocks and 1 wood crystal model are also in these numbers. No. 094 and No. 151 are lost. Nowadays, the samples are numbered in the whole geological collections, and some samples recorded as other minerals in catalog 1823 are classified as zircon. The gemological collection is not only meaningful for the study of Werner’s life and his scientific work, but it is also a very important resource to students, professionals, and amateurs of gemstones.

This study deals with the application of Raman spectroscopy analysis for estimating the degree of metamictization in zircons in the gemological collection of Werner and discusses the influence of metamictization on the gemological properties of zircon.

2 | EXPERIMENTAL PROCEDURE AND MATERIALS

Raman spectra of samples were determined by a LabRam800 HR (Horiba Jobin Yvon) microprobe (Institute of Theoretical Physics, Technische Universität Bergakademie Freiberg). The 532-nm line of a wavenumber-doubled diode-pumped Nd:YAG laser was used. For laser focusing, an Olympus microscope with a 50× objective (0.5 numerical aperture) was employed. The laser power at the sample surface was 20 mW. The spot size in analyzing zircons was 1.3 μm in radius. The scattered laser light was suppressed by an edge filter (Jobin Yvon, cutoff at about 150 cm⁻¹). The resolution of the system was better than 2 cm⁻¹. External calibration was reached using the Raman line of the HeNe lamp (1703.71 cm⁻¹). The Raman spectrum of zircon relies on sample orientation because of anisotropy. Each sample was measured from three different orientations at least three times for each position; the spectra were selected to maximize the intensity of B1g (ν3) mode at 1008 cm⁻¹. The data were exported by the HORIBA LabSpec software and described by symmetric Lorentzian bands with Origin software, which calculated the FWHM of the B1g (ν3) mode.

The color reorganization follows the Munsell color system in hue, value, and chroma with the Munsell Book of Color under the daylight indoors with a closed window. The color data were converted to the CIEL^*Ch^* color system according to the Virtual Atlas from Virtual Colour Systems.

Quantachrome Corporation He-pycnometer Ultrapyc 1200e (Institute of Mineralogy, Technische Universität Bergakademie Freiberg) was used to measure the density of samples. The measurements of each sample at room temperature (20–28°C) ran 10 times with dry helium gas to 103.4 kPa, and the density was calculated as an average.

To avoid the possible influence of different origins on the gemological properties of zircon, only 69 samples from Sri Lanka were selected for testing.

The new number, form, and transparency of all measured zircon samples are listed in Table S1. Almost half of them were polished grains (31 samples), and the other half were fragments (34 samples), whereas only four samples were cut. Most of the samples are translucent; only six transparent zircons and four opaque zircons are found in all these samples.

3 | RESULTS AND DISCUSSION

The peak assignment of Raman spectra is carried out, and the ν3(SiO4) bands are also listed in Table S1.

To estimate the degree of metamictization, the FWHM value of this band is calculated. The results indicate that nine samples are crystallized (FWHM value < 5 cm⁻¹), 11 samples are metamict (FWHM value > 15 cm⁻¹), and the others are intermediate between crystallized and metamict states. The Raman spectra examples of different metamictization levels are shown in Figure 1. The ν3(SiO4) band of No. 109086b is located at 1006.5 cm⁻¹, and its FWHM value is calculated to 4.37 cm⁻¹, which is classified as crystallized zircon. The Raman shift of No. 109028 sample's ν3(SiO4) band is 1000.0 cm⁻¹, and the FWHM value of 14.8 cm⁻¹ indicates the metamictization. With the ν3(SiO4) band at 998.3 cm⁻¹ and FWHM value equaling 23.41 cm⁻¹, No. 109039 sample is metamict. With the increase of metamictization, the Raman shift of the ν3(SiO4) band position decreases and its FWHM value grows. Their correlation can be observed in Figure 2 clearly with Formula 1, and the extremely metamict sample was regarded as the outlier.

\[
\text{FWHM} = -1.3060 \times \text{Wavenumber} + 1321.0664 R^2 = 0.879.
\]

The data according to the Munsell color system show the proportion of samples with different color tones (Table S1). Orange tone is displayed by 31 pieces of
samples, which means they have both red and yellow colors. Respectively, only red and yellow tones are observed in 10 samples and 16 samples. The hues of three samples are determined as green, and the colors of two samples are between yellow and green. The degree of colors can be identified by the hue number. The colors of two gray zircons and five colorless zircons are marked in the table with only value number, no hue, and no chroma in the Munsell color system. To analyze the data in statistical tests, all color data are calculated to L*C*h parameters in the CIE color system. Respectively signed by L* and C*, the lightness and relative saturation show no obvious differences between samples with different structural states. The samples are gray or colorless owing only to the L* parameter. The h parameter of the CIE color system demonstrates the color difference more clearly.

In Figure 3, the color distribution of samples in the different structural states can be seen. The h values of crystallized samples are from 47.31° to 91.93° in a 95% confidence interval, meaning they are almost orange to yellow. These data conform to a normal distribution with skewness of −0.315 and excess kurtosis of −1.521. As intermediate structural state samples, red to yellow are still the main color. The h values of these samples distribute relatively uniformly. Some of them display a strong green tone. Most of the metamict samples are yellow to green with h values from 54.79 to 105.55 in a 95% confidence interval, which is an approximately normal distribution. From the color data, the change of metamictization is followed by a change in color tone, mainly from red to green. The greenish coloration is not only related to the intense absorption by U4+ and Er3+ but also related to a phonon-coupled electron–hole center.[2,12,89–91] The green samples from the literature are not all metamict, especially the samples not from Sri Lanka.[4,11,89,92,93]

With the data of the unit cell volume, the theoretical density of zircon is calculated as 4.61 to 4.76 g/cm³. Comparing the FWHM value and the measured density of samples (Table S1), the data demonstrate trends in different structural states (in Figure 4). The density of the crystallized samples is mainly from 4.57 to 4.70 g/cm³ in a 95% confidence interval with the median at 4.58 g/cm³, whereas the data of samples in the intermediate state are concentrated in the range of 4.60–4.65 g/cm³. In the same confidence interval, the density of metamict is measured as 4.37–4.59 g/cm³. The density of intermediate and metamict samples conforms to a normal distribution. The density range of the crystallized samples overlaps the range of intermediate samples. The low density of crystallized samples may be due to the cleavages or inclusions. Even so, the tendency still can be observed that the density of samples reduces with the metamictization.

Considering that the samples are in different forms, the structural state and the polishing of samples are compared; 80% of crystallized samples are unpolished fragments, whereas only 18% of metamict samples are unpolished. In the intermediate structural state, the unpolished samples (48%) and polished samples (52%) are almost half and half. Although a trend of well-polished samples showing high metamictization degree is observed, only 10 and 11 samples are estimated to be crystallized and metamict; more data need to be measured to support the result. The result of the 48 intermediate samples is more convincing, showing that the form and polishing do not affect the crystallinity of zircon.
Raman spectroscopy is a convenient, efficient, and non-destructive technique that is able to estimate the metamictization degree of zircon, particularly for gem-class or historical samples. The FWHM value of the $\nu_3(\text{SiO}_4)$ band around 1000 cm$^{-1}$ can classify the structural state of zircon as crystallized (FWHM value < 5 cm$^{-1}$), intermediate, and metamict (FWHM value > 15 cm$^{-1}$). Along with the increase of metamictization, the Raman shift of the $\nu_3(\text{SiO}_4)$ band position decreases and its FWHM value grows. The typical color tone of zircon in the different structural states is distinguishable. Crystallized zircon can show more a red tone with yellow. With metamictization, the green tone appears in zircon.

The density of crystallized zircon fits the theoretical density (4.61–4.76 g/cm$^3$) better, and the density of zircon decreases with metamictization. Both color and density of zircon could be an indicator of the metamictization degree.

The metamictization has a significant influence on the gemological properties of zircon. The green tone and low density cannot be considered as an identifying characteristic of metamict zircon, although they are still a sign of metamictization.

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