



New Method for Identification of Blue Topaz —An Application of Cathodoluminescence(CL)

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Abstract

Blue colored topaz is the most commercialized gemstone worldwide at present. Very rare in nature, most of these topazes are treated by laboratory irradiation with gamma ray, neutron or electron, or in combination with them ever since more than 30 years ago. Knowledge about the origin of the blue color in topazes is not well understood, and a method to identify blue topaz nondestructively is a worldwide problem.

In this research, the tested samples were natural blue, colorless topazes and irradiated blue topazes which were firstly tested by using UV lamp ($\lambda=365, 254\text{nm}$). Results showed that the UV fluorescence of the natural blue topazes ranged from very strong to very weak, while those of the irradiated blue topazes were always very weak or even no fluorescence. Based on the UV fluorescence testing, their cathodoluminescence(CL) characteristics were studied emphasisly by using CL-2 cathodoluminescence spectroscope produced by Gemmological Institute of CUG and USB2000 CCD multi-channel spectroscope produced by Ocean Optics, U.S. For this study, CL spectra was acquired at an accelerating voltage of 9.5~10.5 kV, a 0.95~1.05 mA beam current, and entrance and exit slit widths of 4 mm. Results indicated that the maximum of the broad emission bands of all the topazes were always at approximately 500 nm with a side band at approximately 492 nm, and CL of natural blue topazes was the strongest (about 40~50 counts), followed by the natural colorless topazes (about 20~30 counts) and the irradiated blue topazes (less than 15 counts), only 1/3 of the natural blue topazes. Therefore, CL characteristics could be used to separate the natural blue topaz from the irradiated blue topazes rapidly and nondestructively.

Keywords: CL, Natural blue topaz, Irradiated blue topazes, Spectra

1. Introduction

Blue topaz is usually sky blue, with little grey or green hue, similar to aquamarine and its color is pretty. Natural blue topaz is rare, and more than 95% blue topazes in the world are produced in the pegmatite of Minas Gerais in Brazil, near to Silva Rodriguez City (Yukihara, 1999; Gatta, 2006). However, colorless topazes could be greatly available in numerous places, as well as Guangdong province, China. Accordingly, a host of blue topazes in the market are produced using colorless or light topazes through irradiation treatment to change the color. Currently, there are three routine irradiation inducing coloration methods (Leala, 2007; Krambrock, 2007; Silva, 2005), viz. ^{60}Co gamma rays, electron accelerator (charged particles) and nuclear reactor (fast neutron). Topazes treated by gamma rays usually are sky blue or American blue with light color; Topazes by neutron irradiation are London blue with dark color; while those by electron irradiation are Swiss blue with gorgeous and pretty color and less residual radiation, respectively (Figure 1).

Topazes processed by irradiation treatment inducing coloration were homogeneous with stable color, no mottling and color band (Gatta, 2006). They could be preserved for a long period at a high or low temperature, and when exposed to acid, alkali and salt solutions, they were immune to interference. Physical and chemical properties of topazes after and

before irradiation inducing coloration treatment such as hardness, density, refractive index, and birefringence and so on almost coincide with natural topazes excluding color (Table 1).

Although identification methods such as infrared spectroscopy, thermoluminescence and so on were recommended by some researchers (Krambrock, 2007; Silva, 2005), due to the complexity of performance, high temperature of experiment and great damages to samples, the efficacious method to identify blue topazes by irradiation treatment is not available at present. How to differentiate blue topazes in nature or processed by irradiation treatment promptly, conveniently and exactly became a difficulty to gemstone identification currently. In the present paper, CL characteristics of blue topazes in nature or processed by irradiation treatment were studied emphasisly in order to seek an efficacious way to identify blue topazes nondestructively.

2. Experimental samples and methods

Samples for testing included three types: natural blue topaz (9), natural colorless topaz (8) and blue topaz after irradiation treatment (20). Natural blue topazes were produced in Friedi Mine in Brazil. Among topazes after irradiation treatment, 1 was Swiss blue irradiated by electron and others were London blue by neutron.

Topazes were measured by UV lamp used for standard identification of gemstone at the long wavelength of 365nm and the short wavelength of 254nm, and results showed that UV fluorescence of natural topazes varied often: UV fluorescence of some topazes, especially dark blue was strong, green-yellow of middle intensity at long wavelength and weak intensity at short wavelength; UV fluorescence of some blue or colorless samples were weak, light cyan at long wavelength, weak or even no fluorescence at short wavelength. UV fluorescence of blue topazes by irradiation treatment was cyan and weak at long wavelength, while that of Swiss blue samples was stronger. All topazes for testing by irradiation treatment at the short wavelength of UV had no visible fluorescence.

Based on the UV fluorescence testing, their CL images and spectra were investigated by CL-2 cathodoluminescence spectroscope produced by Gemmological Institute of CUG and USB2000 CCD multi-channel spectroscope produced by Ocean Optics, U.S. For this study, CL spectra were acquired at an accelerating voltage of 9.5~10.5 kV, a 0.95~1.05 mA beam current, and entrance and exit slit widths of 4 mm or so) Results were listed in Table 2.

3. CL characteristics of topazes

CL has been used for a long time in petrographic studies to determine the provenance of mineral grains or to distinguish generations of growth within minerals. Recently, CL detectors have been attached to scanning electron microprobes allowing a better control of the electron beam flux and general instrument stability, and permitting higher magnification and spectrometric measurements in the UV and visible ranges. Its basic principle was depicted as follows: high speed electrons with high energy resulting from cathode ray tube converged in the surface of samples, and due to higher energy of electron beam than UV, its electrical excitability was stronger, which facilitated many mineral samples with no UV luminescence have obvious CL. (Yuan, 2005, Barbar, 2001; Lindblom, 2003).

Observations indicated that CL color of different type topazes was similar, and all showed blue fluorescence, but topazes were significantly different in luminous intensity and threshold excitation voltage.

3.1 Luminous intensity characteristics

Under the condition of a high voltage of 9.5~10.5 kV, a 0.95~1.05 mA beam current, CL of natural blue topazes (Fig. 3a) was the strongest with blue light of middle brightness; natural colorless topazes (Fig. 3b) followed with blue light of medium weak brightness; CL of irradiated blue topazes (Fig.3c) was the weakest with weak blue light, only in the sections of edges and corners centralized bombarded by electrons.

3.2 Spectra characteristics

A. CL spectra of natural and irradiated topazes were broad and gentle curves, and the main wavelength of peak were at 492-500nm, which was the reason that topazes possess blue fluorescence. Peak shape and position of natural topazes was approximately identical to irradiated ones.

B. CL of natural blue topaz was the strongest with an intensity of about 40~50 counts, followed by the natural colorless topaz (about 20~30 counts) and the irradiated blue topaz(less than 15 counts), only 1/3 of the natural blue topaz. (Figure 4 and Table 2).

3.3 Threshold excitation voltage characteristics

Through the testing, it was noted that by the bombarding of electron beams, natural topazes (whether blue or colorless) irradiated easily, with a threshold excitation voltage appearing fluorescence at only 4-5kV; While threshold excitation voltage of irradiated topazes was obviously higher, at 6-7kv. Such threshold difference, as well as CL intensity, all suggested that the luminescence property of natural topazes was obviously stronger than that of irradiated ones, which indicated that CL mechanisms of natural topazes were quite different from irradiated ones.

4. Identification flow of blue topaz

- 4.1 Prepare standard samples of a natural colorless (blue) and an irradiated blue topaz;
- 4.2 Compare UV fluorescence intensity of unknown samples with that of standard samples, if UV fluorescence of unknown sample is strong, it is natural blue topaz; If not, a further CL test is necessary;
- 4.3 Put the natural colorless (blue) standard topaz and the blue topaz for checking into sample chamber of gemstone cathodoluminescence spectroscope, and compare their CL intensity. Under the condition of a high voltage of 9.5~10.5 kV, a 0.95~1.05 mA beam current, if its CL intensity is equivalent to natural blue or colorless topaz, the blue topaz for checking is natural blue topaz, otherwise it is irradiated topaz (Figure 5). If CL spectra of topazes are available, the result will be more accurate.

5. Discussions

Our observations indicated that CL of natural blue topazes was markedly higher than that of irradiated blue ones, and UV fluorescence also showed this trend (Tarashchan, 2006). What was the cause for the difference of such luminescence intensity?

Topaz is an aluminum fluorosilicate with chemical formula $\text{Al}_2\text{SiO}_4(\text{F},\text{OH})_2$, in which OH^- may substitute for up to 30mol% of the F⁻. It crystallizes in the orthorhombic space group $Pbnm$ (D_{2h}^{16}) with four molecules per unit cell, but the OH/F substitution turns its symmetry into triclinic (P1) (Pinheiro, 2002, PP.104-301). In the lattice of topaz, a hexagonal close packed structure of O^{2-} and F⁻ ions in ABAC sequence in which the small Al^{3+} and Si^{4+} cations are located interstitially between the layers, respectively, and trace elements such as Cr, Fe, Ti, V, and so on could replace Al^{3+} of the lattice in the form of isomorphism (Yukihara, 1999; Leala, 2007; Krambrock, 2007; Silva, 2005). According to the Electron Paramagnetic Resonance (EPR) study on the natural blue, colorless topaz and irradiated topaz by Dickinson and Moore, EPR features confirmed that impurities in natural blue or colorless topaz was Fe^{3+} in the octahedral or interstitial position and defect centre was X hole center; F hole center only existed in blue topazes, viz. color center of inducing blue which was in the O^{2-} of Si-O tetrahedron surrounded by six F⁻ ions in the same crystal surface (010).

During the process of topazes irradiated by the high speed electrons resulting from CL, hole center precursor, O^{2-} possessed conjugated electrons radiate away when bombarded by high energy particles. Most electrons emitted by O^{2-} were used for forming F color center, but denier electrons were captured by impurities Fe^{3+} to form Fe^{2+} . Fe^{2+} was the most efficacious fluorescence quencher and could greatly attenuate CL effect. Accordingly, it is not tough to elucidate that CL intensity of natural blue topazes was higher than that of irradiated ones.

6. Conclusions

- 6.1 Observations indicated that CL of topazes was usually weak with same color, but CL intensity of natural blue topazes was markedly higher than that of irradiated ones. This difference could be easily recognized in Gemstone cathodoluminescence spectroscope. Especially when these two kinds of topaz were undertaken CL comparison, we could obtain more accurate and effective results.
- 6.2 Results of CL spectra determination indicated that CL relative intensity of natural blue topazes was 2 times higher than that of irradiated ones. Intensity difference was quite obvious.
- 6.3 Irradiated blue topaz usually possessed no or weak UV fluorescence, but some natural blue topazes had strong UV fluorescence, which could be used as a quite convenient and efficacious identification method.

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Table 1. Property variation of topazes after and before irradiation treatment

Property category	Test method or apparatus	Property change before or after irradiation
Chemical composition	Chemical analysis	Aluminosilicate, no change
Crystal Structure	D-max3X ray powder diffraction	Orthorhombic system D_{2h}^{16} , no change
valence bond	PE-983Ginfrared spectrophotometer	Infrared 3644, 1004cm ⁻¹ absorption spectrum, no change
relative density	Hydrostatic weighing method	3.56, no change
Hardness	Mohs hardness scale	8.0, no change
Refractive index	immersion method	Ng=1.624 Np=1.615, no change

Table 2. Testing results of some samples

Serial number	Sample characteristics			cathodoluminescence(CL)			UV fluorescence	
	Property	color	Cutting style	Excitation voltage /KV	Relative intensity/ counts	Peak/nm	Long wavelength	Short wavelength
1	Natural	Light blue	Ellipse	5	20~25	496	Very weak	No
2	Natural	Light blue	Rough stone	5	50~55	492	Very weak	Very weak
3	Natural	Light blue	Rough stone	5	30~35	514	Middle	Weak
4	Natural	Light blue	Emerald	5	85~90	497	No	No
5	Natural	Light blue	Rough stone	5	30~35	497	Weak	Very weak
6	Natural	Light blue	Emerald	5	40~45	495	Very weak	Weak
7	Natural	Blue	Rough stone	5	25~30	497	Middle	Weak
8	Natural	Blue	Ellipse	5	40~45	492	Middle	Weak
9	Natural	Blue	Rough stone	4~5	35~40	510	Middle	Weak
10	Natural	Colorless	Ellipse	5	15~20	500	No	No
11	Natural	Colorless	Rough stone	4	25~30	505	Weak	Very weak
12	Natural	Colorless	Rough stone	4.5	15~20	491	Weak	Very weak
13	Natural	Colorless	Rough stone	4	15~20	499	Weak	Very weak
14	Treated	London blue	Marquise-shaped	6~7	10~15	492	Weak	No
15	Treated	London blue	Brilliant	7	5~10	491	Weak	No
16	Treated	Swiss blue	Ellipse	6	5~10	497	Weak	No



Sky Blue



London Blue



Swiss Blue

Figure 1. Blue topaz produced by three routine irradiation treatments



Figure 2. CL-2 Gemstone cathodoluminescence spectroscope

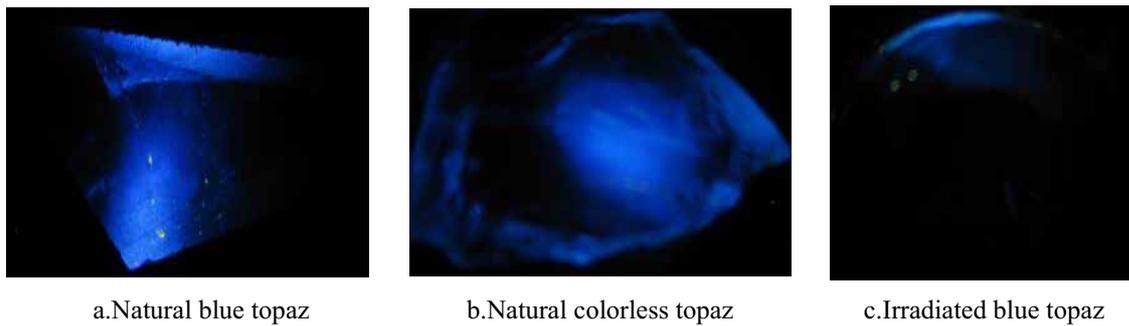


Figure 3. CL characteristics of natural and irradiated blue topazs

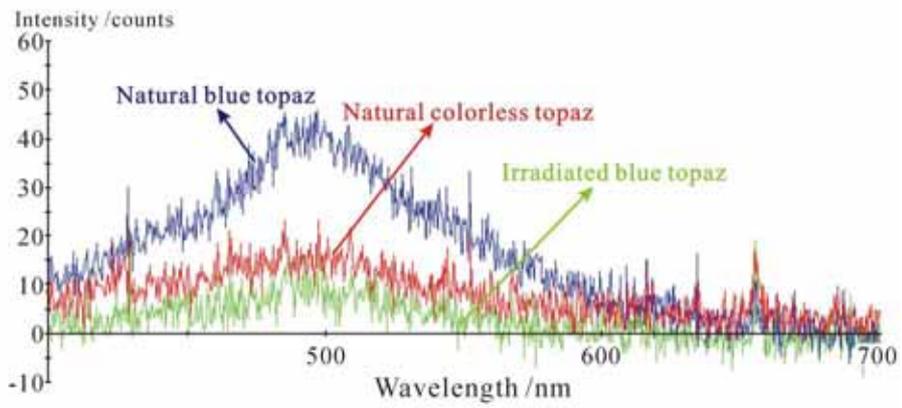


Figure 4. CL spectra characteristics of natural blue, natural colorless and irradiated topazes

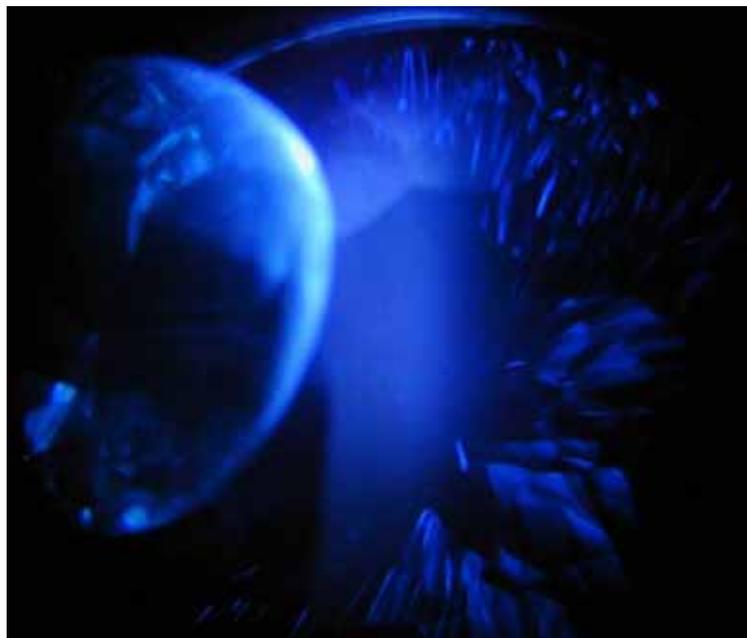


Figure 5. CL brightness comparison of natural and irradiated blue topaz