

Study of neutron irradiation-induced colors in Brazilian topaz

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Abstract

In this work, preliminary results of the investigation of the coloring mechanisms in topaz from different regions of Brazil, irradiated by the TRIGA MARK I IPR-R1 and BR1 nuclear reactors of the CDTN/CNEN (Brazil) and SCK.CEN(Belgium), respectively, are presented. The samples were analyzed by the k_0 -NAA method for impurities and total activity. The color and color centers were investigated by optical absorption and electron paramagnetic resonance (EPR) spectroscopy. The total integrated flux dependence of the induced blue colors and color centers is discussed.

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1. Introduction

Brazil is one of the most important producers of topaz in the world. Most of this topaz has a very low commercial value, because it is colorless or present only weak coloration. Differently from other gems, the color induced in topaz by gamma radiation is not stable. In such cases, the alternative of irradiating the gemstones by neutrons has shown very interesting results in the enhancement of its colors. Topaz is the best example for enhancement of color by commercial application of neutron irradiation. It leads to a deep blue color, called *LONDON BLUE*. Since the past 30 years, such treatments have been commercially applied and blue topaz is the one of the highlights in international gem trading. It is estimated that the market absorbs about 100 million carats per year, and today nearly 100% of such topaz is treated by laboratory irradiation [1].

The reasons why neutron irradiation has not been applied in a systematic way to color enhancing are the difficulty in accessing neutron reactors with a sufficient flux

and at the same time having the material of interest. In this sense, the state of Minas Gerais in Brazil has the privilege of being the most important producer of gem minerals worldwide and of possessing the nuclear research reactor TRIGA MARK I IPR-R1 do Brazilian National Nuclear Energy Commission (CDTN/CNEN). These aspects are very important for evaluating the future economic potential of the irradiation of topaz and other gem minerals [2].

From a physical point of view, it is important to study color enhancing by neutrons in order to understand the coloration processes and the structure of the color centers. In gem minerals, we have two different color mechanisms. One is related to optical transitions involving transition metals, including also charge transfer transitions between two of them or its oxygen neighbors [3]. The other cause of color is related to intrinsic color centers. Two types of centers, electron and hole centers, commonly produce color in minerals and they are produced in general by irradiation. A well-known example is the smoky color of quartz, which is related to a hole localized on the oxygen neighbors of an Al^{3+} impurity, the O^- hole center. It is easily created in colorless quartz that contains silicon replacing Al impurities to a large amount. We have recently identified a

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similar O^- hole center in gamma-irradiated tourmaline causing yellow colors [4]. Electron centers are known in fluorite (CaF_2), where an electron is trapped in a F vacancy causing violet to red colors. In all of the last examples, the color is stable in most cases under natural conditions and can be produced by gamma irradiation using, for example, a ^{60}Co source. The color centers in topaz are still controversially discussed.

2. Experimental

In this work, topaz samples from four different regions in Brazil, namely the State of Rondônia (TR), State of Tocantins (TT), State of Minas Gerais, Hematita (TH) and Marambaia (TM) were analyzed. Samples were prepared by cleaving and cutting large pieces to sizes of about $3 \times 3 \times 6$ mm with optical quality.

The topaz gems were separated in two batches of irradiation, as follows:

- Batch 1: the samples from TR, TT, TM and TH were irradiated by CDTN and SCK (except for TH) for a preliminary k_0 -NAA analysis. The goal here was to obtain a profile of the main impurities existing in the stones of each region, not a comparative k_0 -NAA study between the institutes. The gems analyzed by the CDTN and SCK were from the same region (TR, TT and TM) but not exactly from the same batch. The set of parameters of irradiation and gamma spectra analysis of each institute are described in Table 1. A more detailed description of the sample preparation and other parameters related to k_0 -NAA employed by each institute can be found elsewhere [5].
- Batch 2: five samples of each region, TR, TT, TM and TH, were irradiated by the CDTN for a total time of (3.5, 7, 14, 35 and 70)h in cycles of 8 h in the central thimble of the core, where the thermal flux is $4.0 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$, corresponding to an integrated flux of (5.0×10^{16} , 10^{17} , 2.0×10^{17} , 5.0×10^{17} and 10^{18}) n cm^{-2} , respectively. The objective here was to evaluate the total flux dependence on the induced colors and total activity in the samples of each region.

3. Experimental results and discussion

3.1. Radioactivity and impurities

A fundamental aspect to be considered for a future potential economic feasibility of colored topaz induced by neutrons is the time needed for the irradiated gemstones to decay. Radioactivity from some long-life elemental impurities would require long-time storage of the gems before being delivered. Table 2 shows the results of the elemental analysis of samples of batch 1 found by the k_0 -NAA method performed by SCK.CEN and CDTN. Table 3 shows its level of concentration C , in mg kg^{-1} , divided into

Table 1
Parameters of k_0 -NAA of topaz used by SCK.CEN (Belgium) and CDTN (Brazil)

Experimental	CDTN	SCK.CEN
Reactor channel	TRIGA MARK I	BR1 -Y4
Thermal flux ($\text{n cm}^{-2} \text{ s}^{-1}$)	6.4×10^{11} at 100 kW	3×10^{11} at 700 kW
Irradiation cycles (h)	8	8
Detector nominal efficiency (%)	15	40
Software used for acquisition	GeniePC	Accuspec Genie
Spectra Spectra analysis	Hyperlab [6]	Hyperlab [6]
Sample mass (g)	0.1	0.1

Table 2
Impurities found by neutron activation in the topaz samples from different regions of Brazil

Element	Nuclide	Half-life	Sample			
			TR	TM	TT	TH
Ag	Ag-110	249.76d			X	
Al	Al-28	2.24m			X	
As	As-76	26.32h	X	X		
Au	Au-198	2.70d	X	X	X	
Br	Br-82	35.3h	X	X		
Ce	Ce-141	32.5d		X		
Cl	Cl-38	37.24m	X	X	X	X
Co	Co-60	5.27y	X	X	X	
Cr	Cr-51	27.7d		X		
Cs	Cs-134	2.062y		X		
Eu	Eu-152	13.33y	X	X		
Fe	Fe-59	44.4d	X	X	X	X
Ga	Ga-72	14.1h	X	X	X	
Hf	Hf-181	42.39d	X	X		
K	K-40	$1.28e+09$ y	X	X	X	
La	La-140	40.27h	X	X	X	
Mg	Mg-27	9.46m	X	X	X	X
Na	Na-24	14.96h	X	X	X	X
Rb	Rb-86	18.66d		X		
Sb	Sb-122	2.7d	X	X	X	
Sc	Sc-46	83.1d	X	X	X	
Ta	Ta-182	114.5d	X		X	X
Th	Th-233	22.3m	X	X		
Tm	Tm-170	128.6d		X		
U	U-239	23.47m		X		
W	W-187	23.9h	X	X	X	
Yb	Yb-175	4.19d	X		X	
Zn	Zn-65	243d	X	X	X	

four different ranges: I ($C > 100$), II ($1.0 < C < 100$), III ($0.1 < C < 1.0$) and IV ($C < 0.1$). The higher number of elements found in TR, TM and TT compared with TH samples is due to the higher flux and efficiency of the gamma spectra acquisition system of SCK.CEN compared with CDTN, as can be seen from Table 1.

In this sense, the qualitative results of the k_0 -NAA analysis are important to know all the possible impurities present in the samples from such regions in concentrations below the lower limit of detection of the CDTN, where the

future irradiation will be performed. Due to the limitations of space and the scope of this work, the quantitative results of concentration of each element will not be presented here separately.

Among all the 20 samples of batch 2, just two TH samples, irradiated by 35 and 70 h, presented some final radioactivity—3 times higher than the background—after 6 months of irradiation, and were not released for optical and EPR measurements. This activity is due to the higher concentration, compared with TR, TT and TM samples, of the elements Fe and Ta with half-life of 44.4 and 113.5 days, respectively, obtained for batch 1, as shown in Table 3.

3.2. Optical absorption and electron paramagnetic resonance

Fig. 1 shows the optical absorption spectra of samples from TR as a function of dose in the spectral range from 350 to 800 nm measured at room temperature. As can be noticed from the figure, the band centered at 620 nm increases with the dose and is still not saturated for the highest dose (70 h) applied. This band together with the absorption tail in the UV region is responsible for the blue color of the topaz leaving an absorption valley at about

Table 3
Concentration ranges of elements found from k_0 -NAA performed by CDTN for topaz samples from the four different regions TR, TT, TM and TH

Range	TH	TT	TR	TM
I	Fe, Mg, Na	Mg, Na	Mg, Na	Cl, Mg, Na
II	Cl, Ta, Sc	Al, Cl	Cl	
III	Sb	Sb	Sc	
IV		Au, Sc		

The concentrations, C , in mg kg^{-1} are divided into four different ranges: I ($C > 100$), II ($1.0 < C < 100$), III ($0.1 < C < 1.0$) and IV ($C < 0.1$).

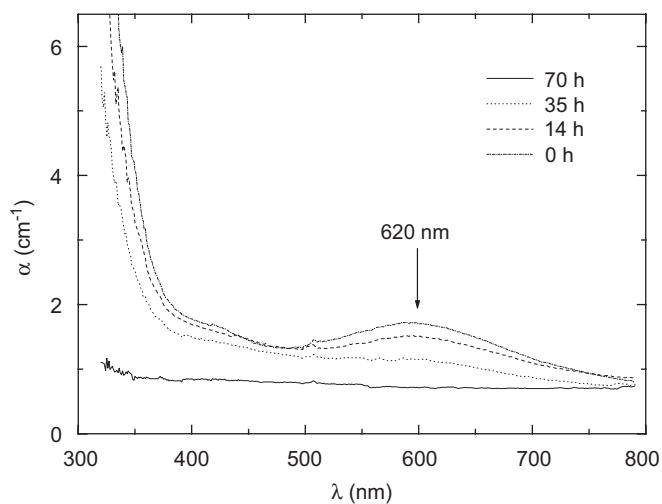


Fig. 1. Optical absorption spectra of topaz for different total times of irradiation (0, 14, 35, 70 h).

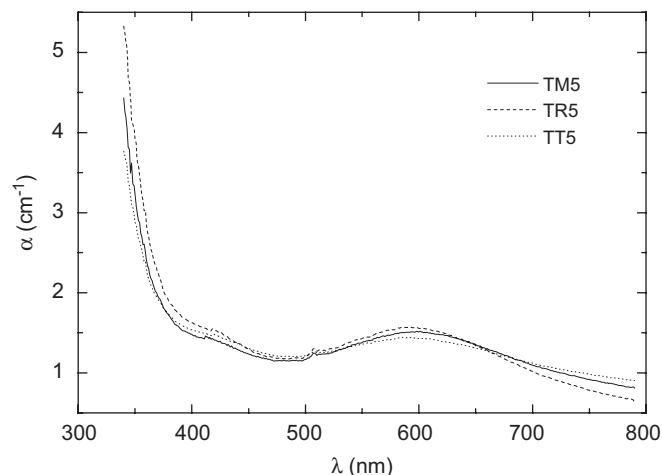


Fig. 2. Optical absorption spectra of topaz samples from TR, TT and TM for the highest total neutron flux of 70 h.

480 nm. However, increasing the irradiation to the doubled time increases the absorption band at 620 nm by only 10%.

All the samples from the different regions in Brazil show the same optical absorption spectra, and the same trend on neutron irradiation, i.e., the absolute absorption is the same for all samples investigated, as shown in Fig. 2 for the different samples irradiated with the highest flux applied (70 h). It means that the produced colors and color centers do not depend on the origin of samples. The induced blue color on gamma irradiation on the other hand depends strongly on it.

Our detailed electron paramagnetic resonance studies on the same samples show that the optical absorption band centered at 620 nm is intimately correlated with an O^- center interacting with two Al ions of the topaz structure. This O^- center is produced by the irradiation on the hydroxyl sites which substitutes fluorine in the topaz structure [6]. The concentration of the O^- center (i.e., the integrated area under the EPR spectra) is correlated absolutely with this absorption band [7] and also has the same thermal stability [8].

4. Conclusion

Except for the samples from TH from the Minas Gerais state in Brazil, all topaz samples presented a very low final activity, allowing the characterization of defects and color centers induced by neutron irradiation. The irradiated samples were analyzed by optical absorption for their color and by electron paramagnetic resonance for radiation-induced paramagnetic defects. From the analysis, it is shown that the blue color induced by neutrons is independent of the origin of topaz and correlated with an O^- defect. Its concentration and the blue color are increased nearly linearly by dose, and both are still not saturated for the highest applied dose. At present, neutron irradiation in Brazil for commercial use is prohibited by law, and all topaz treatments are done in foreign countries. The results

obtained in this study can open different economic perspectives for the country in international gem trading.

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