*Radiation Effects*, 1988, Vol. 106, pp. 143–150
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# IRRADIATION AND HEATING EFFECTS IN TOPAZ CRYSTALS FROM MINAS CERAIS, BRAZIL

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The origin of the blue color induced by irradiation in topaz crystals from the region around Governador Valadares, Minas Gerais, was examined through chemical analyses and heat treatments before irradiation. No correlation between impurities and the induced blue color was found. Heat treatments above 300°C before irradiation inhibit the formation of color.

*Key words:* color centres, topaz, gamma radiation, annealing, impurity measurements.

## INTRODUCTION

Topaz is a silicate class mineral, for the group "$Al_2SiO_5$" with chemical formula $Al_2(F, OH)_2 SiO_4$.[1] It occurs commonly in high temperature veins, probably formed by igneous intrusions in the presence of fluorine and water vapour. This results in the substitution of fluorine atoms by hydroxyl. Samples of topaz from several places show 15 to 20% fluorine. The specific gravity varies from 3.4 to 3.6 and the optic axial angle ($2V_\gamma^+$) varies from about 48° to about 65° with decreasing replacement of F by OH.[2]

The irradiation of different species of colorless topaz with radium radiation,[3] produces a brownish amber color. Irradiation with X-rays and $\gamma$-rays of colorless blue samples of topaz produces smokey brown to orange shades of color,[4,6] which is removed by heat treatment or by exposure to sunlight. The irradiation of 86 colorless topaz stones of probable Brazilian origin, produced after a moderate heating, 21 blue stones.[6] Standard gemological tests showed that blue color in topaz by irradiation is indistinguishable from that of natural blue stones.

The optical absorption spectra of blue topaz shows a strong E//a polarized band at about 15,200 $cm^{-1}$ and weak bands at 23,700, 24,200 and 24,800 $cm^{-1}$.[7] The 15,200 $cm^{-1}$ band is bleached by heating at 220°C. It was suggested that this band may be due to Ti or Fe impurities.

In previous work, we have carried out X-ray fluorescence quantitative analysis for Fe, Mn, Cr and V in colorless, brown, green, blue and imperial topaz.[8] It was shown that there is no correlation between the blue color and these impurites.

The purpose of the present work is to report on an investigation of the origin of the blue color in topaz through a new comparative study of impurity concentrations in different colored samples and the effect of heating before irradiation on the color induction by gamma ray irradiation.

## EXPERIMENTAL PROCEDURES

The samples were obtained in the region around Governador Valadares, Minas Gerais, and were of different colors: colorless (natural), slightly brown (natural), brown (irradiated) and blue (irradiated). The brown topaz and the sample of blue topaz were irradiatated with $\gamma$-rays of $^{60}$Co. Clear blue and dark topaz were irradiated in the nuclear reactor in Instituto de Pesquisa Energéticas e Nucleares (IPEN) (thermal neutrons were suppressed with a Cd absorber).

Neutron activation analyses were obtained for two samples of colorless topaz and for brown and blue topaz at IPEN. Semiqualitative analysis with X-ray fluorescence and atomic emission spectroscopy were also carried out at IPEN.

The optical absorption (AO) spectra were measured with a Cary 17D spectrometer at IPEN. The spectra were obtained with nonpolarized light and reference beam in air. Low temperature measurements were made in a cryostat described elsewhere.[9]

The thermal treatments were carried out in air.

## RESULTS

In Figure 1 we show the optical absorption spectra of irradiated topaz heated at 260°C for different times. The spectrum of the sample irradiated with a 4 MGy dose shows a strong UV band-edge rising from 1200 nm and with a shoulder around 600 nm. The absorption of violet, blue and green light associated with the 600 nm shoulder gives the brownish tone for irradiated topaz. After 33 minutes of heat treatment, the UV band edge shifts to lower a wavelength revealing an optical absorption band at 620 nm. For longer heating times the 620 nm band intensity decreases considerably. The combination of the UV band-edge and the 620 nm band is the origin of the greenish-blue tone, characteristic of irradiated blue topaz.

In several minerals the color is due to impurities.[10,11] So to determine the origin of the 620 nm band we first examined the possibility of a correlation between color and impurities. In Table 1, we show X-ray fluorescence counts corresponding to various metal impurities. No correlation between the color of the samples and the transition metal concentrations was observed. Rare earths were not detected within the limit of detection of the equipment. In Table 2 we show the atomic emission spectroscopic qualitative analysis for Ti, V, Cr, Mn, Fe; Co; Ni, Cu; Be, Mg, Mo and Pt. Again no correlation was found between these impurities and color. Finally, we see from neutron activation data in Table 3 that there is no apparent correlation between the color and the observed impurities: Sb; Ga, Sc, Ta, La, Au, W, Ce, U, Th.

In irradiated crystals, color can arise from valence changes of impurities or from formation of lattice defects.[12] From the above chemical analyses we found no direct correlation between impurities with color. We therefore conclude that irradiation induced color is probably due to the presence of lattice defects. If this is true, heating before irradiation may change the radiation yield. To check this possibility,

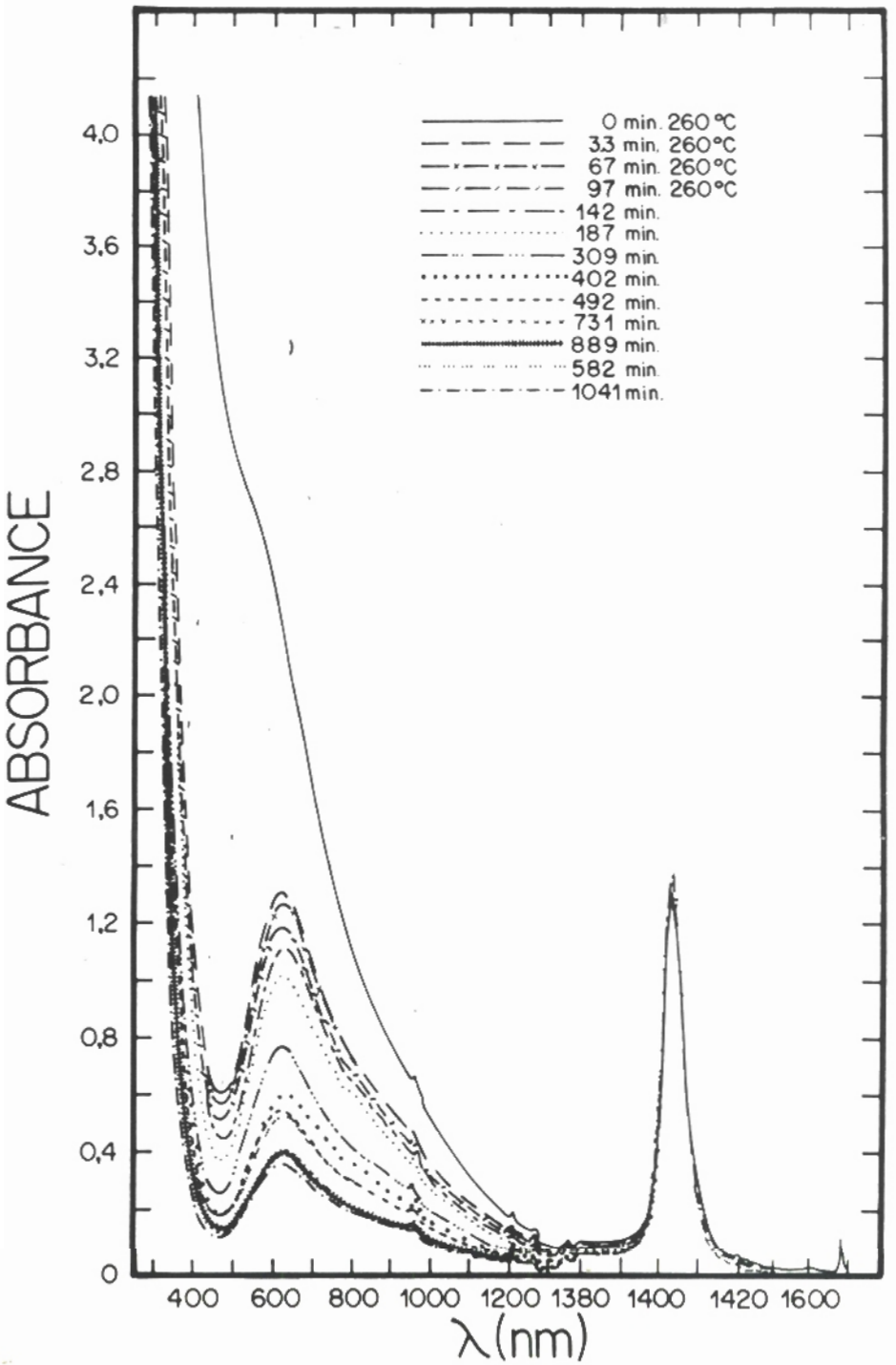


FIGURE 1 Optical absorption spectra of topaz irradiated with $^{60}Co$ $\gamma$-rays at room temperature and then heated to 260°C for different times.

TABLE I
X-ray fluorescence countings (counts/1005)

| Topaz samples | Ti | V | Cr | Mn | Fe | Co | Ni | Cu |
|---|---|---|---|---|---|---|---|---|
| Colorless | 530 ± 190 | 1510 ± 200 | 1790 ± 90 | 19170 ± 140 | 5060 ± 200 | 3570 ± 80 | 3090 ± 120 | 8790 ± 1030 |
| Slighty brown | 1040 ± 20 | 1510 ± 260 | 1610 ± 120 | 19900 ± 150 | 5420 ± 370 | — | 11020 ± 270 | 2660 ± 480 |
| Brown | 580 ± 80 | 1580 ± 220 | 1440 ± 210 | 18840 ± 450 | 5020 ± 240 | 3280 ± 140 | 4210 ± 120 | 10800 ± 440 |
| Blue | 580 ± 70 | 1710 ± 140 | 1620 ± 150 | 18500 ± 180 | 5470 ± 100 | 2670 ± 70 | 3240 ± 60 | 11470 ± 660 |
| Clear blue | 1480 ± 120 | 2860 ± 50 | 1720 ± 70 | 20910 ± 190 | 3710 ± 90 | 2820 ± 170 | — | — |
| Dark blue | 480 ± 70 | 1790 ± 140 | 1520 ± 140 | 21320 ± 110 | 4140 ± 200 | — | — | — |

Y, Lu, Er, Gd, Ho, Th, Yb, Tb, Dy, Sm, Eu, La, Pr, Ce, Nd: were below detected limit
—below limit of detection.

samples of topaz obtained from a single crystal were heated for 24 hours at several temperatures. These samples were then irradiated with $^{60}Co$ $\gamma$-rays for 4 MGy dose and then heated at 180°C for 24 hours. The spectra of these samples are shown in Figure 2. We see that the UV band-edge increases for samples heated at temperatures above 900°C before irradiation, and that the radiation yield, as shown by the 620 nm band height, decreases.

The increase in the band-edge for samples preheated at temperatures above 900°C is probably due to the liberation of (OH, F) above this temperature.[1]

In Figure 3, we show the correlation between the normalized absorbance of the 620 nm band (normalized to an unheated sample) and the temperature of heating before irradiation. We see that pre-heating at temperatures below 300°C does not affect the formation of 620 nm band. For pre-heating temperatures above 300°C the 620 nm decreases. Above 600 °C we see a sharp decrease of the 620 nm band.

In Figure 4, we show the absorption spectra for blue topaz at room and liquid nitrogen temperatures with a shift of the 620 nm band to 640 nm.

TABLE II
Qualitative atomic emission analysis

| Topaz samples | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Be | Mg | Ca | Mo | Pt |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Colorless | # | – | # | + | + | + | + | + + | – | + | # | – | # |
| Slightly brown | + + | – | # | + | + | – | # | # | – | + + + | + | – | – |
| Brown | # | – | # | + | + | + | # | + + | – | + | # | – | + |
| Blue | # | – | # | + + + | + | # | # | + + | – | # | # | – | # |
| Clear blue | + + | – | – | # | # | # | # | – | + | + + | + | # | – |
| Dark blue | + + | – | – | # | # | + + | – | – | # | # | # | + | – |

+, Indicates relative intensities of emission.
#, Traces.
–, Below limit of detection.

TABLE III
Data from neutron activation analysis

| Topaz samples | Sb (ppb) | Ga (ppm) | Sc (ppm) | Ta (ppb) | La (ppb) | Qualitiative identification |
|---|---|---|---|---|---|---|
| Slightly brown | 75.8 | 6.2 | 1.51 | 55.7 | — | W, Au |
| Blue | 12.4 | 10.6 | 0.51 | 14.3 | — | As, Au |
| Colorless | 19.7 | 10.2 | 0.64 | 10.7 | 23.2 | |
| Brown | 35.0 | 18.8 | 0.63 | 9.1 | 55.5 | W, Au, Ce, U, Th |

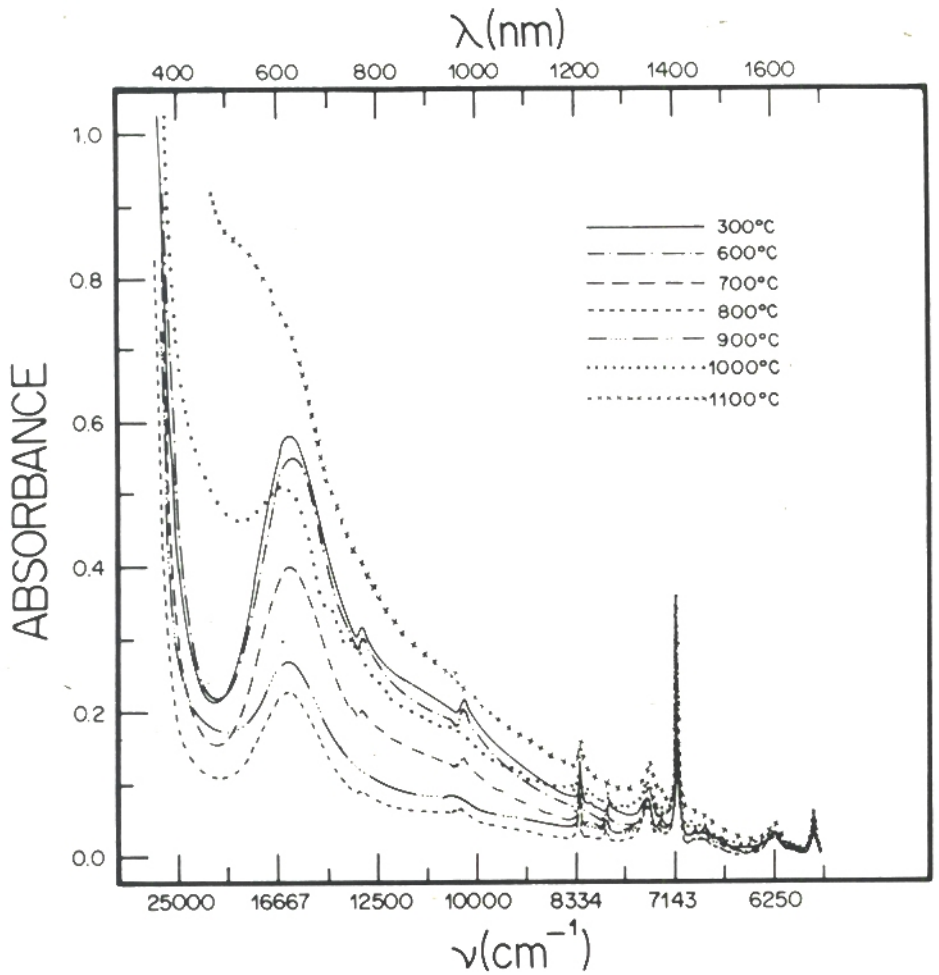


FIGURE 2 Optical absorption spectra of topaz samples heated before irradiation, irradiated with $^{60}Co$ γ-rays at room temperature and then heated at 180°C for 24 h.

## CONCLUSION

The chemical analysis of impurities through X-ray fluorescence, optical emission and neutron activation spectrospcopy failed to show direct correlation between color and impurities in topaz. On the other hand, pre-heating before irradiation showed a decrease of the radiation yield for temperatures above 300°C with a particularly sharp decrease at 600°C. This shows that the 620 nm band is formed from some state of the crystal which is changed by heat treatments before irradiation. Also, low temperature measurements show a shift of the 620 nm band to 640 nm, probably due to the coupling of the color center with the lattice. These observations suggest that the 620 nm band is due to a lattice defect.

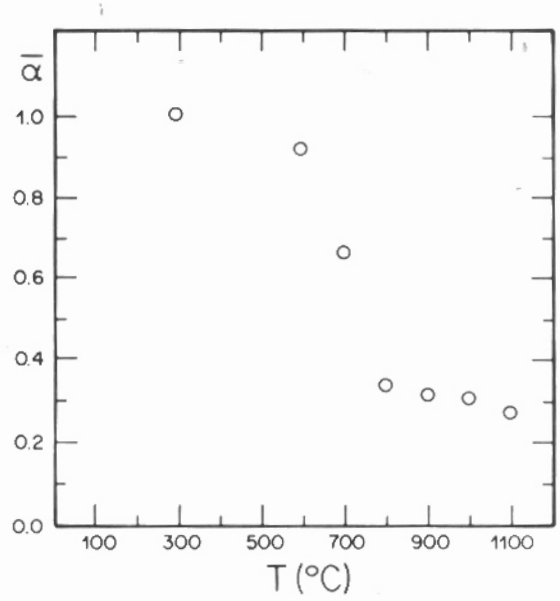


FIGURE 3 Correlation between normalized absorbance of the 620 nm band and heating temperature before irradiation.

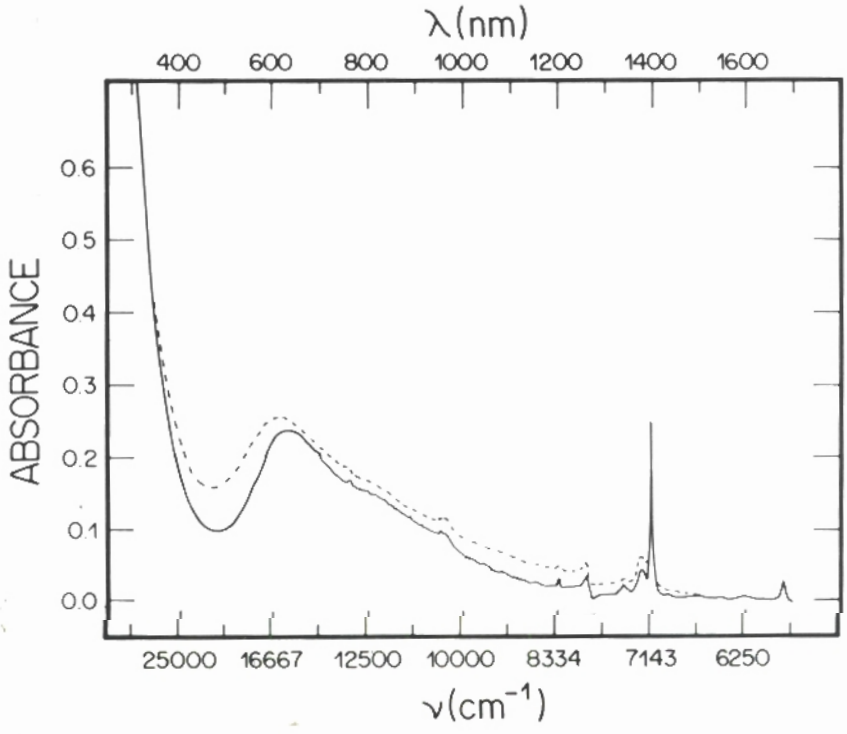


FIGURE 4 Optical absorption spectra of blue topaz at room and liquid nitrogen temperatures.

ACKNOWLEDGMENT

We would like to thank Prof. Shigueo Watanabe for discussions and support. Our thanks to Virgilio Tamberlini Neto for the offer of clear blue and dark blue topaz samples. This work was partially supported by grants from CNPq and FINEP.

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