

## Blue and Brown Topaz Produced by Gamma Irradiation

KURT NASSAU AND BETTY E. PRESCOTT

*Bell Laboratories, Murray Hill, New Jersey 07974*

### Abstract

The well-known brown color produced by the irradiation of topaz has been reexamined, in particular with respect to the kinetics of the color formation. The known color is produced at two different rates: fast coloration with a half coloration dose of 0.058 megarads of  $\gamma$  rays from cobalt 60 (15 min in the cell) produces a yellow to "sherry" color which fades rapidly on exposure to light; the slow coloration with a half dose of 12.6 megarads (18 hours) saturates to a dark brown which fades more slowly. Not all specimens go through both stages. Heating to 200°C for a few hours removes essentially all the color of the specimens tested. Topaz from Mexico and some from Brazil appear to be most resistant to light fading.

Some rare colorless topaz specimens (of unknown origin but probably from Brazil) after irradiation and heat bleaching become blue. This coloration is stable to light and heat and indistinguishable by standard gemological tests from natural blue topaz, both showing an absorption band at 0.62  $\mu\text{m}$ .

### Introduction

The observation that topaz turns yellow, tan, orange, or brown on irradiation by radium emanations, X rays, gamma rays, *etc.*, as well as the rapid fading of this color on exposure to light or heat, has been frequently noted (*e.g.*, Wild and Liesegang, 1923; Lind and Bardwell, 1923; Pough and Rogers, 1947; Lietz and Klug, 1956). That some of this material also develops the 0.62  $\mu\text{m}$  absorption band characteristic of natural blue topaz on irradiation and becomes blue when the accompanying brown is removed by heating does not, however, appear to have been previously noted.

The understanding of the causes of the various colors in topaz is not well-developed. The only unambiguous assignment is that of chromium, which causes pink and red, as well as the reddish component in some orange or "sherry" colored material (some of which turns pink on heating). Chromium as the colorant was first proposed by Wild and Liesegang (1923) and later confirmed by optical (Grum-Grzhimailo, 1953) and paramagnetic resonance (Dickinson and Moore, 1967) spectra. Vanadium has also been suggested as the cause of pink (Howard, 1935), as has  $\text{Fe}^{3+}$  (Lemlein and Melankholin, 1951).

Natural yellow and brown colors in topaz have been attributed to iron (Grum-Grzhimailo, 1953), chromium (Howard, 1935), or to color centers

(Dickinson and Moore, 1967; Samoilovich and Novozhilov, 1965). Chromium may be the colorant in those yellow topazes that turn pink (possibly the change  $\text{Cr}^{6+} \rightarrow \text{Cr}^{3+}$ ?) but certainly not in most other yellow topazes which usually lack significant amounts of chromium. Iron has been suggested as the cause of the blue color in topaz (Wild and Liesegang, 1923; Howard, 1935; Lemlein and Melankholin, 1951), as has a color center (Dickinson and Moore, 1967).

The electron paramagnetic resonance work of Dickinson and Moore (1967) is most significant. They recognized ten distinct EPR centers, four from impurities (two  $\text{Fe}^{3+}$ ,  $\text{V}^{4+}$ , and  $\text{Cr}^{3+}$ ), and six from defect centers (designated A, B, X, Y, Z, and F). The  $\text{Cr}^{3+}$  center was identified with pink, but  $\text{Fe}^{3+}$  centers occurred in colorless, blue, and yellow topaz, and hence are probably not color causing. Unfortunately  $\text{Fe}^{2+}$  is not seen in EPR. The A and B defect centers, both of the trapped electron type, appeared to correlate with the natural yellow color lost by heating to 500°C but recovered on irradiation. Y is a hole center associable with a yellow color produced by further heating of this now colorless material to 1000°C. The hole center designated X correlated with the blue color (lost by heating to 500°C), and the hole center designated F was correlated with the intensity of the irradiation-induced yellow-orange observed in crystals of any color and lost again on heating to 500°C. This last center, having a *g* value of about 2.09,

was interpreted as possibly being a hole trapped "on that oxygen of a silicon tetrahedron which is coplanar with and surrounded hexagonally by six fluoride ions in the (010) crystal plane" (Dickinson and Moore, 1967).

Samoilovich and co-workers (1965, 1969) also used EPR to study irradiation induced color centers in topaz. They correlated a resonance at  $g = 1.982$  with the depth of the color and the amount of irradiation (up to a saturation limit), and also interpreted the defect as an F center type, consisting however of an electron trapped at a fluoride vacancy. This is clearly inconsistent with the F center involving a hole described by Dickinson and Moore (1967).

### Experimental

A total of 123 topaz specimens were examined, some in crystal form and some as cut gem stones. Except for five crystals from Mexico and two from Topaz Mt., Thomas Range, Utah, these specimens were either from Minas Gerais, Brazil, or of unknown origin, probably also from Brazil. The initial colors used and the results obtained are summarized in Table 1.

Irradiations were carried out in a Co-60 gamma cell with an irradiation intensity of 0.70 megarads per hour. At least 10 megarads was used on each specimen. Heating was carried out in a muffle furnace with the samples buried in sand and heated and cooled slowly to prevent cracking.

Polarized optical spectra were run on a Cary 14R spectrophotometer; faceted stones were immersed in carbon tetrachloride in a fused silica cell.

TABLE 1. Color Changes on the Gamma Irradiation of 123 Topaz Specimens with 10 Megarads

Initial Color	Irradiated Color	No. of Specimens
Colorless	No change to pale-yellow	28
	Med. yellow to light brown	26
	Brown to dark brown	32*
Pale Yellow	No change to darker yellow	14
	Medium to dark sherry	17
Sherry	Slightly darker	1
Blue to Green	Pale brown (with an olive or greenish tint)	2
	Medium to dark brown	3

\*Heating of these produced a blue color in 21 specimens some of which had an olive or greenish tint; in all the other 102 specimens heating merely restored the original color.

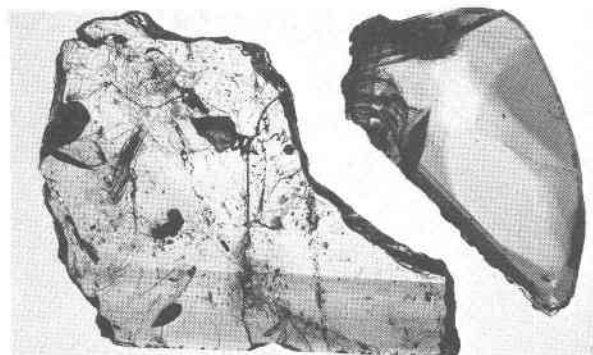


FIG. 1. Cleavage fragments of originally colorless topaz showing unevenness of coloration upon irradiation.

### The Irradiation Induced Brown Color in Topaz

As expected, all specimens acquired a more-or-less yellow to orange to brown coloration (Table 1), the exact shade depending on the original color, the length of exposure to gamma rays, and the susceptibility of the material to coloration. This last varied greatly even within a crystal. In Figure 1 are shown two topaz cleavage sections originally colorless, irradiated with 2 megarads. Both striations and patches of brown have developed, some of which follow crystal faces and some of which do not.

The polarization and the rate of coloration with irradiation dose were studied on a near cube approximately 8 mm to a side, oriented with the crystallographic axes. The three polarized spectra are shown in Figure 2 for two different levels of irradiation (15 min = 0.175 megarads, 20 hours = 14 megarads). The basic change is the shift of the absorption edge, near  $0.3 \mu\text{m}$  before irradiation, across the visible region, to produce the brown coloration. The only structure seen is the absorption band on the side of the edge near  $0.35 \mu\text{m}$  in the spectra with E parallel to the  $c$  axis. There is pronounced pleochroism (Fig. 2) with  $\alpha$  (dark brown)  $> \beta$  (med. brown)  $\gg \gamma$  (tan).

Using the absorption coefficient at  $0.5 \mu\text{m}$  as a measure of the intensity of coloration with irradiation dose, the data points of Figure 3 were obtained. This is for the polarization with E parallel to the  $b$  axis, but the other orientations gave essentially the same results. As can be seen there is an initial rapid coloration, saturating in less than one hour, as well as a much slower component, saturating only after some days (the "infinity" point was measured after a 30 day irradiation).

An exponential type coloration equation is:

$$\alpha_{\text{max}} - \alpha_t = \alpha_{\text{max}} \exp(-\lambda_t t) \quad (1)$$

or

$$\alpha_{\max} - \alpha_d = \alpha_{\max} \exp(-\lambda_d d) \quad (2)$$

where  $\alpha_{\max}$  is the saturation absorption coefficient,  $\alpha_t$  or  $\alpha_d$  is the same coefficient after irradiation time  $t$  or dose  $d$ , and  $\lambda_t$  and  $\lambda_d$  are constants.

Rewriting this in terms of the half coloration time,  $t_{1/2}$  where:

$$t_{1/2} = 0.693/\lambda_t \quad (3)$$

or the half coloration dose,  $d_{1/2}$ , where

$$d_{1/2} = 0.693/\lambda_d \quad (4)$$

and using superscripts ' and '' for two separate coloration processes occurring simultaneously gives:

$$\alpha_t = \alpha'_{\max} + \alpha''_{\max} - \alpha'_{\max} \exp(-0.693 t/t'_{1/2}) - \alpha''_{\max} \exp(-0.693 t/t''_{1/2}) \quad (5)$$

and

$$\alpha_d = \alpha'_{\max} + \alpha''_{\max} - \alpha'_{\max} \exp(-0.693 d/d'_{1/2}) - \alpha''_{\max} \exp(-0.693 d/d''_{1/2}) \quad (6)$$

By plotting on a logarithmic scale (Fig. 4) the two components were separated and gave for the data of Figure 3 the values shown in Table 2 (more precise than those given by Nassau, 1974). The solid curves in Figure 3 were drawn using these parameters of

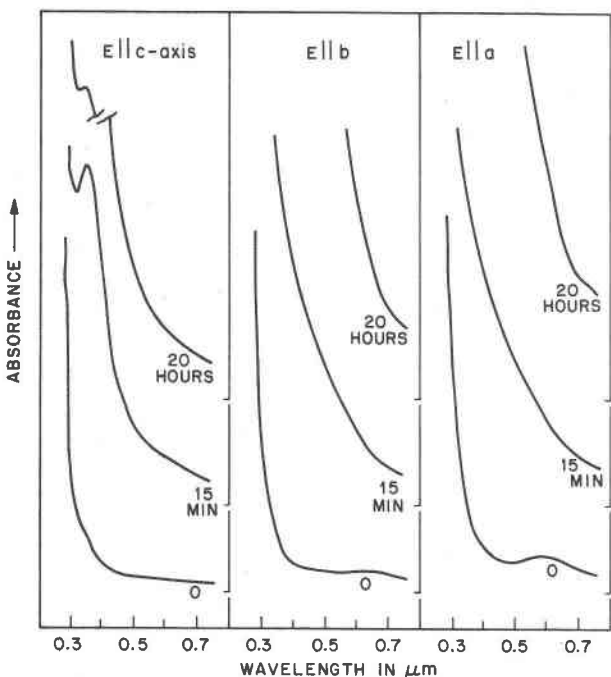


FIG. 2. Polarized absorption curves of a colorless topaz that turned brown on gamma irradiation.

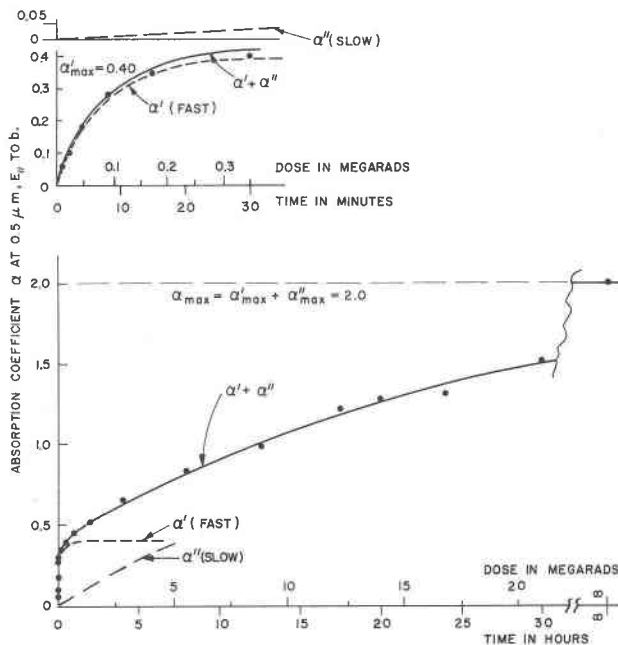


FIG. 3. Development of the color in the initially colorless topaz of Figure 2 on gamma irradiation. Points are experimental; the curves are calculated from Equation (5). The "infinity" point was the result of irradiation for 720 hours.

Table 2 and can be seen to represent the two coloration processes well within the experimental error.

Color photographs corresponding to the two stages of coloration of Figures 2 and 3 were published by Nassau (1974). The color after 15 min is a warm "sherry" brown; after 20 hours, the color is much darker "cinnamon" brown and less attractive. These two coloration stages also react differently to light exposure; the rapidly formed sherry brown color (yellow if only a very short irradiation) fades after a 1 or 2 day exposure to sun/daylight, while the slower forming but darker color requires several weeks to

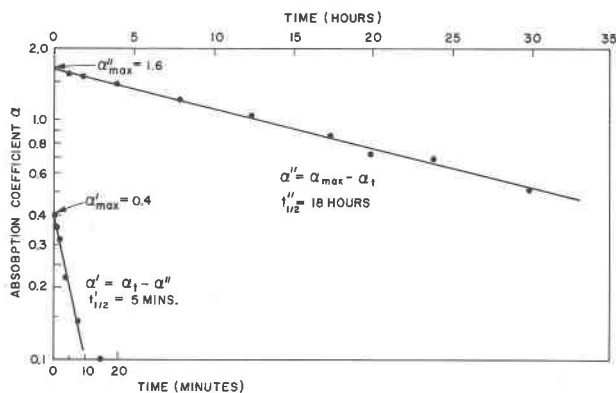


FIG. 4. Logarithmic decomposition of the data of Figure 3 into two components.

TABLE 2. Coloration Parameters for the Topaz of Figures 2 and 3

	Rapid Coloration	Slow Coloration
Saturation Absorption Coefficient	$\alpha'_{\max} = 0.40$	$\alpha''_{\max} = 1.60$
Half Coloration Time	$t'_{1/2} = 5.0$ mins.	$t''_{1/2} = 18$ hours
Half Coloration Dose (Megarads)	$d'_{1/2} = 0.058$	$d''_{1/2} = 12.6$

fade. Most topaz was found to go through both stages. However some yellow specimens from Brazil (e.g., the center stone, Fig. 9, Nassau, 1974) only showed the rapid coloration even on extended irradiation and faded very quickly. Some colorless topaz from Brazil, as well as colorless topaz from Mexico (e.g., center crystal, lower row, Fig. 10, Nassau, 1974), turned very dark and still retained significant color after some months of exposure to light. Heating to as little as 200°C for a few hours removed all this irradiation-induced color.

Some variation not only in the saturation coloration but also in the half coloration time  $t_{1/2}$  was noted

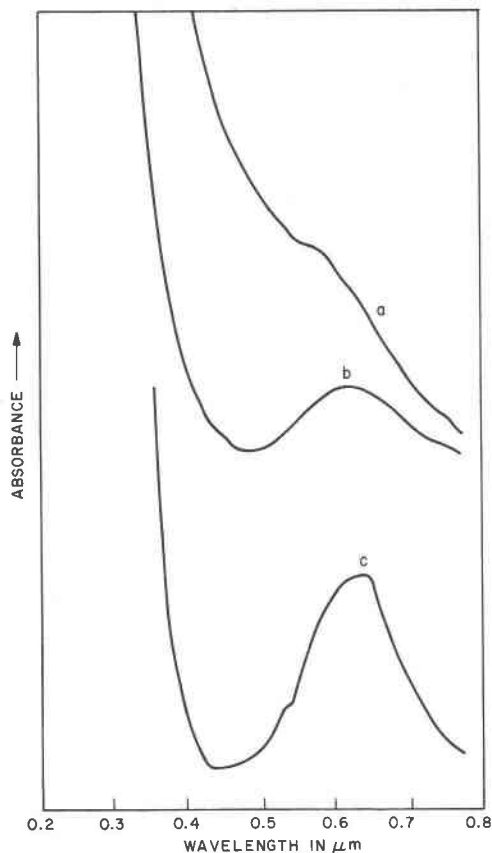


FIG. 5. Unpolarized absorption curves of (a) a colorless topaz turned brown after 20 hours irradiation; (b) same as (a) but after it turned blue through heating overnight at 200°C; (c) a natural blue topaz.

in the case of the Maxixe type deep-blue color center in beryl (Nassau, 1974), and some variation may also be anticipated in topaz. Thus the saturation coloration of  $\sim 1.5 \times 10^7 R$  of Samoilovich and Chentsova (1969) can be considered as being in reasonable agreement with our  $d_{1/2}$  of 12.6 megarads.

Samoilovich *et al* (1965, 1969) obtained a brown color with a saturation dose of 15 megarads in their electron type F center topaz, while Dickinson and Moore (1967) noted a "pale amber-yellow" color obtained with 5 megarads in their initially colorless hole type F center topaz. These observations would not be inconsistent with each other and with our current results, if the hole type F center with  $g > 2$  of Dickinson and Moore correlates with the rapidly produced yellow to sherry color, and if the electron type F center with  $g < 2$  of Samoilovich *et al* (1965, 1969) correlates with the more slowly produced dark brown color. This is merely a suggestion for the resolution of this inconsistency and clearly needs corroborating data.

Crowningshield (1974) noted that one of these irradiated dark brown topaz crystals (origin unknown) when partially light bleached became "smoky," *i.e.*, similar in appearance to smoky quartz without a significant brown component, an apparently previously unreported color.

#### The Irradiation Induced Blue Color in Topaz

This was first noted during a study of the development of the smoky color and its destruction by heating in a group of colorless quartz stones loaned by R. Crowningshield of the Gemological Institute of America, when one stone turned an olive or greenish-brown on irradiation and became blue on heating overnight at 250°C. Tests showed it to be topaz and not quartz.

The spectrum of this stone, which had been initially colorless, is shown in Figure 5 both before and after reirradiation and compared with a natural topaz. The blue color in both is due to a broad absorption at 0.62  $\mu\text{m}$ . Both by this test and by standard gemological tests (e.g., Webster, 1972; Liddicoat, 1972) carried out by R. Crowningshield, this blue irradiation-produced color proved to be indistinguishable from naturally-occurring blue topaz. It also behaved on exposure to light in the same way as much natural blue topaz, fading slightly in the first two days but showing no significant further change in the next two months.

Heating to 250°C overnight had no effect on the blue color, but at 500°C decoloration occurred as it

does in natural blue topaz (Dickinson and Moore, 1967; Lemlein and Melankholin, 1951). A natural deep blue topaz, which had paled significantly on light exposure, did not return to the original color but remained pale after the irradiation treatment. When completely bleached to colorless by heating to 500°C, the blue color could be partially restored by gamma irradiation followed by gentle heat treatment at 200°C for a few hours. Color photos of these changes have been published by Nassau (1974).

Of the 86 colorless topaz specimens in Table 1, 21 were turned blue by this treatment. The effect is much rarer than this would indicate since the 21 blues were found in the first 48 colorless specimens tested (mostly from old collections), and no more were found in the next 38 colorless specimens tested (from more recent sources). It is likely that only material from one or a few localities has the specific precursor to this blue color, which is in all probability the hole type X center of Dickinson and Moore (1967). An explanation for the lack of success in finding additional colorless material which would turn blue may perhaps be found in the report by Crowningshield (1974) that gem grade blue topaz has recently been appearing in abundance and that some of this is stated to have been treated—presumably by the gamma ray process here described. Apparently this process has been discovered more than once. Cinnamon brown topaz also seems to be becoming widely available.

### Summary

Two distinct types of yellow to orange to brown color in topaz, produced by gamma irradiation, have been observed with different formation rates. One or both may occur in a specimen, and they may relate to two different hole and electron type F centers previously observed in topaz by EPR. There is considerable variation in the rate of fading on exposure to light.

Some colorless topaz becomes blue after irradiation followed by gentle heating. This transformation has not been previously reported, and the resulting material appears to be indistinguishable from naturally occurring blue topaz.

### Note Added in Proof

The testing of over 100 additional specimens (pebbles from Brazil, courtesy of R. V. Gaines of Pottstown, Pennsylvania) has confirmed two factors which had previously been suspected: (a) that topaz which turns blue shows an unusually strong

tendency to cleave during heating after irradiation, and (b) that topaz which is already pale blue turns darker blue only very rarely. A possible deduction from the latter observation is that natural blue topaz may have become blue from natural irradiation; since the accompanying brown is not usually seen, this also implies that the accompanying brown color bleached at ambient temperature over geological time periods.

### Acknowledgments

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