# COLOR CENTERS IN THE α-QUARTZ CALLED AMETHYST*

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## ABSTRACT

The absorption spectra of six amethyst specimens from different geographical areas are compared over the wavelength range 200 to 1400 mμ.

All the amethyst studied exhibited characteristic absorption bands with maxima in the vicinity of 340, 540, and 950 mμ. Certain of the specimens studied in the 200–300 mμ spectral region exhibited bands with maxima variously at 225 and 266 mμ. The absorption bands with maxima at 225, 266, 340, 540 and 950 mμ are produced or enhanced by x-irradiation and have the attributes of color centers. The 340 mμ band is anisotropic and centered at 360 mμ for light with electric vector vibrating along the c-axis. The green color remaining after bleaching a Brazilian amethyst appears to be due to a separate microscopic phase. Results of emission analyses for impurities in amethyst are tabulated and compared to those of a fused silica and a solarized complex silicate glass both containing a 540 mμ color center. It is concluded that the color centers at 340, 540 and 950 mμ are associated with one or more specific unknown chemical impurities present in the quartz structure.

## INTRODUCTION

Holden (1925) concluded that amethyst owes its color to a ferric compound and not to manganese. His analyses of 17 samples showed the $Fe_2O_3$ content varying from 0.004 to 0.35 per cent, $TiO_2$ from a trace to 0.001 per cent and MnO from none to 0.008 per cent. He found amethyst commonly associated with limonite, hematite and siderite and containing among others the elements S, Cu, Zn, As, Ag, Ba, Au, and Pb which he stated are rarely present in smoky quartz. His paper contains a selected bibliography of papers on smoky and amethyst quartz through 1924. Holden reported an absorption maximum in amethyst at $0.53 - .54\ \mu$.

Vedeneeva (1940) reports an absorption maximum in amethyst at 5400 Å. He attributes the color to highly dispersed inclusions of elementary iron reduced from the ferric state by ionization accompanying natural radioactivity. Pough and Rogers (1947) found that x-irradiation has little effect upon the violet color although there is some suggestion of darkening.

Lemmlein (1951b) has reported absorption maxima at 250, 360 and 540 mμ in amethyst and has discussed (1951a) the concentration of the

color on the pyramidal (10$\bar{1}$1) faces. The relationship of the latter phenomenon to Brazil twinning has been discussed earlier by Frondel (1945) who suggests it may be "profitable to investigate order-disorder and defect-structure phenomena and mosaic structure" in distinguishing alpha- and beta-quartz.

The first quantitative spectroscopic study of amethyst was made by Bappu (1952, 1953). He has shown (1952) that the 550 m$\mu$ band found in Deccan amethyst is similar to the F band found in alkali halides. He is able to produce an F'-like band by excitation of the F-like band. The present author (1954) has pointed out the similarity of this 550 m$\mu$ band to the 540 m$\mu$ band in fused silica. Bappu (1953) reported absorption bands in amethyst at 7850, 8350 and 9200 Å. The 7850 Å band was found to fade on thermal treatment, while the 8350 Å band increased. The 9200 Å band was found to decrease on heating but not to fade completely.

Rose and Lietz (1954) published the spectrum of "greened" amethyst from the Montezuma Mine in Minas Gerais, Brazil, before and after thermal treatment. They mention an absorption band at 350 m$\mu$ in amethyst as well as the familiar band at 540 m$\mu$. After thermal treatment of a specimen at 510° C., the 350 and 540 m$\mu$ peaks faded and a new absorption peak was found in the vicinity of 700 m$\mu$. This absorption peak was subsequently removed by heating in hydrogen at 550° C.

On the basis of the findings of pleochroism and optical biaxiality by Pancharatnam (1954), Raman and Jayaraman (1954$a$) suggested that amethyst belongs to a lower symmetry class than colorless quartz. Pancharatnam finds amethyst to conform to the symmetry of the monoclinic class, and the visible absorption maximum to be near 5000 Å for light vibrating along an $a$-axis and to be near 5750 and 5250 Å for two vibrations in the perpendicular planes 45° on either side of the $c$-axis. In a later paper Raman and Jayaraman (1954$b$) conclude that the change in structure of amethyst from trigonal to monoclinic symmetry occurs as a result of growth of the crystal from ferric-containing material. They conclude after some qualitative magnetic measurements that amethyst is diamagnetic in contradiction to the earlier work of Leela (1953) and to indications that the 5400 Å color center is an F-like center.

Arnold (1955) has measured the absorption spectrum of a Brazilian amethyst specimen cut perpendicular to the $c$-axis and finds bands with maxima near 230, 270, 350 and 540 m$\mu$ which is in close agreement with the data presented in this paper.

Although pleochroism in amethyst was studied over a hundred years ago by Haidinger (1854) no extensive investigation of the possible anisotropy of its characteristic absorption bands has as yet been made.

## EXPERIMENTAL DATA

The amethyst specimens were cut to various thicknesses suitable for optical study depending on the depth of color of the given specimen, and polished. All of the material available for study exhibited both Brazil twinning and the finer *d-l*-twinning characteristic of amethyst, and for that reason this study is limited to presentation of qualitative data. After extensive search no specimens suitable for quantitative solid state investigations have been located.

The *x*-ray source was a Picker industrial *x*-ray unit using a Machlett type *AEG-50T* tube with beryllium window, run at 50 PKV and 20 milliamperes. The characteristics of this tube are described by Pough and Rogers (1947). The specimens being *x*-rayed were placed 8.5 cm. below the center of the focal spot of the tungsten target. The dosage in air at the surface of the specimens under these conditions was approximately $2.5 \times 10^4$ *r* per minute.

The absorption spectra data were taken on a Beckman model *DU* Spectrophotometer serial No. 77626 with photomultiplier attachment. The Beckman instrument was modified to extend the wavelength limit in the near infrared from 1000 m$\mu$ to greater than 1400 m$\mu$ by use of a polished Corning filter No. 2550 to largely eliminate scattered light of lower wavelengths.

Studies using polarized light in the 320–625 m$\mu$ region were made by use of polarized J-film placed between the variable slit of the Beckman Spectrophotometer and the sample holder and by balancing the instrument vs. air. The photomultiplier photocell was found to give nearly the same response to both the extraordinary and ordinary ray of plane polarized light. The usual light used for absorption spectra studies other than that polarized as described above will be called normal light in the succeeding text. All the spectra reported were measured versus air, and no reflection corrections have been made. The optical density, *O. D.*, is defined by the equation, $O. D. = \log_{10} I_0/I$, where $I_0$ is the incident light and $I$ is the light transmitted by the sample.

The samples were prepared for emission analysis in some cases by grinding duplicates in a "Diamonite" ($Al_2O_3$) mortar and in a "Plattner" iron mortar and comparing levels of impurity introduced by different crucible material. The majority of the samples were ground in a boron carbide mortar which proved the most satisfactory in keeping down introduction of impurity.

## RESULTS AND DISCUSSION

All the amethyst investigated exhibited the threefold distribution of Brazil twinning characteristic of quartz that originally crystallized below

the alpha-beta inversion temperature (see Frondel, 1945). The amethyst color was all distributed on the loci of the $(10\bar{1}1)$ faces. In some cases these faces were uniformly colored; in others the color appeared in alternate bands. In several specimens from Brazil the colored $(10\bar{1}1)$ faces were sometimes $d$- and sometimes $l$-. On certain $(10\bar{1}1)$ faces in which color banding was present, the coloration was specific to either of the laminar $d$- or $l$- twins, not to both; in other cases the laminar $d$- and $l$- twins were both colored, the twins being distinguished only by the opposite direction of rotation of plane polarized light in a basal section cut from the apex of the given crystal. The observation that color is not specific to either $d$- or $l$- twins indicates that the impurity with which the color is associated is not attracted to a given face (or laminar twin) preferentially because of stereoisomerism of the impurity ion in solution. More likely, it is because of a piezoelectric charge on the growing face which can either attract a charged ion or repel it depending upon the sign of the charge on the face or the laminar $d$-$l$-twins of which it may be composed and whether the ion is a complex cation or anion. It is hoped that further work in this laboratory concerning the charge on the
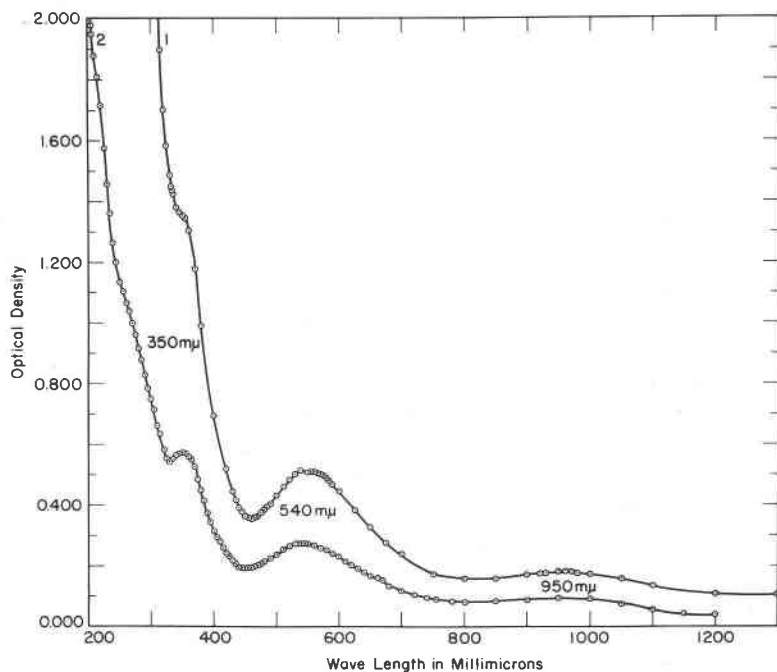


FIG. 1. Absorption spectra of amethyst sections cut parallel to $c$-axis using normal light. Locality: 1. Bidell, Saguado County, Colorado. 2. Minas Gerais, Brazil.

colored and uncolored twins developed by pressure will throw more light on this question.

Figure 1 shows the typical spectra of amethyst sections cut parallel to the *c*-axis. Spectrum 1 is that of a specimen from Bidell, Saguado County, Colorado, and spectrum 2 is that of a specimen from Minas Gerais, Brazil. These spectra indicate that there is an intense absorption band in the 200–400 m$\mu$ region upon the tail of which a band at 350 m$\mu$ of lower optical density is located. A third weaker band is centered at 540 m$\mu$ and a weak, almost indistinguishable, band is centered at 950
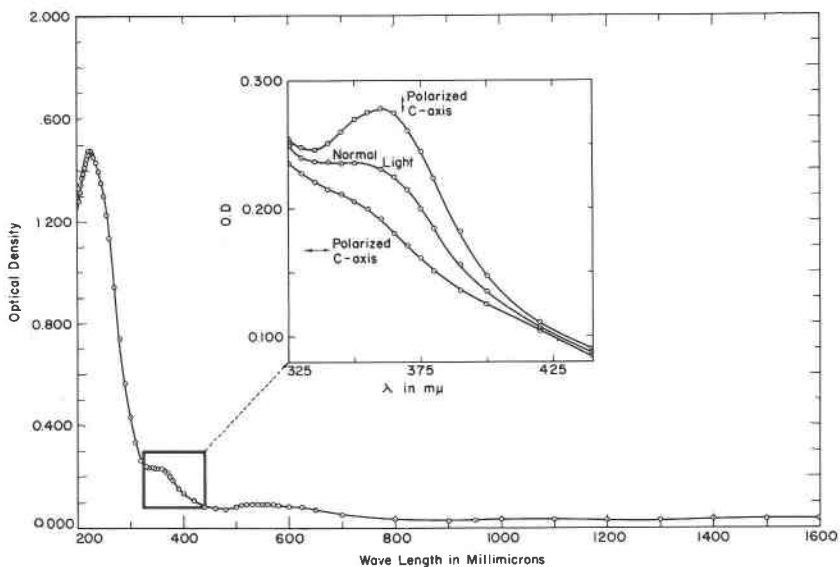


FIG. 2. Absorption spectrum of amethyst used in Fig. 1, spectrum 2 after thinning section. Inset spectrum illustrates the anisotropy of the 350 m$\mu$ absorbing center.

m$\mu$. When the section giving spectrum 2 is reduced to about 20 per cent of its original thickness the spectrum illustrated in Fig. 2 results. It is seen that the lower wavelength absorption is due to an intense absorption band with maximum at 225 m$\mu$. This band may be characteristic to the quartz lattice in general; however it is in the 225 m$\mu$ region in all amethyst studied in this region of the ultra-violet while it appears to be at a slightly different wavelength in smoky quartz (see Cohen, 1956).

Evidence for the anisotropy of the 350 m$\mu$ band is also presented graphically in Fig. 2. It is seen that plane polarized light with electric vector parallel to the *c*-axis is more highly absorbed than the light with electric vector perpendicular to this axis in the region of this band. The

550 m$\mu$ band has become less evident in this thinner wafer and the 950 m$\mu$ has apparently faded and cannot be resolved from the background absorption. Figure 3 gives the spectrum of the same section after nine hours of x-irradiation. It should be noted by comparing Figs. 2 and 3 that the 225, 350, and 540 m$\mu$ peaks have been enhanced. This is evidence that the 225 and 350 m$\mu$ bands are color centers as Bappu has proven earlier for the 540 m$\mu$ band. Although it is not intended to dwell at length on the anisotropy of the color centers in amethyst in this paper as has been done recently for smoky quartz (Cohen, 1956), there is much information to be gained from even the qualitative experimental work
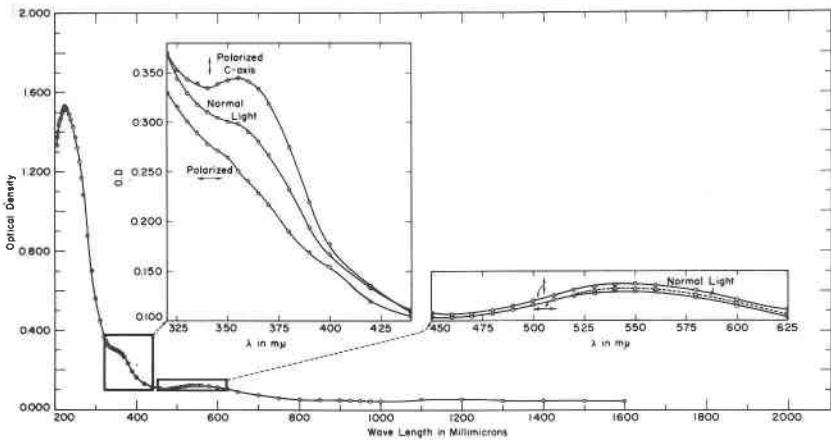


FIG. 3. Absorption spectrum of amethyst illustrated in Fig. 2 after $13.5 \times 10^6$ r of x-irradiation. Insert spectra show detailed anisotropy of the 350 m$\mu$ color center and the very weak anisotropy of the 540 m$\mu$ color center.

here presented. The insert in Fig. 3 gives plots of the e-ray, o-ray and normal spectrum of the 350 m$\mu$ band which are all of higher optical density than the corresponding plots in Fig. 2 before x-ray treatment. The insert of the 540 m$\mu$ color center band illustrates its slight anisotropy. This center may be isotropic, the anisotropy observed being due to the tail of the anisotropic 350 m$\mu$ band extending into this region. Comparisons of the anisotropy of the e- and o-rays at the 360 m$\mu$ maximum of the so-called 350 m$\mu$ band in sections cut parallel to the c-axis are presented in Table 1. The ratio remains constant within experimental error for this center in the Brazilian amethyst for the original coloration and after 3 and 9 hours of x-ray treatment. An investigation of the anisotropy of the natural coloration in specimens from Alexander County, North Carolina, and Lake Superior, Michigan, indicates that

TABLE 1. RELATIVE ANISOTROPY OF COLOR CENTERS IN AMETHYST, SECTIONS
CUT PARALLEL TO *c*-AXIS

| Locality | Color Center Maximum in m$\mu$ | $O. D._{e-\text{ray}}$ | $O. D._{o-\text{ray}}$ | $\pi^1$ |
|---|---|---|---|---|
| Minas Gerais, Brazil | | | | |
| (a)  no *x*-ray | 360 | 0.278 | 0.192 | 1.45 |
| | 540 | 0.096 | 0.096 | 1.00 |
| (b)  after 3 hours *x*-ray, $4.5 \times 10^6$ *r* | 360 | 0.335 | 0.226 | 1.48 |
| | 540 | 0.124 | 0.113 | 1.10 |
| (c)  after 9 hours *x*-ray, $13.5 \times 10^6$ *r* | 360 | 0.342 | 0.241 | 1.42 |
| | 540 | 0.136 | 0.130 | 1.05 |
| Alexander County, N. C. | 360 | 0.930 | 0.805 | 1.16 |
| | 530 | 0.680 | 0.650 | 1.05 |
| Lake Superior, Michigan | 360 | 0.360 | 0.321 | 1.12 |
| | 540 | 0.207 | 0.210 | 0.99 |

[1] $\pi = \dfrac{O. D._{e-\text{ray}}}{O. D._{o-\text{ray}}}$.

the 360 m$\mu$ center is also anisotropic but the ratio $\pi$ is lower. The ratio $\pi$ for the 540 m$\mu$ band in the three cases illustrated is nearly unity. The deviations from unity are all much less than those for the 360 m$\mu$ ratio in the same specimen. This may be taken as support for the isotropy of the 540 m$\mu$ band. It should be mentioned that the 225 m$\mu$ band could be anisotropic; if this were true it would complicate the study of the 360 m$\mu$ band. That the $\pi$ ratios remain fairly constant for different times of irradiation indicates either the 225 m$\mu$ band is isotropic or its rate of growth in this instance is the same as that of the 360 m$\mu$ band.

Figure 4 gives the absorption spectrum of a twinned amethyst crystal from Alexander County, North Carolina. The spectrum, using normal light entering the crystal perpendicular to a (10$\bar{1}$0) face of one of the Brazil twins exhibiting amethyst coloration, is typical except for absence of the 950 m$\mu$ band. The apparent shift of the 540 m$\mu$ peak to 525 m$\mu$ is accounted for by the non-parallelism of the opposite *m* faces of the uncut crystal used. The data on anisotropy in Table 1 show the 360 m$\mu$ band to be anisotropic and the 540 m$\mu$ band to be very weakly anisotropic (as measured at 530 m$\mu$).

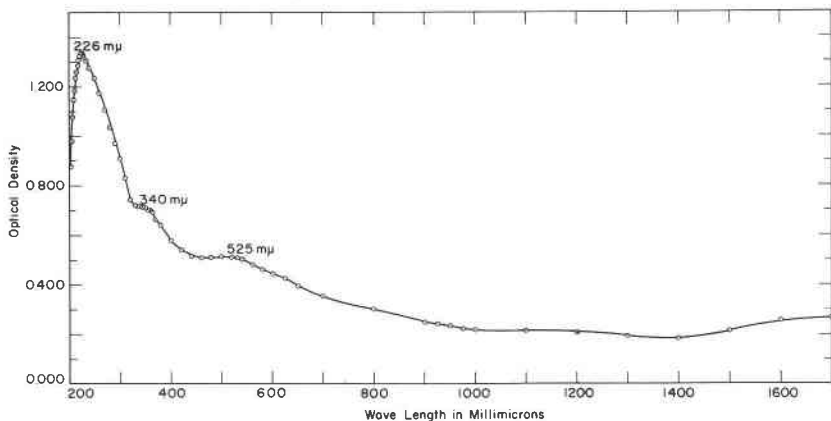The spectra in Fig. 5 are those of a Brazil-twinned amethyst section

FIG. 4. Absorption spectrum of an amethyst from Alexander County, North Carolina, using normal light transmitted perpendicular to the (10$\bar{1}$0) face of a Brazil twin.

from Lake Superior, Michigan, cut perpendicular to the *c*-axis. Normal light from the spectrophotometer entered the specimen parallel to the *c*-axis. Spectrum 1 is the original absorption of the amethyst. Spectra 2 and 3 are after one hour and fourteen hours of *x*-irradiation respectively.
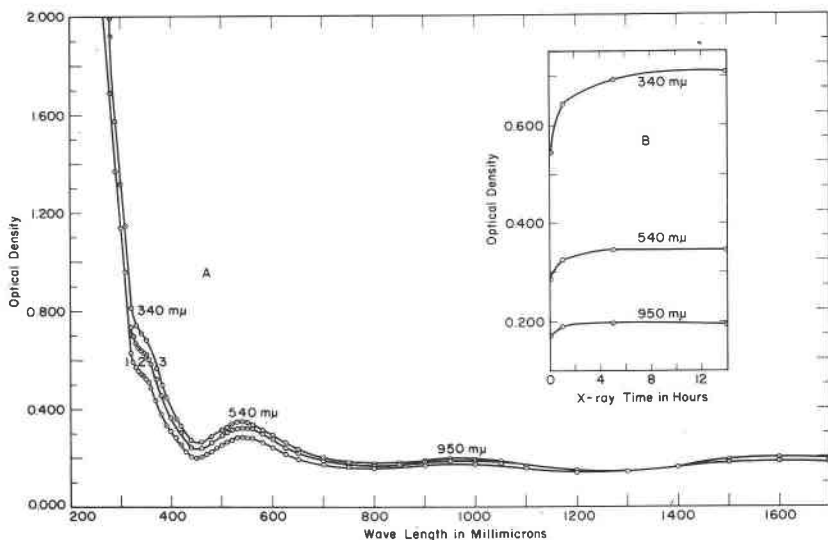


FIG. 5. Enhancement of color centers in amethyst from Lake Superior, Michigan, cut perpendicular to *c*-axis. *A:* Spectrum 1, natural absorption of section. Spectrum 2, after 1 hour, $1.5 \times 10^6 \, r$ of *x*-irradiation. Spectrum 3, after 14 hours, $21 \times 10^6 \, r$. *B:* Plot of optical density of center *vs.* time of *x*-ray.

The insert $B$ at the right gives the growth of band maxima with time of $x$-ray. It is observed that the 950 m$\mu$ band saturates after one hour, the 540 m$\mu$ at approximately five hours, and the 340 m$\mu$ band intermediate between five and fourteen hours. The enhancement of the spectrum in the near infrared region, 1400–1700 m$\mu$ is noticeable in this figure. This weak effect has not been studied in detail as yet because of its nearness to the long-wavelength limit of the spectrophotometer used. The fact that colored amethyst specimens are not saturated in respect to $x$-irradiation is probably due to the partial fading of the naturally produced color centers by sunlight, since the saturation values of optical densities are not appreciably higher than the original values. Another possibility is that some traps may be created by natural radioactivity that are not completely filled by the same type of radiation. Table 1 shows the relative anisotropy of the 360 and 540 m$\mu$ centers in a section from the same Lake Superior, Michigan, crystal as discussed here, cut parallel to the $c$-axis. The 360 m$\mu$ band has approximately the same anisotropy as that in the North Carolina specimen. The 540 m$\mu$ center appears to be isotropic within experimental error.

Two $Z$-cut wafers of synthetic quartz grown around an amethyst seed at 325° C. were presented to the writer by Dr. D. R. Hale, Head, Crystal Growth Section of the Brush Laboratories Company, Cleveland. Dr. Hale found that the amethyst color of the seed did not fade at this temperature.* The wafer was heated for one hour at 400° C. in this laboratory without change in the absorption spectrum in confirmation of the observation of Dr. Hale. The natural spectrum of the seed was typical of other amethyst studied with absorption bands centered at 350, 540 and 950 m$\mu$. Upon $x$-irradiation the seed developed a new color center with apparent maximum at 266 m$\mu$ on the shoulder of a shorter wavelength band which decreased in optical density after the $6 \times 10^6$ $r$ of $x$-ray dosage. The synthetic portion around the seed did not show any change in absorption spectrum after irradiation nor did it originally have any of the centers characteristic of amethyst. Apparently it either does not contain the impurities necessary for development of amethyst color or the defect environment surrounding the impurities if present is not that required for color center formation. To investigate these possibilities, emission analyses were run on the amethyst seed and the non-coloring synthetic $\alpha$-quartz surrounding it. The results are shown in Table 2. It appears that the only impurity in the amethyst not common to both is a small trace of nickel, much less than 0.003 per cent. All other impurities found were common to both materials but in slightly differing

* Personal communication.

TABLE 2. COMPARISON OF EMISSION ANALYSES OF AMETHYST SEED AND NON-COLORING
SYNTHETIC QUARTZ GROWN AROUND SEED[1]

| Impurity | Amethyst Seed[2] %[3] | Relative Concentration | Synthetic Quartz Grown Around Amethyst %[3] | Carbon Blank |
|---|---|---|---|---|
| Ag | ≪0.0005 | < | <0.0005 | N.F. |
| Al | >0.005 | = | >0.005 | Trace |
| Ba | N.F. | | N.F. | N.F. |
| Be | N.F. | | N.F. | N.F. |
| Ca | >0.0005 | > | >0.0005 | Trace |
| Cr | ∼0.002 | > | ≪0.002 | N.F. |
| Cu | >0.0005 | > | <0.0005 | ≪0.0005 |
| Fe | >0.005 | > | <0.005 | N.F. |
| Ge | N.F. | | N.F. | N.F. |
| Mg | >0.0005 | > | <0.0005 | ≪0.0005 |
| Mn | N.F. | | N.F. | N.F. |
| Pb | N.F. | | N.F. | N.F. |
| Ni | ≪0.003 | > | N.F. | N.F. |
| Ti | N.F. | | N.F. | N.F. |
| Zr | N.F. | | N.F. | N.F. |

[1] Specimen courtesy of Dr. D. R. Hale, Brush Laboratories Co., Cleveland 8, Ohio.

[2] Analysis differs slightly from that of same material given in Table 3, probably due to sampling from different portion of crystal, the main difference being that Ti is not found in this case.

[3] Absolute value believed to be between $\frac{1}{3}$ and 3 times the values indicated. N.F.=not found.

amounts except for aluminum which was present in approximately the same amount in both quartzes. In a subsequent analysis of the amethyst seed reported in Table 3, 0.002 per cent of titanium was found to be present. No conclusion can be reached from these analyses as to the given impurity related to the color centers in amethyst $\alpha$-quartz; however, nickel and titanium as well as the ever present iron, will bear watching.

The difference between the spectra of the amethyst seed before and after 4 hours of $x$-irradiation is plotted versus wavelength in Fig. 6. This plot indicates that a band at 215–220 m$\mu$ fades upon $x$-ray treatment as an apparent 266 m$\mu$ band (centered at 280 m$\mu$ in the difference plot) grows. This crystal appears unique among those studied in respect to this observation as well as to the stability of the 350, 540 and 950 m$\mu$ centers on heating. Heating of the seed after irradiation caused only the apparent 266 m$\mu$ color center to fade and the shorter wavelength center to return to its original value. This indicates that the band in the 215–220 m$\mu$ region and the apparent 266 m$\mu$ band are interrelated and

TABLE 3. EMISSION ANALYSES OF AMETHYST AND GLASS SPECIMENS

| Impurity | Holden[1] % as oxide | Colorado[2] %[8] | North Carolina[2] %[8] | Lake Superior[2] %[8] | Minas Gerais Brazil[3] %[8] | Brazilian "Greened"[4] %[8] | Brush Seed[5] %[8] | Ultrasil Grade Fused Silica[6] %[8] | Solarized Soda-Lime-Magnesia-Silica Glass[7] %[8] |
|---|---|---|---|---|---|---|---|---|---|
| Ag | — | N.F. | N.F. | N.F. | N.F. | <0.0005 | <<0.0005 | N.F. | N.F. |
| Al | 0.06 | 0.1 | 0.3 | 0.06 | 0.08 | 0.005 | <0.005 | 0.007 | 0.2 |
| Ba | none | N.S. | N.S. | N.S. | N.S. | <0.08 | N.F. | est <0.001 | est <0.001 |
| Be | — | 0.00004[9] | N.F. | 0.00005[9] | 0.00004 | N.F. | N.F. | trace | N.F. |
| Ca | 0.03 | 0.04 | 0.03 | <0.01 | 0.03 | >0.0005 | 0.0005 | 0.002 | 1.0 |
| Cr | trace? | 0.02 | 0.02 | 0.002 | 0.01 | <0.002 | <<0.002 | 0.002 | 0.01 |
| Cu | — | 0.002 | 0.004 | 0.007 | 0.003 | <0.0005 | <0.0005 | >0.02 | 0.004 |
| Fe | 0.05 | 0.03 | 0.02 | 0.2 | 0.009 | >0.005 | 0.005 | 0.007 | 0.1 |
| Ge | — | N.F. | N.F. | N.F. | N.F. | N.F. | N.F. | trace | N.F. |
| Mg | trace | 0.01 | 0.01 | 0.01 | 0.008 | <0.0005 | 0.0005 | 0.0009 | 2.0 |
| Mn | 0.0001 | 0.004 | 0.006 | 0.005 | <0.001 | N.F. | N.F. | N.F. | >0.07 |
| Pb | — | N.F. | N.F. | N.F. | N.F. | <0.05 | N.F. | N.F. | 0.2 |
| Ni | — | <0.001 | <0.001 | 0.01 | <0.001 | 0.001 | <<0.003 | 0.005 | <0.002 |
| Ti | 0.001 | 0.004 | <0.001 | 0.003 | N.F. | N.F. | 0.002 | N.F. | 0.05 |
| Zr | trace? | N.F. | N.F. | N.F. | N.F. | 0.001 | N.F. | N.F. | 0.06 |

[1] Amethyst of unknown origin, analyzed chemically by Holden (1925).
[2] Specimen courtesy Dr. E. R. Eller, Carnegie Institute Museum, Pittsburgh 13, Pa.; see Figs. 1, 2, 3.
[3] Specimen purchased from Ward's, Rochester 9, N. Y.; see Figs. 1, 4 and 5.
[4] Specimen courtesy Eldot and Company, New York 23, N. Y.; see Fig. 7.
[5] Specimen courtesy Dr. D. R. Hale, Brush Laboratories Co., Cleveland 8, Ohio; see Fig. 6.
[6] Specimen purchased from Amersil Co., Hillside 5, N. J.; see Fig. 8.
[7] Specimen collected in Mojave Desert near Little Lake, California, by the author; also contains 10% Na, 0.1% Sr, trace Li and K, and 0.01% Sn; see Fig. 8.
[8] Absolute value believed to be between ⅓ and 3 times the values indicated.
[9] Presence uncertain.
N.S. = not sought.
N.F. = not found.

possibly occupy the same trapping site. It should be mentioned in passing that the Brazil twinning of the seed extended through the synthetic portion of the crystal.

Another unusual material studied was the so-called "greened" quartz or "greened" amethyst (Pough, 1954) from the Montezuma mine near Rio Pardo in Minas Gerais, Brazil.

Optical and electron microscopic examination of the green bleached amethyst reveals fine laminar $d$-$l$-twinning in all of this material and the green color appears to be due to a separate green phase, possibly chlorite, oriented between the laminar microcrystalline layers composing the
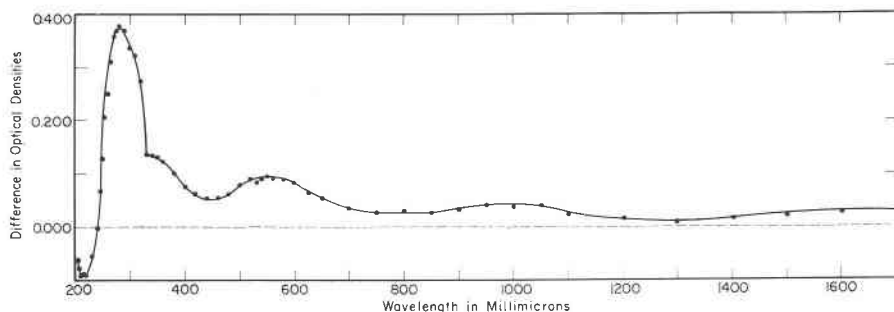


FIG. 6. Plot of difference of spectra of $Z$-cut amethyst seed before and after $6 \times 10^6 \, r$ of $x$-irradiation.

twins. The twinning is so fine that the optical rotation of plane polarized light entering along the $c$-axis is no longer apparent. The mode of formation of this unusual quartz may be another illustration of the growth spiral interaction suggestion of Hendricks (1955) to account for orderly alternation of layers of differing composition such as chlorite-mica-chlorite.

Figure 7, spectrum 1 is that of the "greened" quartz after heat-bleaching of the amethyst color. The material is ordinarily imported into this country in this state and an unbleached specimen could not be obtained. However, the color centers were regenerated by $x$-ray treatment as shown in spectra 2 through 4. The absorption band centered at 725 $m\mu$ in the bleached material is not a color center but an ordinary impurity band related to the separate phase giving the green color. It begins to be swamped by the 540 $m\mu$ color center after 0.5 hr. of $x$-ray dosage as shown in spectrum 2. After 3.5 hours it is no longer noticeable as shown in spectrum 3. The apparent location of the 540 $m\mu$ band maximum at 500 $m\mu$ after 25 hours of $x$-ray is clearly demonstrated in spectrum 4. This shift is probably due to the fact that the tails of three other
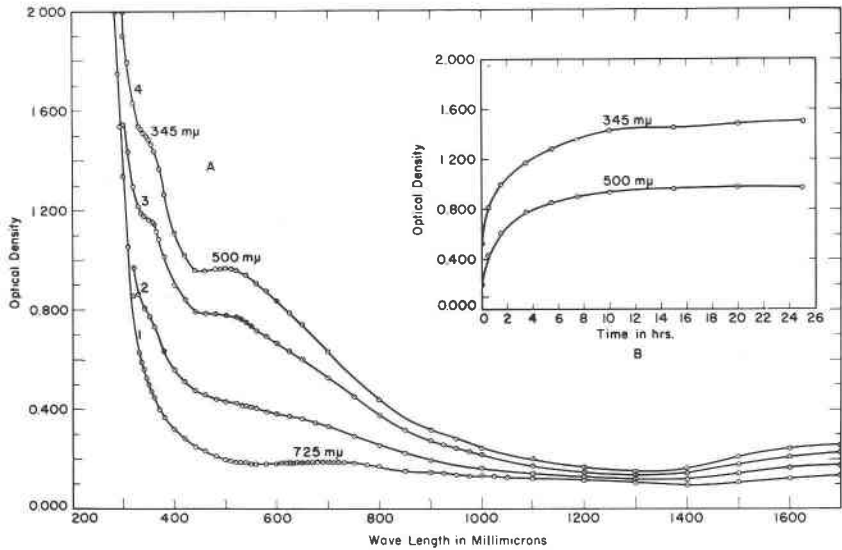
FIG. 7. The spectra of "greened" amethyst section cut nearly parallel to *c*-axis.

*A*. 1. After removal of amethyst color by heat treatment, as received in this labora-
tory;
2. After 0.5 hrs., $0.75 \times 10^6 r$ x-ray dosage;
3. After 3.5 hrs., $5.25 \times 10^6 r$;
4. After 25 hrs., $37.5 \times 10^6 r$.

*B*. Plot of growth of color centers during x-ray treatment.

bands overlap this region in this material. The *B* plot illustrates the smooth growth of the two color centers upon x-irradiation of the bleached specimen.

In order to show the general structural relationship between allo-tropic forms of silica and to show that a trapped electron associated with an impurity which together compose the 540 mμ color center band, sees little of its environment except nearest neighbors, Fig. 8 showing this color center in a high-purity fused silica and a solarized soda-lime-magnesia-silica glass is included in this paper. Spectrum 1*a* is that of ultrasil grade, homogenized fused silica produced by the Hereaus Company in Germany and imported through the Amersil Company of Hillside, New Jersey. A 1.5 mm.×1 cm.×2 cm. polished wafer was heated in silicon powder at 1400° C. for two hours and quenched. This caused enhancement of the three color centers present (Cohen, 1955*b*) at 220, 300 and 540 mμ after two hours of x-ray dosage. In spectrum 1*b* the same wafer has received a total of 204 hours of x-irradiation. The 300 mμ color center has long ago been saturated and swamped out by the intense 220 mμ color center band. This is the saturation spectrum, e.g.
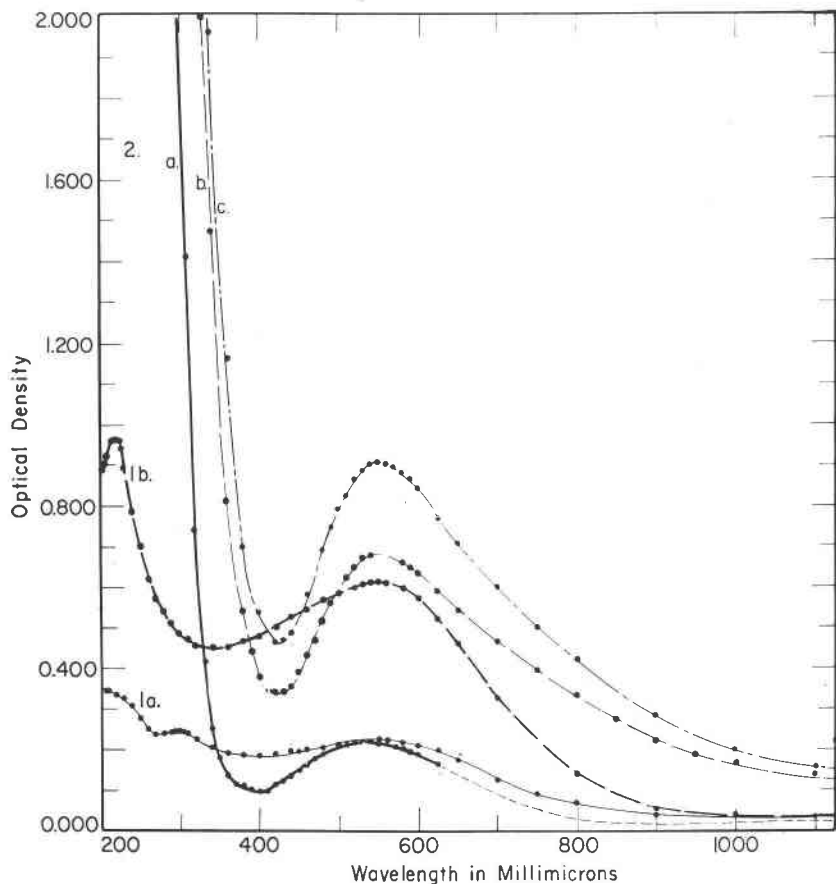
FIG. 8. Color center in silica glasses.

Spectra of:

1. (*a*) Ultrasil grade, homogenized fused silica after reducing treatment in silicon pow-
   der at 1400° C. followed by 2 hours of x-ray, $3 \times 10^6$ *r*.
   (*b*) Same sample after total of 204 hours of x-ray, $3 \times 10^8$ *r*.
2. (*a*) Solarized soda-lime-magnesia-silica glass as collected in Mojave Desert near
   Little Lake, California.
   (*b*) After 3 hours of x-ray, $4.5 \times 10^6$ *r*.
   (*c*) After total of 10 hours of x-ray, $15 \times 10^6$ *r*.

further x-irradiation leaves the spectrum of the fused silica unchanged
after this particular reducing treatment. High purity Corning fused
silica after undergoing the same treatment exhibits neither the 300 nor
540 m$\mu$ bands. This is indirect evidence that these two color center bands
are associated with impurities.

The writer collected several specimens of solarized beverage bottles

from the gold mining area of the Mojave Desert in California several years ago. A plane polished wafer was made from a fragment of a quart flask found near Little Lake, California. Its spectrum is shown in 2a. Spectra 2b and c are of the same wafer after a total of 3 and 10 hours of x-ray treatment, respectively. It is seen that the 540 mμ band in this complex glass is also a color center as it is enhanced by x-irradiation as well as sunlight. Furthermore, heating or exposure to intense unfiltered line spectra from a mercury lamp with quartz envelope will cause the color in this glass to fade. The similar shape, wavelength, reaction towards ultraviolet light, heat, and method of production or enhancement of the 540 mμ bands in α-quartz, fused silica, and complex glasses suggest that the color center is the same in these three different materials and that the identification of the given impurity atom associated with any one will solve the problem for all.

The impurity levels of the amethyst and glass samples discussed in this paper are compared in Table 3. An earlier analysis of Holden (1925) is also included. The table shows that all specimens with the 540 mμ color center contain aluminum, calcium, chromium, copper, iron, magnesium, and nickel. The amethysts all have 360 mμ and 950 mμ bands as well as 540 mμ bands. These studies do not permit a conclusion to be drawn as to the specific impurity or impurities responsible for these three color center bands.

## Conclusions

Some tentative postulates may be made concerning several of the color centers in the α-quartz called amethyst which are in accord with the experimental findings of this paper.

*Postulate 1: All or most of the color centers are associated with impurity atoms. In the case of the anisotropic center (at 360 mμ), the impurity atoms are electropositive and replace silicon atoms in the lattice. The impurity atoms are of lower valency but electroneutrality is preserved by concommitant introduction of additional positive impurity atoms into interstitial positions of the lattice.*

This proposal resembles that of O'Brien (1955) for smoky quartz color centers where aluminum atoms replace silicon atoms in the lattice to give the anisotropic centers observed at 460 and 625 mμ, but electroneutrality is maintained by sodium, lithium, or hydrogen atoms which take up unspecified positions in the structure and whose effects have not as yet been directly observed. Postulate 1 anticipates anisotropic centers from substitutional impurities (360 mμ band), and permits isotropic behavior of bands from interstitial impurities (540

$m\mu$ band). A symbiotic relationship between centers due to substitutional impurities and those due to interstitials might be expected since electroneutrality requirements pair the introduction of both. This deduction is in harmony with the relative constancy of intensity ratios of the 360 and 540 $m\mu$ centers observed throughout the amethyst samples. For example, the ratio of these two bands in the amethyst from Minas Gerais, Brazil, is 2.4 before $x$-ray, 2.5 after three hours of $x$-ray and 2.2 after nine hours of $x$-ray treatment. In the Alexander County, North Carolina, amethyst the ratio is 1.3 and in the Lake Superior, Michigan, amethyst it is 1.6. A corollary to this postulate appears in the possibility that both types of sites are occupied by impurity atoms of the same element. For example, if divalent nickel atoms go equally into lattice and interstitial positions, electroneutrality will be maintained, several different centers are possible, and intensity ratios will again be constant. Finally, if nickel (for example) were to appear in both valence states and if situations intermediate to that of postulate one and its corollary were possible, then a spectrum with many bands could result from a sample containing only two impurities. Indeed, a single impurity present in two valence states and occupying both types of position could give four or more bands.

*Alternate*

*Postulate 1: One or more species of impurity atom substitute for silicon in the lattice but electroneutrality is preserved by an appropriate number of accompanying oxygen vacancies.*

If, say, divalent nickel replaces tetravalent silicon, one anion vacancy is created to preserve the electroneutrality. Upon irradiation this anion vacancy would capture an electron and an F-like center associated with the nearby $Ni^{+2}$ in a tetrahedral position would be produced. Several F-like centers of different energies would be produced if different impurities were present; however, more than one absorption band could be associated with a given impurity depending on the energy scheme. The absorption bands associated with a given impurity would have coupling of intensity ratios.

*Postulate 2: Anion impurities (such as halides) in the lattice are accompanied by cation vacancies.*

Upon irradiation these vacancies become V-like centers. Whereas postulate one and alternate one may account for the bands of longer wavelength viz. the 350, 540 and 950 $m\mu$, this postulate may account for the bands of higher energy at 225 and 266 $m\mu$ (see Seitz, Fig. 4 and related text, 1954).

*Postulate 3: The fine laminar d-l-twinning of amethyst is genetically connected with the presence of an impurity associated with one or more color centers.*

Perhaps impurity atoms assist nucleation in spiral growth or because of their size force twinning in the lattice to relieve strain, thus it may be impossible to find untwinned amethyst. X-ray powder diffraction studies are in progress in the Institute in order to relate the unit cell dimensions of the quartz lattice to different impurity contents. Precise measurements on amethyst, smoky, rose and colorless natural and synthetic quartzes are in progress.

In conclusion it is hoped that an understanding of the coloration of amethyst will be placed upon a sounder basis if it becomes possible to perform quantitative studies on uniformly colored, untwinned crystal sections and couple these results with those of electron spin resonance studies.

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