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On the Coloration of Quartz Crystals Induced by X-ray Irradiation

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Abstract

A strong x-ray source was constructed to investigate the x-ray induced coloration of quartz crystals. A large number of quartz crystals were irradiated with x-rays, some of which became colored to green, gray or brown, while others did not. The coloration was found to approach saturation with more than about 10^8 r. Chemical and spectroscopic analysis revealed that quartz crystals containing relatively large amount of impurities became dark-colored on irradiation and those containing only small amount of impurities do not become colored. Artificial quartz crystals containing different amount of aluminum were synthesized, and these behaved in the same manner as natural ones on irradiation. Thermoluminescence and accompanying bleaching of colored quartz crystals were studied, from which the activation energy for the thermal bleaching of the coloration was obtained. Finally the atomic mechanism of the coloration was explained with models of the color center.

I. Introduction

Not all quartz crystals are colorless. Some are produced naturally in violet or yellow colors, which are prized highly as jewels. Smoke quartz crystals are also present in nature. On the other hand, it has been known that even transparent quartz crystals can be colored by x-ray irradiation. Interesting enough, the x-ray induced colors are quite different from natural ones, being green, gray or brown. These artificially caused colors are stable at room temperatures and can be studied in the same manner as in the case of ordinary colored crystals. When the temperature is raised, however, the coloration becomes unstable with the beginning of radiative dissipation of the excess energy stored in the crystal lattice by the irradiation, or the thermoluminescence. Quartz crystal is then brought to the original colorless state. This is a reversible change, very convenient for the study of this kind of coloration.

Coloration of minerals can be divided into two kinds, one due to impurities and the other due to remaining various causes. In case of quartz crystals, several

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researchers confirmed that the coloration is caused by aluminum. Recently, it was discovered that colored quartz crystal shows the electron spin resonance, the intensity of which is proportional to the degree of coloration, and its spectrum has a fine structure resulting from aluminum nuclei. O'Brien proposed an atomic model of the color center conforming to these results.¹⁾

The author has studied the coloring of glass, quartz crystals and other minerals by x-ray irradiation since 1928, and published a part of the results pertaining to the thermoluminescence of quartz crystals irradiated with x-ray in 1938.²⁾ In this paper are assembled these and other experimental results accumulated during a period of over 30 years, and the results are discussed from the standpoint of solid state physics, in as much since quantum mechanical studies of ionic crystals and semiconductors at large have made remarkable progress in recent years.

In chapter II are described the improvements made in the x-ray apparatus used for the irradiation. Subsequent chapters from III to VIII deal with a large number of coloring experiments of natural quartz crystals with x-ray irradiation and their results, and also the syntheses of artificial quartz crystals with controlled amount of impurities to determine the relationship between the impurities and the coloration. In chapter IX are given measurements of the degree of coloration, optical properties and characteristics of the thermoluminescence of artificially colored quartz crystals, with relevant discussions. In chapter X theories are given of the coloration, the thermoluminescence and the thermal bleaching of artificially colored quartz crystals, based on the atomic character of color centers.

II. X-ray apparatus

The x-ray source which has been used for a long time in this study is Coolidge enclosed tubes of tungsten target. For comparison a tube of copper target was used also. The target is cooled by flowing water. Fig. 1 is a photograph of the apparatus used from twenty five years ago. Two x-ray tubes were used simultaneously, the positive and negative half portions of the alternating current passing through each tube. A small transformer supplied enough power in spite of its small iron core, as greater power can be taken out in this method than by the usual rectification method.

The present apparatus³⁾ is shown in Fig. 2. The x-ray tube was manufactured recently for trial. The target is kept in rotation and water cooled, for which Wilson's sealing method is applied to keep vacuum. The electron beam converges electrostatically with a Wehnelt's cylinder, resulting in a marked increase in the x-ray intensity. When the voltage applied to the W-target is 150 KV, the shortest wavelength of the x-rays is 0.082 Å, and is about 0.11 Å at the maximum intensity. When the applied voltage is 100 KV, the corresponding wavelengths are 0.124 Å and 0.26 Å each. The irradiation was done mostly at one of these voltages in

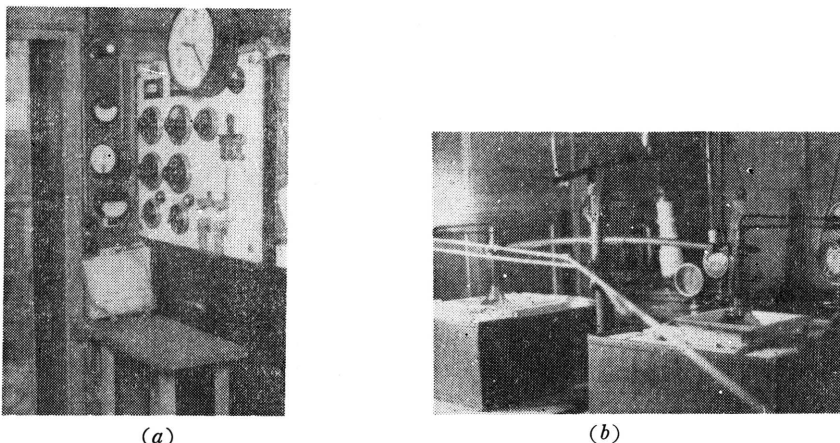


Fig. 1. X-ray apparatus for irradiation of quartz, constructed 25 years ago.

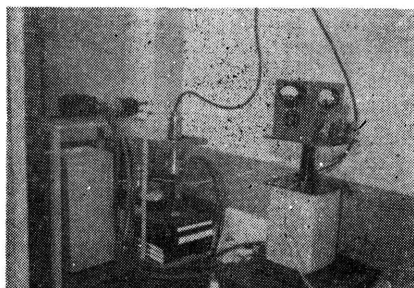


Fig. 2. Present x-ray apparatus for irradiation of quartz.

the following experiments. In the case of a Cu-target with a relatively low applied voltage, the radiation of the characteristic rays is more pronounced than that of continuous rays. The wavelength of the characteristic x-rays of copper is 1.54 \AA . As for the intensity I of x-rays from a W-target, the following expression was obtained experimentally.

$$I = (k/R^2) V i^2 (Z/74),$$

where the unit of I is roentgen per second, V the voltage applied to the target in kilovolts, i the tube current in milliamperes, R the distance from the target in meters and the value of k is 3.4×10^{-6} for the new apparatus. In case some other metal than tungsten is used, its atomic number Z divided by 74, the atomic number of tungsten, should be used. The radiation intensity is quite high: when V is 150 KV and i is 20 mA, I becomes 38.3 r/sec at a point R equal to 0.2 m in case of W-target. When V is 100 KV and i 20 mA, I becomes 17.0 r/sec at the same distance. If the target is copper, and V is 12 KV and i 20 mA, I becomes 0.383 r/sec at 0.1 m distance. The irradiation for 1 hour with a W-target at 150 KV corresponds to 2 hours and 13 minutes at 100 KV, and 100 hours with a Cu-target.

Radioactive cobalt 60 was used as a source of γ -rays for comparison. The energies of the γ -ray quanta are 1.173 and 1.342 MeV, the corresponding wavelengths being 0.001,61 Å and 0.001,49 Å. As the amount of cobalt 60 was 100 curies and the distance was 0.3 m, the intensity of γ -rays was 0.34 r/sec. The irradiation by γ -rays amounts to the same dose as above with 107 hours; γ -rays are far weaker in the ionizing power, in photographic action and in fluorescence action.

III. Classification of the x-ray induced coloration

There are three principal colors induced by x-ray in quartz crystals; green, brown and gray, though intermediate ones are present also. Among colored specimens prepared from quartz crystals collected from all over this country 5 % were green, 15 % brown and 80 % gray. Two subclasses are present among gray ones, one bearing some resemblance to the green type and the other to the brown. Not all quartz crystals become colored. Quartz crystals which become colored by irradiation contain aluminum as impurity in different amounts, as will be explained later.

The x-ray induced color can be bleached by heating. And when a quartz crystal is irradiated again with x-rays after the thermal bleaching of the first x-ray coloration, it regains the same color, showing the reversibility of this type of coloration. On the other hand, quartz crystals which are naturally colored to violet or yellow become gray on irradiation after the thermal bleaching of the original coloration, which is an irreversible change.

IV. Preparation of quartz crystal samples

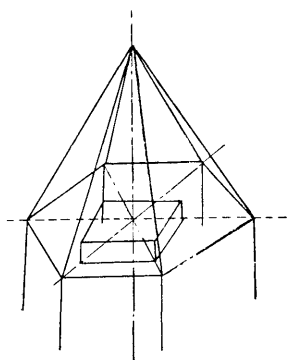


Fig. 3. Relative orientation of a quartz sample with respect to crystallographic axes.

A large number of samples were prepared for the experiment. First, quartz crystals were irradiated with x-rays, most of which became colored. Then, samples were cut from each crystal and ground to a size of 1.5 cm square and 0.5 cm in thickness as shown in Fig. 3. The principal plane of these rectangular plate samples was perpendicular to the principal axis of the crystal, and the sides were cut to an angle of 120° with the second crystallographic axes.

After being investigated for color type and the light absorption coefficient, the samples were bleached by heating. Gray samples with light absorption coefficient 0.5 were taken as the standard for these experiments. The absorption coefficient was measured with an incandescent lamp as the source and a phototube as the detector, unless otherwise stated.

V. Change of the degree of coloration with x-ray dose

To correlate the degree of coloration with x-ray dose, tests were done as follows: A quartz crystal plate was put in a hollow of a lead block and irradiated with x-rays on one of its principal faces. The degree of coloration or the light absorption coefficient depends on the amount of impurities as well as the time of irradiation. Besides, the surface facing the incoming x-rays reaches saturation sooner than the other, though the thickness of the specimen is not very large in this arrangement, that is, only 5 mm. In these tests the maximum value of the light absorption coefficient k after uniform saturation was 0.57 for green quartz crystal, 1.23 for brown and 4.69 for gray in units of cm^{-1} . The saturation is brought about with x-ray dose of more than 10^8 r in ordinary cases.

The x-ray dose needed to bring a sample to the same absorption coefficient differs according to the color type. It was measured under the condition of 150 KV, 20 mA and 20 cm distance for which I was 38.3 r/sec. A quartz crystal of the green type reached the absorption coefficient 0.5 by 1.8×10^8 r, whereas that of the brown type attained the same coefficient by 6.6×10^8 r. It takes 11 days for the former to reach the saturation if the irradiation is done for 12 hours in a day, while 40 days are required for the latter. Fig. 4 shows the increase of the absorption coefficient with x-ray dose for a green type and a brown type quartz crystal, where both have nearly the same saturation value.

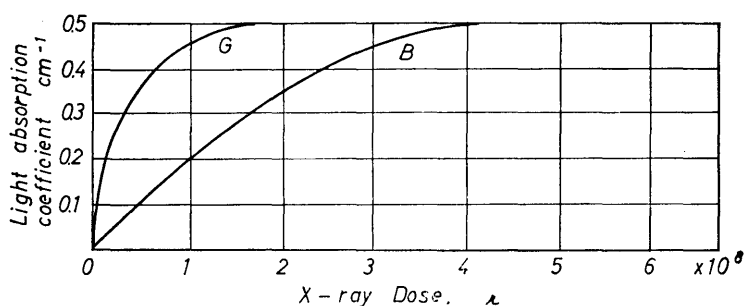


Fig. 4. Increase of the light absorption coefficient with x-ray irradiation of quartz crystals of green and brown types.

The degree of coloration decreases with the depth of x-ray penetration in a sample, for the x-ray intensity is weakened by the absorption in quartz crystal. To see this, the next experiment was done in the following manner. Each quartz crystal sample was placed in a lead holder so as to be irradiated with x-rays on one of its sides. The x-ray induced coloration of quartz crystals is shown in Fig. 5 and the transmission of these samples is given in Fig. 6. In these figures (a) is a standard sample of the gray type irradiated for 5 hours at 150 KV, the x-ray dose amounting to 689,400 r, (b) was irradiated for 20 hours at the same voltage, (c) and (d) were irradiated for 11.4 hours (689,520 r) and 45 hours respectively at

100 KV, (e) and (f) are for the irradiation of 500 hours (689,400 r) and 2,000 hours each with a Cu target. (g) and (h) were irradiated with γ -rays from cobalt 60 for 535 hours (690,000 r) and 2140 hours respectively. The difference of coloration in the samples due to absorption is evident, as almost the same dose was given to each series in the figure, where the samples of the lower series were irradiated with the dose four times as much as those of the upper series. Analysis follows.

Direction of incoming radiation \rightarrow

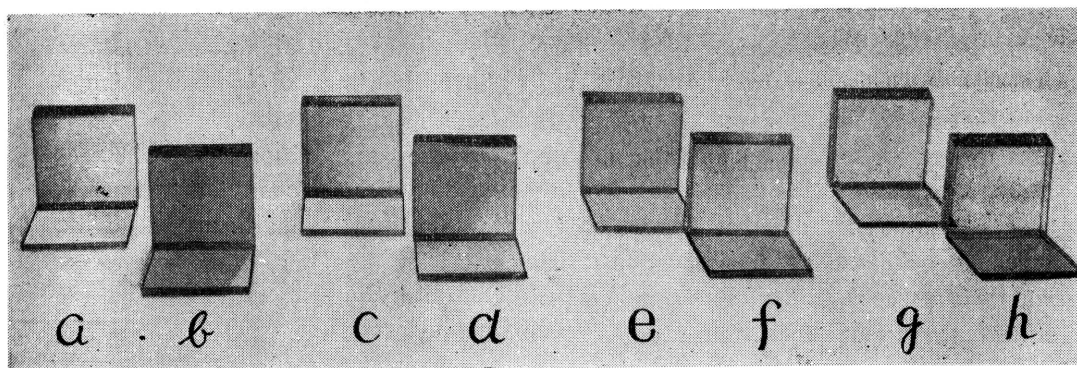


Fig. 5. Quartz samples irradiated from the left side with x- or γ -rays. Conditions of irradiation and the light transmission coefficient normal to the face of respective samples are given in the next figure.

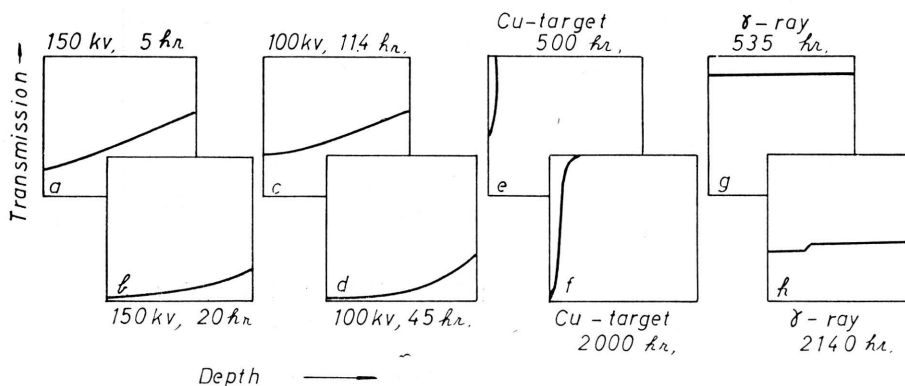


Fig. 6. The light transmission coefficient normal to the face of quartz samples irradiated from the left side. Samples corresponding to the upper series were given irradiation of 69×10^4 r each, while those corresponding to the lower series 276×10^4 r, 4 times as much as the former.

First, the x-ray absorption coefficient was measured. The equation of the x-ray intensity as function of the penetration depth x takes the same form as that for light, that is, $I = I_0 \exp(-\mu x)$, where μ is the absorption coefficient. The absorption

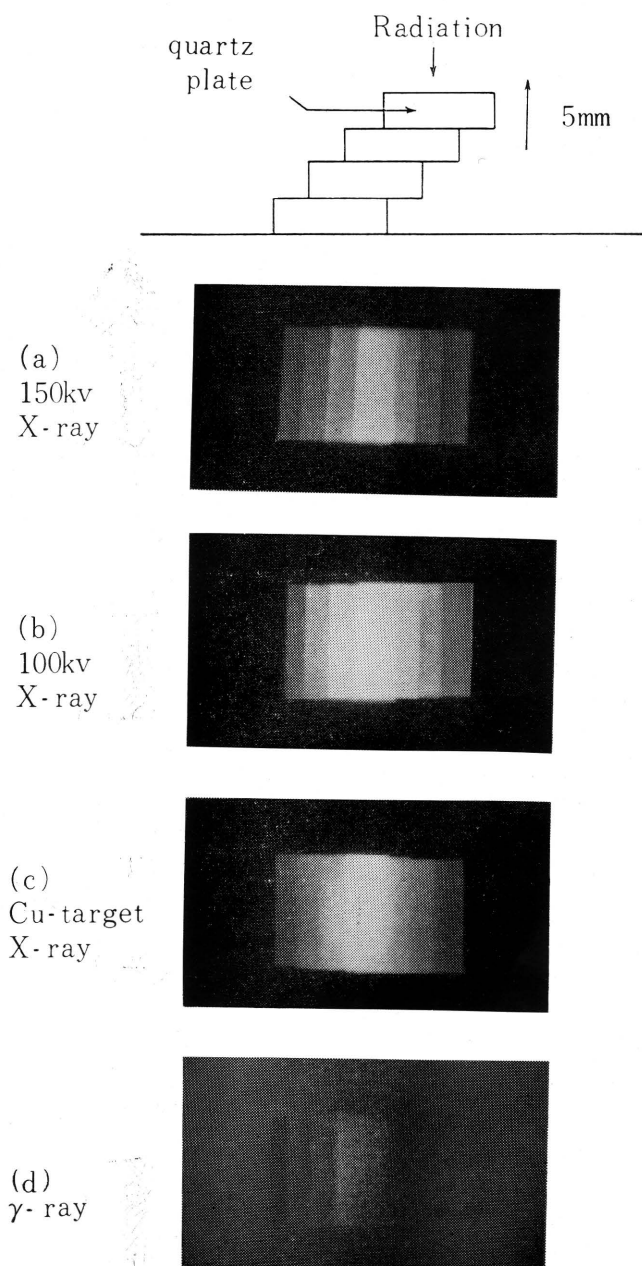


Fig. 7. Change of blackening of photographic plates with thickness of quartz crystal plates at different radiation wavelengths.

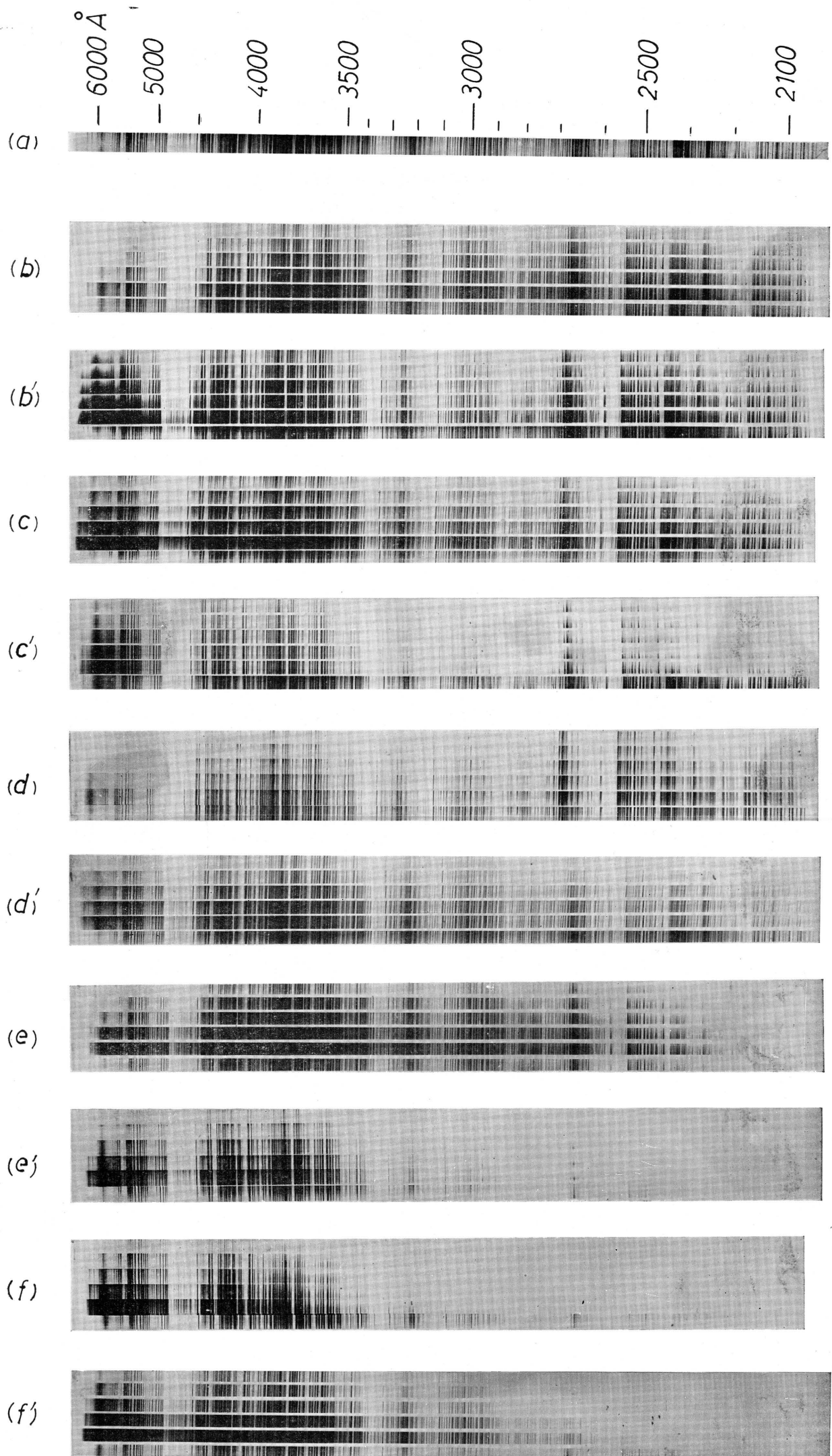


Fig. 8. Absorption spectra of colored quartz crystals. (a) Iron arc as light source with indication of wavelengths, (b) and (b') green quartz crystals, (c) and (c') brown quartz crystals, (d) and (d') gray quartz crystals, (e) and (e') yellow quartz, and (f) and (f') violet quartz crystals. The primed series are for samples of higher degree of coloration.

coefficient in quartz crystal can be calculated from those of silicon and oxygen, yielding 0.42 for 150 KV and 0.53 for 100 KV x-ray in case of a W-target, and 92 in case of a Cu-target. To test this result qualitatively, four quartz crystal plates were piled up like an echelon on a photographic film and exposed to x-rays. Photographs from (a) to (c) of Fig. 7 indicate the validity of the above calculation. The same experiment was done with γ -rays. As seen in (d) of the same figure, quartz crystals gave no shadows; instead, the blackening of the photographic plate was more pronounced where quartz crystal plates were near to it than that of the background was. The reason of this phenomenon is that x-ray and γ -rays were excited by the primary γ -rays. To measure the absorption coefficient directly, an x-ray counter (GM 134, Kobe-Kogyo Inc.) was used with a thin quartz crystal plate 0.5 mm thick. The result was 1.48 for 150 KV, 0.58 for 100 KV and 74 for 12 KV x-rays from a Cu-target. The first and the second values agree with the calculation. That the third value is less than expected is due to the mixing of continuous x-rays with the characteristic ones.

Now, the degree of coloration or the light absorption coefficient k should be proportional to the number of color centers formed from impurity atoms. The energy of x-ray absorbed in the lattice is partly transferred to impurities and changes them to color centers. Accordingly, it is natural to consider that the degree of coloration increases with a rate proportional to the number of impurity atoms which have not been transformed to color centers as yet, as well as the amount of x-ray absorbed in unit time. We get then,

$$\begin{aligned} dk/dt &= \nu(-dx)(k_{\infty}-k) \\ &= \nu \mu I(k_{\infty}-k) \end{aligned}$$

Here, ν is a constant, I the intensity of x-ray and k_{∞} the saturated value of the light absorption coefficient. Hence,

$$\begin{aligned} k &= k_{\infty}\{1 - \exp(-\nu \mu I t)\} \\ &= k_{\infty}\{1 - \exp(-\nu \mu I_0 t) \cdot \exp(-\mu x)\} \end{aligned} \quad (1)$$

where I_0 is the intensity of x-ray at the surface.

Usually, k is far smaller than k_{∞} , so that

$$k \cong \nu \mu I_0 t \cdot \exp(-\mu x) k_{\infty} \quad (2)$$

Values of k calculated from either (1) or (2) as function of x and t fit closely in the curves of Fig. 5 and 6, showing that the assumption made to derive (1) is correct.

VI. Absorption spectra of irradiated quartz crystal

A quartz spectrograph was used to study the absorption spectra of irradiated quartz crystal, for which two methods of detection were applied: one, the photographic method and the other with photoelectric cells. An iron arc was used as

the light source in both cases. The emission spectra of the iron arc is shown in Fig. 8 (a).

Absorption spectra taken photographically by the spectrograph in the visible and the ultraviolet region are given in Fig. 8 (b)~(f') for different samples. Here, the product of the absorption coefficient k and the thickness x of colored samples were made to take a common value 0.57 at respective peaks regardless of the color type, green, brown or gray, for unprimed series (b), (c), (d), (e) and (f). In this series the top spectrum is for an exposure for 2 sec. the second for 4 sec., the third for 8 sec., the fourth for 16 sec., and the fifth for 32 sec. respectively. The bottom spectrum is for the bleached state of the same samples, taken with an exposure for 2 sec.

In primed series of the same figure are shown the cases of the high degree of coloration or large thickness. Here, kx 's are far greater than 0.57, so that the time of exposure was longer than the above except that for the bleached samples, which was 2 sec. again. These spectra were not used for further calculation, though they served as convenient references.

If the illumination on the photographic plate is between 10^{-5} and 10^{-6} lux, the Bunsen and Rescoe's law holds for the spectrum lines. But, beyond and below this range, the law of the photogaphic blackening can not be applied as Hurter-Diffield and Scheiner state. For this reason, only the cases where the blackening of spectra of colored samples is of the same order as that of bleached ones were studied analytically. Results from this photographic method are omitted here, as they are nearly equivalent to those obtained from the next method using photoelectric cells.

Absorption spectra were then examined with a photoelectric cell as the detector. The arrangement of the apparatus and the measuring circuit are shown in Fig. 9

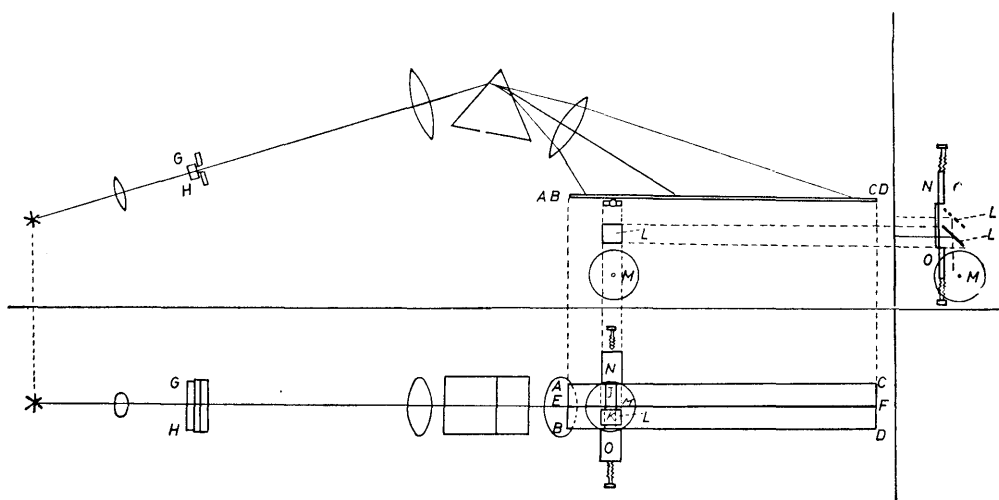


Fig. 9. Quartz spectrograph with an attachment for measuring absorption spectra.

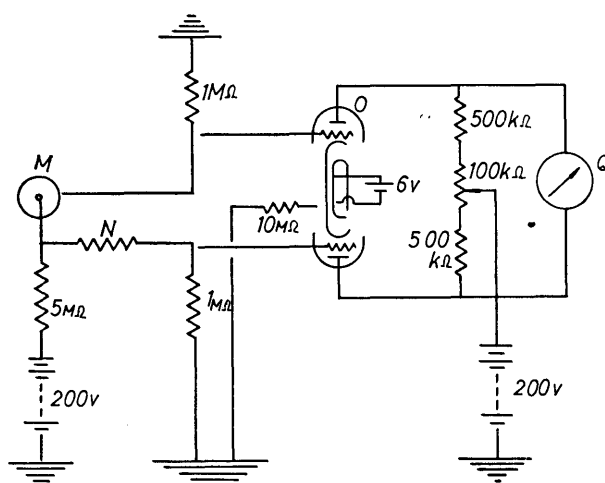


Fig. 10. Electric circuit for measurement of light intensity.

and 10. The spectrum from the spectrograph is projected at $ABCD$, which is divided into upper and lower halves. Corresponding to the upper half a colored quartz sample G is placed in front of the slit to examine its absorption, while to the lower half a bleached sample H is placed at the neighboring position. Both samples are from the same colored quartz crystal cut in half, one of which, G , being left as it was, and the other H having been bleached by heating. In this way the absorption spectra of the colored and bleached samples appear on the upper and lower positions each. The spectrum $ABCD$ is covered with a shutter that is equipped with windows J and K . The light which passes through the windows is deflected by the mirror L and sent to the photoelectric cell M . When the mirror is placed at the position shown by solid lines, the light entering through the window K is sent to the photoelectric cell, and when the mirror is displaced to the position depicted with dotted lines, the light passing through the window J is sent to the cell. The displacement of the mirror can be done instantaneously.

The cathode of one of the photoelectric cells is made of a complex material of silver and cesium and is enclosed in a glass valve, for use in the range of from $7,000 \text{ \AA}$ to $38,000 \text{ \AA}$. Another cell has a cathode made of a complex of cesium and antimony and is enclosed in a fused silica valve useful in the range of from $3,800$ to $2,000 \text{ \AA}$. These valves are filled with inert gases.

The value of the resistance N in Fig. 10 is equal to the internal resistance of the photoelectric cell. O is a valve 6SL7-GT. P is for the adjustment of the unbalance working as a potentiometer, and Q is a galvanometer with a sensitivity of $200 \mu\text{A}$ maximum. The windows J and K are of a rectangular shape, 5 mm wide and 1 cm high. But the height can be shortened with the plate N or O .

The successive interval of the spectrum range adopted in this experiment, which

was realized by the shift of the window from the long to the short wavelength is from 40 \AA at the wavelength of $2,000 \text{ \AA}$ to 600 \AA at the wavelength of $7,000 \text{ \AA}$. The variation of the intensity of the iron arc spectrum was measured by taking the sample G away, closing the window K and reading the deflection of the galvanometer, which value is given in the same table as the intensity.

The spectral transmission or the absorption of colored samples were determined in the following manner. Measuring the intensity of the light beams that passes through the window J and K , the height of the window K was regulated so that both light beams possess the equal intensity. The ratio of the height of the window K to that of L gives the ratio of the transmission of the colored quartz crystal to that of the colorless sample as given in Fig. 11.

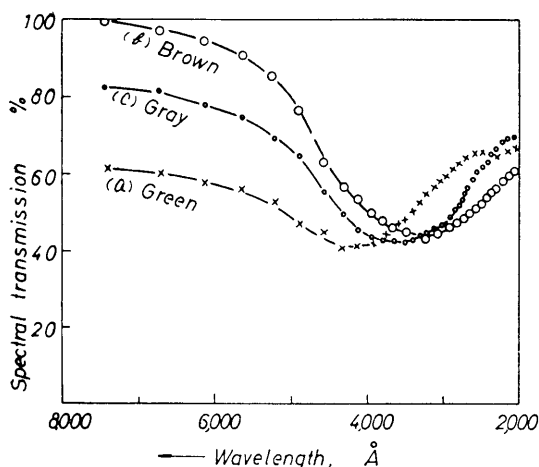


Fig. 11. Spectral transmission coefficient of colored quartz crystals: (a) a green quartz, (b) a brown quartz, and (c) a gray quartz crystal.

As seen in the figure, the spectral absorption for the different color types have respective peaks in the visible region, which are

green type	4,100 \AA
gray type	3,500 \AA
brown type	3,200 \AA

It is likely that these curves have another peak each in the ultraviolet region below $2,100 \text{ \AA}$. If it is so and the ultraviolet absorption is more pronounced than those in the visible region, we can not expect that the oscillator strength for the visible absorption would be very high. Assuming its value to be of the order of 10^{-1} and taking the maximum value of the visible ab-

sorption coefficient to be 1 cm^{-1} and the half-value width 3 eV , the number of color centers in unit volume can be calculated from

$$nf = 1.31 \times 10^7 n_0 (n_0^2 + 2)^{-2} \alpha_{max} W,$$

and becomes about 3×10^{16} . Here, n is the number density of color centers, f the oscillator strength, n_0 the refractivity, α_{max} the maximum absorption coefficient, W the half-value width in eV. This value is still an order of magnitude smaller than the impurity content in quartz crystal as will be seen later. There is a possibility that not all aluminum atoms can contribute to the formation of color centers.

VII. Analysis of impurities and cause of coloration

Quartz crystals which do not become colored by the x-ray irradiation are quite colorless and perfectly transparent in appearance, whereas those which become colored are slightly white, light yellow or light blue. It is natural to suspect that the irradiation-induced coloration is due to the presence of impurities.

J. H. E. Griffiths, J. Owen and I. M. Ward⁴⁾ presented a report on the impurities in quartz crystal at a conference on defects in crystalline solids. They performed spectroscopic analysis and stated that quartz crystal contains 1×10^{-4} Na, 1×10^{-4} Al, 5×10^{-4} Li, and other traces such as K, Fe, Mn, Mg, Ca and I.

Quartz crystals from Brazil and Madagascar contain aluminum of the order of 10^{-4} according to another paper by Griffiths, Owen and Ward⁵⁾ and also to M. C. M. O'Brien.¹⁾ They state that the cause of the absorption band due to the x-ray irradiation is the presence of aluminum, and either lithium or sodium, the latter two being present in very small amounts.

J. S. van Wieringen and A. Kats⁶⁾ state that aluminum impurity is the cause of coloration. An ordinary quartz crystal contains aluminum of the order of 10^{-4} . When aluminum is completely absent in quartz crystal, coloration does not occur. They state that the mechanism of coloration is the appearance of an absorption band resulting from the capture of electrons in positive holes that are formed at the missing oxygen sites which in turn are caused by the substitutionally existing aluminum atoms.

The author of this paper applied chemical and spectrographic method to analyze the impurities in quartz crystal specimens, independently of the above researches. The method for chemical analysis followed the standard technique, which is very complicated in procedures. In Table 1 are given the contents of elements investigated.

Table 1. Results of chemical analysis of impurity elements in colorless and colored samples.

	colorless	green	brown	gray	violet	yellow	black
K	—	1	1	1	1	1	1
Cu	—	4	1	5	2	1	3
Mg	—	1	1	1	5	0.1	2
Ca	—	1	2	5	5	9	8
Al	—	1	3	6	1	0.1	20
Sn	—	—	—	—	2	1	1
Mn	—	0.5	1	1	0.5	0.5	0.8
Fe	—	1	1	1	2	2	10

The analysis of lithium and sodium was left to the spectroscopic method.

The spectroscopic quantitative analysis was done with a carbon arc on powdered quartz crystal samples. Results are as follows :

Table 2. Results of spectroscopic analysis of impurity elements in colorless and colored quartz crystals.

	colorless	green	brown	gray	violet	yellow	black
Li	—		1	5	1		1
Na	2	1	1	4	2	1	3
K	—	1	1	1		1	1
Cu	—	2	—	4	1	1	0.5
Mg	—	1	1	1	0.5	1	2
Ca	—	1	1	5	10	5	10
Al	—	1	5	1	0.1	1	10
Sn	—	—	—		2	2	0.5
Mn	—	0.1	0.5	1	0.5	0.5	1
Fe	—	1	1	5	1	1	0.5

It can be said that results of the above two tables agree roughly with each other, especially when account is taken of the difficulty of analysis. In addition to these two methods of analysis, the radio-chemical method, by which impurities are detected by γ -rays emitted in $n\text{-}\gamma$ reaction, was applied also. This has an extremely high sensitivity. For this object some quartz crystal samples were entrusted to Dr. S. Bando of the Japanese Atomic Power Research Institute, whose results confirmed the forgoing data as far as common elements were concerned.

Thus, it was made clear that quartz crystals containing relatively large amount of impurities become dark-colored, while those with slight amount of impurities light colored. It is not easy to say which element determines the color type, but as will be explained shortly afterwards aluminum is the one that plays the principal role.

VIII. Synthesis of quartz crystal containing determined amount of aluminum

To confirm that aluminum impurity is the cause of coloration of quartz crystal irradiated with x-ray, artificial quartz crystals containing aluminum impurity were synthesized, according to the method of A. C. Walker¹²⁾ who is famous for the formation of artificial crystals. Fig. 12 shows the vessel in which quartz crystals were grown.

Four artificial quartz crystals containing 1×10^{-4} , 2×10^{-4} , 4×10^{-4} and 8×10^{-4} aluminum respectively were synthesized in this way, and colored by x-ray irradiation. The quartz crystal with 1×10^{-4} aluminum became green, that with 2×10^{-4} brown, 4×10^{-4} greenish brown and 8×10^{-4} gray, as shown in Fig. 13. Thus it was clearly demonstrated that the cause of coloration is the presence of aluminum and the color type is determined by its content.

Some remarks will be given here about manganese as impurity in quartz crystal. Generally speaking, the color of a valence crystal is affected mostly by atoms which

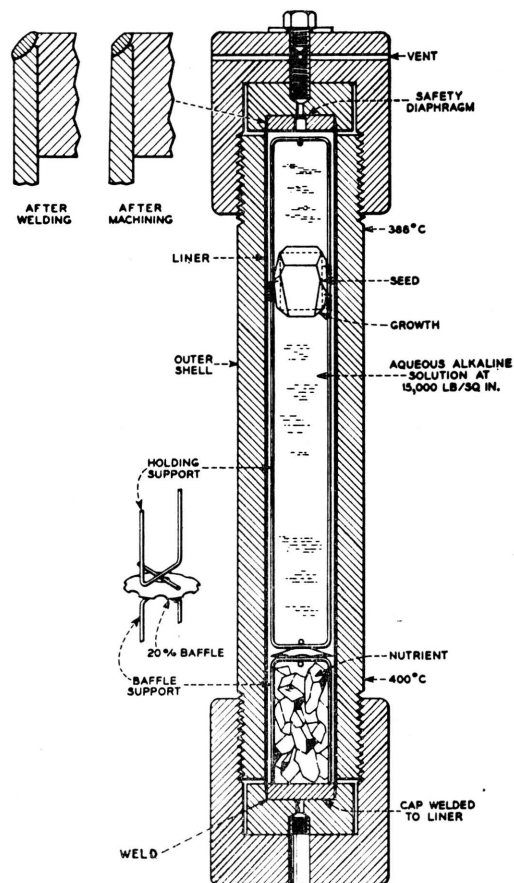


Fig. 12. Apparatus for growing quartz crystals.
(by courtesy of Dr. A. C. Walker, U. S. A.)¹²⁾

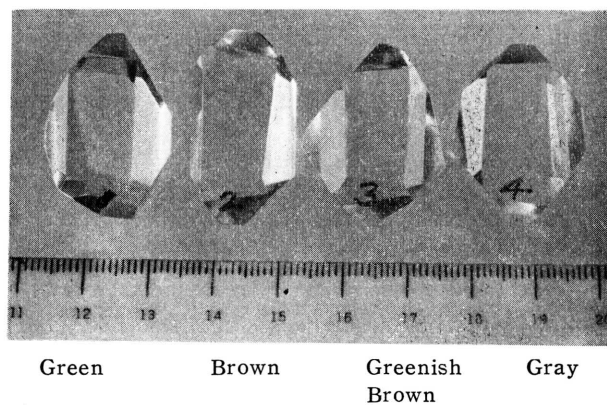


Fig. 13. Quartz crystals grown artificially and colored with x-rays.

ionize easily, while that of an ionic crystal is determined principally by atoms which combine readily with valence electrons of the host atoms. Therefore, manganese atoms should have a great influence upon the color of ionic crystal, as is known widely, but in case of valence crystals they would have only minor effects on their color, contrary to aluminum atoms which are liable to ionize and color such crystals as quartz, a typical valence crystal. This is the reason why the author holds the opinion that aluminum is the determining factor in the coloring of quartz crystal by x-ray irradiation, in spite of the presence of manganese in natural quartz crystals.

Though its effect being minor, manganese can color quartz faintly to light-crimson in case of natural crystals. To make clear further the role of manganese, artificial quartz crystals were grown with manganese impurity. When the content of the impurity is less than 10^{-4} , fairly large crystals can be obtained but they are colorless. For a content of about 10^{-3} , light gray quartz crystals were produced, being very small, however. Both can not become colored by x-ray irradiation, quite different from the case of aluminum impurity. Fig. 14 shows these crystals.

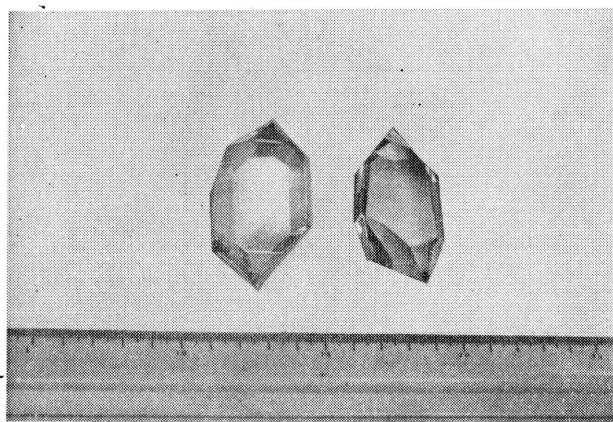


Fig. 14. Artificial quartz crystals containing manganese. The manganese content is less than 10^{-4} in (a), while it is about 10^{-3} in (b).

IX. Thermoluminescence of colored quartz crystals

In the beginning an interesting phenomenon observed in the course of the investigation will be described.

A quartz plate was irradiated with x-ray, which became colored dark green in the inner part. When it was heated at 150°C , luminescence occurred and the color faded gradually. But the edge part remained light brown from the beginning, even though its color was almost unnoticed at first. In the subsequent rise of temperature to 200°C , the edge part emitted a luminescence and bleached out. The quartz crystal was irradiated again with x-ray at room temperature, which

resulted in the same coloring as before. Fig. 15 shows this transformation from (1) to (7). Undoubtedly the edge part grew at a later period than the inner part, in surrounings different in impurity contents and types.

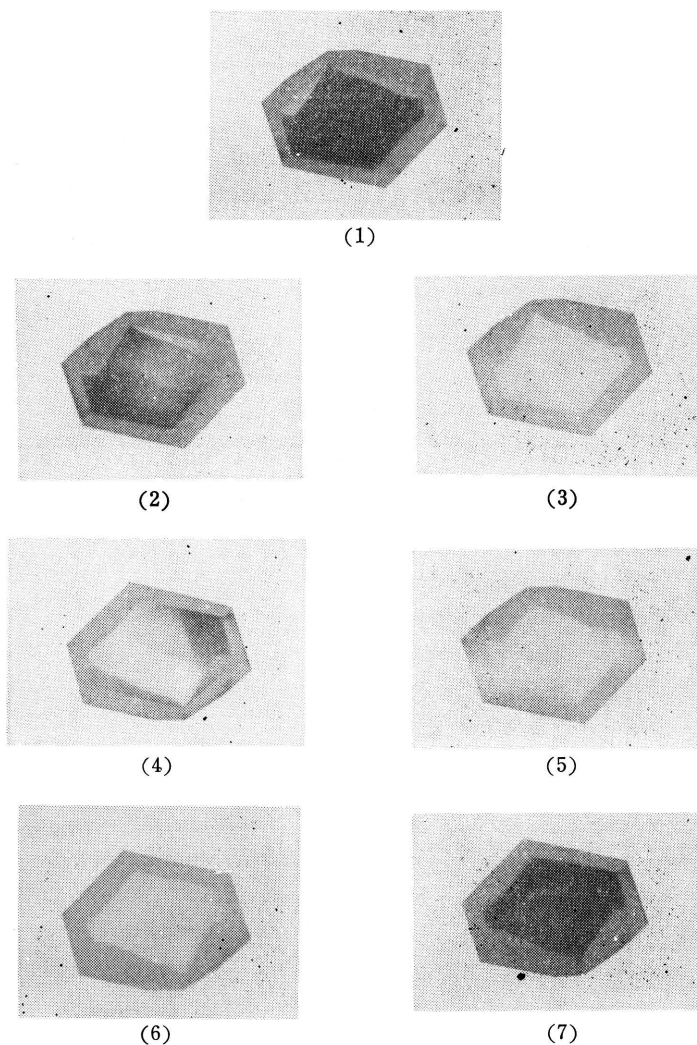


Fig. 15. X-ray induced coloration and subsequent bleaching by heating of a "double-layered" quartz. (1) As colored by x-ray irradiation, (2) and (3) heated at 150°C, (4), (5) and (6) heated at 200°C, (7) colored again by x-ray irradiation.

Almost fifty years ago Goldschmidt⁷⁾ made studies on the thermoluminescence of quartz crystal. He tested samples from 24 different localities, and found that all but five samples had the property of thermoluminescence. It is now well known that quartz crystal shows thermoluminescence at temperatures above 665°C, as

was studied extensively by Nichols and Howes.⁸⁾

On the other hand, it was found by Nichols and Wilber⁹⁾ that precipitated silicon dioxide shows a low temperature luminescence of pale greenish-white color. It begins very sharply at 85°C, ending soon, and appears again when the temperature is raised to 367°C. In 1953 R. Yokota¹⁰⁾ studied the luminescence of quartz crystal colored by x-ray irradiation. According to him the thermoluminescence begins at about 90°, reaching to the first maximum intensity at about 180°, turns then weak and arrives to the second maximum at about 300°.

Our experiments were made as follows: A quartz crystal sample 0.5 mm thick and 2.25 cm² in area was colored by x-ray irradiation to 0.5 in its light absorption coefficient. The sample was placed in the measuring apparatus in such a way that the emitted light was focussed on a photoelectric cell by a lens. In this way

several samples colored by x-ray or naturally were examined.

Green quartz crystals radiate a luminescence detectable by our cell at temperatures above 100°C, at which temperature it ceases after about 20 minutes with the bleaching out of the sample. Brown quartz crystals begin to radiate above 180°, at which temperature the luminescence lasts for about 20 minutes the same as above.

The duration of the light emission shortens with the rise of temperature. The intensity of luminescence as a function of time at given temperatures is shown in Fig. 16. The curves in the figure are by no means singly exponential, indicating some complex mechanisms are acting in the crystal.

Natural violet and yellow quartz crystals were studied, and the results are given in Table 3 along with those of artificially colored ones.

Gray quartz crystals show a peculiar behavior. If they are heated at a temperature above 100°C but

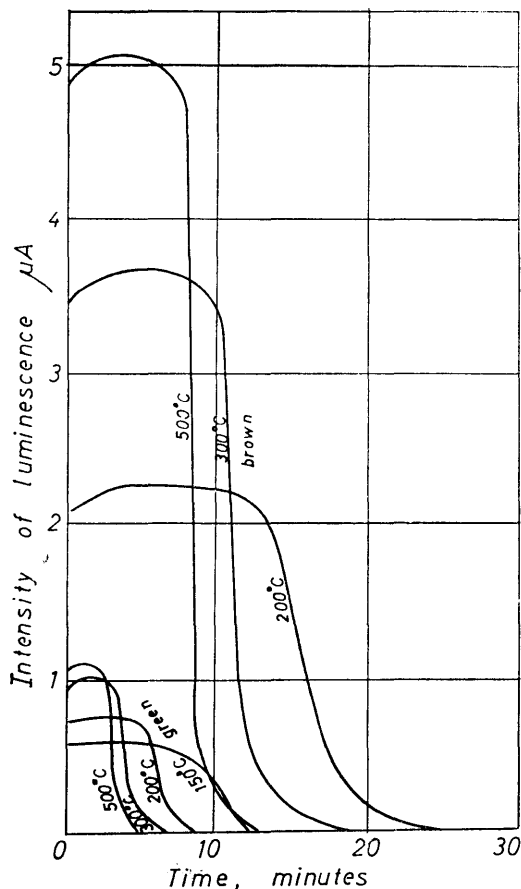


Fig. 16. Change of the intensity of light emitted from colored quartz crystals with heating time at different temperatures.

below about 150°, a luminescence the same as that of green quartz crystals occurs and the color changes to brown. The luminescence fades out after a while, and when the temperature is raised subsequently to above 150° a luminescence of brown quartz crystals is emitted.

Table 3. Thermoluminescence of colored quartz crystals.

Color type	Heating temperature	Light intensity at its maximum	Duration
Green	100°C	0.25	20 min.
	150	0.50	10
	200	0.70	7
	300	1.0	5
	500	1.2	4
Brown	200	2.2	18
	300	3.6	11
	500	5.0	8
Natural violet	300	0.83	11
	400	1.3	7
	500	1.5	6
Natural yellow	800	0.53	8
	850	0.71	6

It is of interest to determine the lowest temperature, above which these colored quartz crystals become bleached eventually, even though the associated thermoluminescence might not be detected by our apparatus. Thus, it was found that no bleaching occurs for heating of one month (30 days) at temperatures below

75°C for green

117°C for brown

239°C for natural violet and

750°C for natural yellow quartz crystals.

The thermal luminescence associated with the thermal bleaching is a process by which the color centers formed by x-ray irradiation or by some other mechanism in case of naturally colored quartz crystal return to their original state. The number density n of color centers should decrease as

$$dn/dt = -p_T n,$$

at a constant temperature T . Here, p_T is the probability of dissipative radiation of a color center in unit time. The subscript T means that p is a function of the temperature. The lifetime of a color center, τ_T , is the reciprocal of p_T .

$$\tau_T = p_T^{-1}$$

The probability p_T takes approximately the following form

$$p_T = p_\infty \exp(-E/\kappa T)$$

where E is the activation energy for this process and k is the Boltzmann's constant, being 1.3805×10^{-16} erg. deg $^{-1}$. p_{∞} is the probability at infinite temperature.

Hence we get

$$\tau_T^{-1} = \tau_{\infty}^{-1} \exp(-E/kT)$$

The activation energy E can be determined using this equation from the observed values of τ_T and the temperature of measurement T . The result is

- 0.075 eV for green quartz crystal,
- 0.088 for brown quartz crystal,
- 0.105 for natural violet quartz crystal,
- 0.24 for natural yellow quartz crystal.

It can be seen that the activation energy is appreciably higher for natural quartz crystals than artificially colored ones, as was expected from the difference of the lowest bleaching temperature. Actually the activation energy is nearly proportional to the lowest bleaching temperature expressed in degree Kelvin as shown in Fig. 17.

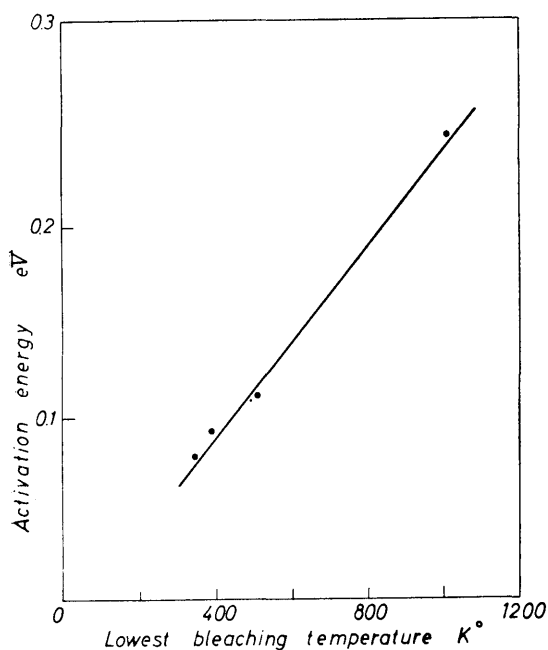


Fig. 17. Relation between activation energy for thermoluminescence and the lowest bleaching temperature.

Miscellaneous phenomena observed in the course of study will be described. A certain natural smoky quartz crystal transforms into a yellow quartz when heated, which in turn becomes colorless by further heating at a higher temperature. Some quartz crystals colored naturally to yellow or violet lose color on heating, whereas some violet ones become yellow by a weak heating, which on further heating turns milky white (translucent). All of these quartz crystals become gray by x-ray irradiation, and the same thing happens by γ -ray irradiation, which are irreversible changes.

Natural colorless quartz crystals which become colored to violet or yellow by the irradiation of x-rays or γ -rays were

not found as yet. On the other hand, there were no natural quartz crystals that are colored green, brown or green like those induced by artificial irradiation.

A kind of smoke quartz crystal resembles in appearance to gray quartz colored artificially, but the temperature of the thermoluminescence or the bleaching is definitely different between both. The bleaching temperature of naturally colored quartz crystals is far higher than that of x-ray colored ones.

It is very probable that many naturally produced quartz crystals had been colored green, brown or gray due to irradiation by cosmic rays. They must have been bleached by heating at temperatures above 117°C but below 239°C, so that only violet and yellow quartz crystals were saved. It should be remembered that the temperature of the earth has never been very high, because of the presence of sea water.

Emission spectra of the thermoluminescence were photographed by a quartz crystal spectrograph. They are shown in Fig. 18, where (a) is for a green quartz crystal, (b) for a brown, (c) for a natural violet and (d) for a natural yellow. The time of exposure was 24 hours each, but the temperature of heating was different, 100° for green, 200° brown, 250° for natural violet and 800° for natural yellow. The width of the emission band and the position of the maximum intensity are as follows.

Table 4. Continuous spectra of thermoluminescence of colored quartz crystals.

Color type	from	maximum	to
green	4250 Å	4700	4950
brown	4200	4490	4750
natural violet	3400	4300	4500
natural yellow	3500	3800	4000

In this table, green, brown and natural yellow quartz crystals are to turn bleached after the emission of the luminescence, but violet quartz becomes yellow, and as for the gray quartz, which is not listed here, heating changes it to brown after luminescence as said before.

X. Mechanism of coloration and thermal bleaching

Historically the coloration of otherwise transparent colorless crystals was divided into two categories, types A and B. In the A type were included such phenomena as the coloration of ruby or sapphire, which are corundum containing impurities. The mechanism of coloration of this kind was concluded to be the formation of a complex salt structure in the crystal. On the other hand, in the B type artificial coloring of colorless crystals was included.

The first discovery pertaining to the B kind was the coloring of a colorless fluorite to pink by an irradiation from sparks of a Leyden jar, which was discovered by Thomas J. Pearsal,¹¹⁾ an assistant to Farady. Actually this was a coloration caused by ultraviolet rays. The coloration by x-rays of minerals was discovered

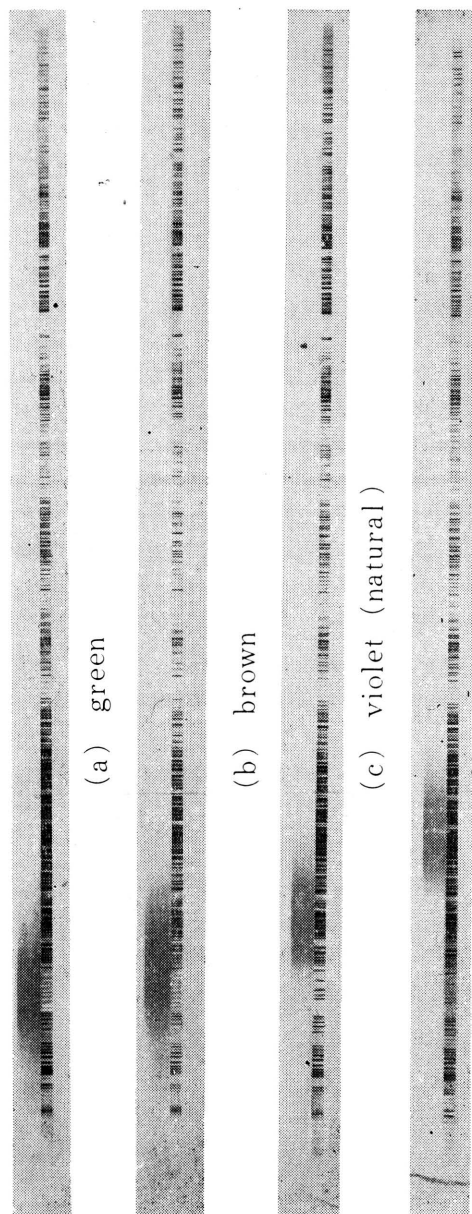


Fig. 18. Spectra of thermoluminescence of colored quartz crystals. Iron arc spectrum is given for indication of wavelengths.

by Becquerel¹³⁾ in 1885, who, however, did not study this appreciably. Extensive researches were undertaken by Goldstein,¹³⁾ Curie, Roentgen and others, immediately after the first manufacture of x-ray tubes in 1890. Then quantum-mechanical theory began to be applied in the study of these phenomena, which revealed the existence of color centers in the cases of the B type as well as in the A type and made it meaningless to distinguish the one kind from the other. Though both kinds of coloration are present in quartz crystals: naturally colored and artificially colored ones, the existence of color centers was confirmed in either case.

The structure of color centers in a smoke quartz crystal was studied by Griffith, Owen and Ward with the electron paramagnetic resonance. It was found that the intensity of the resonance absorption is proportional to the optical absorption, and that the spectrum shows a hyperfine structure caused by the magnetic interaction between the unpaired electron of the color center and the nucleus of an impurity atom.

The hyperfine structure is composed of six lines, revealing that the impurity atom is aluminum which has a nuclear spin $5/2$ at 100%.

O'Brien¹⁾ offered the following model of the color center in irradiated quartz crystal. As shown in Table 1 and 2, quartz crystal contains several kinds of impurities beside aluminum. Aluminum atoms enter into the lattice, substituting silicon sites, while alkali metals form interstitial ions. The atomic arrangement before the x-ray irradiation would be like that shown in Fig. 19 (a). In this model M^+ is a positive ion such as Na^+ and Li^+ . The arrow in Fig. 19 (b) means a coordinate bond, for which an electron pair is supplied by the oxygen atom to link the aluminum atom and the oxygen ion.

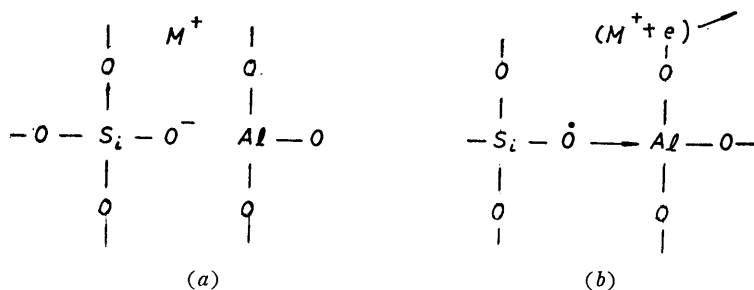


Fig. 19. Atomic model of a color center. (a) is for the state before x-ray irradiation, and (b) for the state as colored by x-ray. ($M^+ + e$) means that a metallic ion M^+ becomes combined with the electron ionized from oxygen ion in (a).

By the x-ray irradiation an electron is emitted from a lone electron pair belonging to oxygen and then captured by M^+ , which loses positive electric charge and wanders away from the color center. The remaining unpaired electron on the oxygen atom acts as the color center as shown in Fig. 19 (b).

O'Brien discussed the electronic structure of the color center. She regarded the Si—O and O→Al bonds as the same, and analyzed the structure of Si—O→Al. The symmetry group of this isosceles triangle is C_{2v} , so that the atomic orbitals $2s$, $2p_x$, $2p_y$ and $2p_z$ of oxygen become irreducible representations of it respectively, belonging to a_1 , b_1 , b_2 and a_1 each. On the other hand, we can get linear combinations from the atomic orbitals of Si and Al participating in the bonds, which belong to A_1 and B_2 . Combining these, molecular orbitals can be obtained as

A_1 (s) : from $2s_1$ $\phi_{Ox} + \phi_{Al}$ and $2p_z$

B_1 (x) : from $2p_x$

B_2 (y) : from $2p_y$ and $\phi_O - \phi_{Al}$

A_2 (z) : from $2p_z$ $\phi_{Ox} + \phi_{Al}$ and $2s$

Here, bonding orbitals are (s) and (z), whereas remaining orbitals are nonbonding.

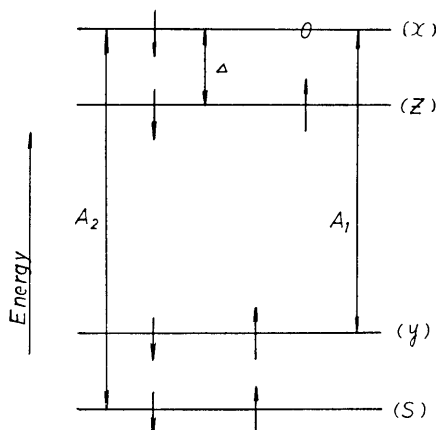


Fig. 20. Energy levels in a color center of quartz, according to O'Brien.

The energy levels are as shown in Fig. 20, where one of the electrons in (s) and (z) comes from Si. The ground state of the color center is $(s)^2 (y_y)^2 (z)^2 (x_x)$ and the first excited state is $(s_z)^2 (y_y)^2 (z) (x_x)^2$. Spin-orbit coupling mixes (z_z) and (x) , making the transition $(z_z) \rightarrow (x)$ allowable, which is observed as two absorption peaks 2,918 and 2,846 cm^{-1} in the infrared regions in a smoke quartz crystal. The level differences Δ between $(z)_z$ and (x) is therefore about 3,000 cm^{-1} . The absorption in the visible region is due to the allowable transition $(s) \rightarrow (x)$, which gives a strong absorption band A_2 (in smoke quartz crystal, $2.6 \text{ eV} \approx 21,080 \text{ cm}^{-1} \approx 474 \text{ m}\mu$), and

the forbidden transition $(y) \rightarrow (x)$, that causes a weak absorption band A_1 (in smoke quartz crystal, $2.0 \text{ eV} \approx 16,200 \text{ cm}^{-1} \approx 617 \text{ m}\mu$). It would be redundant to say that the paramagnetic absorption is due to the unpaired electron in (x) . In this way the characteristics of the color center in smoke quartz was explained with success.

O'Brien's model of the color center is reasonable as far as the absorption of visible and infrared light is concerned, but it does not explain the mechanism of the thermoluminescence. For this reason a new model will be presented here. It does not seem to be very appropriate to regard the Si—O and Al—O bonds as the same, as was done in O'Brien's theory. We will take the approach of localized bonds in contrast to the molecular orbital approximation.

The electronic structure of a color center before the x-ray irradiation is nearly the same as that of O'Brien, as shown in Fig. 21 as Model I. Here the notation

Model I

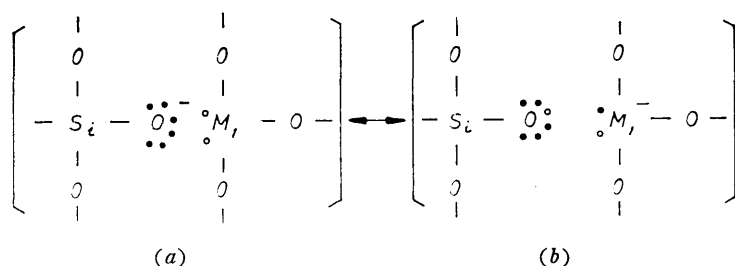


Fig. 21. Proposed atomic model of a color center in quartz before x-ray irradiation, called Model I in text. Structures (a) and (b) are considered to be resonating with each other.

\leftrightarrow means the resonance between both structures. This resonance gives a certain amount of a semi-polar bond nature between oxygen and M_1 . M_1 and M_2 are impurity atoms, the latter being in an interstitial position as an ion. This positive charge is balanced by the negative charge of the oxygen ion. Though there are many kinds of impurities in quartz crystal, aluminum is preferred as M_1 , because it has an ionic radius of the same order as that of silicon as seen in Table 5. This choice coincides with the result of the paramagnetic resonance absorption. At the ground state the contribution of the structure (a) should be more than that of (b), for oxygen has much higher electronegativity than aluminum. As for M_2 , comparison of the data given in Table 5 indicates that Na^+ or Li^+ are most probable ions for they have rather small electronegativity.

Table 5. Comparison of various ions.

Ionic radius		ratio	Mulliken's electro-negativity, $\frac{1}{2}(I + A)$			
Si^{4+}	0.41 A	1.00		SP^3	V_4	6.00 P
Al^{3+}	0.50	1.22	M_1	SP^2	V_3	4.06 P
Fe^{3+}	0.60	1.46				
Li^+	0.60	1.46	M_2	S	V	2.96 S
Mn^{3+}	0.62	1.51				
Mg^{2+}	0.65	1.59				
Sn^{4+}	0.71	1.73				
Fe^{2+}	0.75	1.83				
Mn^{2+}	0.80	1.95				
Na^+	0.95	2.32	M_2	S	V	2.94 S
Cu^+	0.96	2.34				
Ca^{2+}	0.99	2.42				
K^+	1.33	3.24	M_2	S	V	
O^{2-}	1.40	3.42		S^2P^4	V_2	0.00 P

Now, when quartz crystal is irradiated with x-rays, the above structure Model I suffers an ionization and changes to the structure shown in Fig. 22 as Model II.

The electron emitted from oxygen is captured by M_2 which then returns to a neutral atom. M_2 moves away from the color center as the coulombic attraction is now absent, aided by the local high temperature that is caused by the x-ray absorption. As will be stated later, M_2 plays an important role in the thermal luminescence and bleaching.

Model II

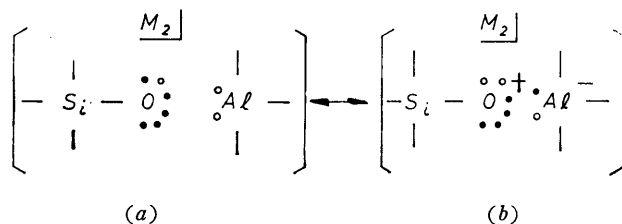


Fig. 22. Proposed atomic model of a color center in quartz crystal after x-ray irradiation, called Model II in text, Structures (a) and (b) are considered to be resonating with each other.

The local structure between oxygen and aluminum is considered to be as follows. For the sake of simplicity we assume that $2p_y$ orbital of oxygen is directed to aluminum, while $2s$ to silicon. The vacant orbital $3p_y$ of aluminum can accommodate the unpaired electron in the $2p_x$ orbital of oxygen by excitation, resulting in the structure (b) of Model II. Actually, the ground structure of the color center would be a mixture of both, so that the ground and excited structures become as follows.

$$\text{Ground state: } \Psi_g = C_a \phi_a + C_b \phi_b, |C_a|^2 \gg |C_b|^2$$

$$\text{Excited state: } \Psi_e = C_a \phi_b - C_b \phi_a.$$

The cause of coloration is the transition between the above states. A simple calculation gives as the level difference

$$h\nu_{abs} \cong \sqrt{(I_0 - A_{Al} + V_5 - V_6)^2 + 4\beta}$$

Here, I_0 is the ionization energy of oxygen, A_{Al} the electron affinity of aluminum, V_5 the dipole—dipole interaction, V_6 the dielectric relaxation energy and the resonance energy.

In our model the thermoluminescence is explained in the following manner. The metallic atom M_2 which had received an electron from a color center by x-ray irradiation and moved far away begins to wander through the lattice when the temperature is raised, and approaches to one of the color centers. The recombination of the color center with the valence electron of M_2 is the cause of the thermal luminescence, different from the cases of ordinary phosphorescent substances in that the migration of metallic atoms is concerned. The electron from M_2 enters into a triplet level instead of the lowest vacant level of the color center,

followed by the emission of luminescence and the adiabatic recovery of the original state of the color center. The configuration diagram relevant to all of these changes is given in Fig. 23.

Some observation will be made about the implications of our model. We assumed above that only aluminum atoms are in the position of M_1 , but it is possible that iron can take part also. In that case the absorption peak of the color center should be different, because the charge transfer acts now between oxygen and iron. This and similar things are expected to explain the difference of the color types. Experimentally, the emission spectrum of the thermal luminescence shows a fairly narrow band about $3,000 \sim 4,000 \text{ cm}^{-1}$ wide, in contrast to the absorption spectrum of the color center

that has a very broad band extending from the ultraviolet to the α -visible region. This is explained in our model as due to long lifetime character of the triplet level that is formed initially by the recombination of the electron from M_2 and the color center. Besides, as transition between the ground state of the color center before irradiation and that triplet level is forbidden, a quartz crystal shows hardly any absorption in the visible region before irradiation. As for the relation between the spectra of the absorption and the thermal luminescence, the "mirror-image" relationship can not be observed. But, as implicated in the configuration diagram given above, we can say from experimental result

$$h\nu_{abs} > h\nu_{thermal\ lumt}$$

holds.

XI. Summary and conclusions

An x-ray apparatus capable of intense radiation was constructed to study the artificial coloring of quartz crystals. A large number of naturally produced quartz crystals were tested, some of which became colored, while others did not. Among colored samples, about 5% were green, 15% brown and 80% gray, though the distinction of color was not always clear. The coloration approaches saturation with increasing x-ray dose. The saturation is brought about with more than about 10^8 r in ordinary cases, differing somewhat according to color type. Experiments were made to see the change of coloration with penetration depth of x-ray in quartz crystal, by use of x-ray of different wavelengths and γ -rays from cobalt 60.

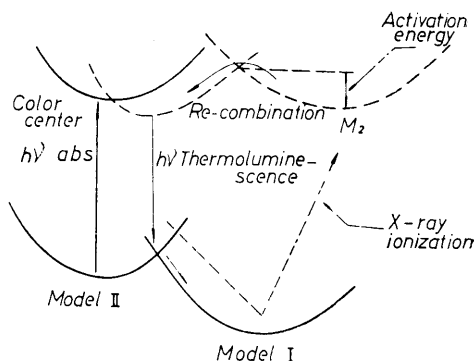


Fig. 23. Mechanism of x-ray induced coloration and thermoluminescence of quartz crystal.

An equation describing the change of coloration with time and depth in sample was derived and found to fit the experimental result. Spectral light transmission coefficient of samples of different color types were measured, the absorption peak of each color type differing with each other, being from 3000 to 4100 Å.

Chemical and spectroscopic analysis of quartz crystal samples were conducted, and it was made clear that those containing relatively large amounts of impurities become dark-colored on irradiation while those with slight amounts of impurities light-colored, and samples which do not become colored contain only even less amount of impurities. To confirm that aluminum is the cause of coloration of quartz crystals irradiated with x-rays, artificial quartz crystals containing this metal as an impurity were synthesized. When irradiated, a quartz crystal with 1×10^{-4} Al became green, one with 2×10^{-4} brown, one with 4×10^{-4} greenish brown and another with 8×10^{-4} gray. Quartz crystals containing manganese as impurity were grown and irradiated also, resulting in light gray coloration.

The thermoluminescence of x-ray colored quartz crystals was studied, and the highest temperatures below which no bleaching occurs was determined for each color type. These temperatures are lower for the x-ray colored crystals than for the naturally colored ones. Activation energy for the thermoluminescence or bleaching was calculated from experiment, and it was shown that high activation energy is associated with higher value of the critical temperature, and actually the activation energy is proportional to the critical temperature expressed in degree Kelvin. Emission spectra of thermoluminescence were photographed, the peak of which is at shorter wavelengths for samples with higher activation energy of thermal bleaching.

Finally, the atomic mechanism of the x-ray induced coloration of quartz crystals was explained on a plausible model of the color center, which is also suitable for explanation of the thermoluminescence.

XII. Acknowledgement

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