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Electrical and Optical Investigation of Charge-Carrier
Trapping in Rutile Single Crystals

by

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ELECTRICAL AND OPTICAL INVESTIGATION OF CHARGE-CARRIER
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Abstract: Low-frequency absorption centers, observed by electrical measurements in single crystals of rutile, can be produced by thermal quenching or optical irradiation in the edge of the eigenabsorption region (4200Å). They are observed when electric fields are applied parallel to the optic axis (crystallographic c axis) and are not visible with the field perpendicular to this axis. The temperature dependence of the principal dispersion indicates an activation energy of 0.18 eV. The centers can be explained by a localized electron transfer process along the optic axis. The introduction of silver and copper by thermal diffusion did not produce low frequency absorption spectra.

Introduction

Titanium dioxide holds a key position in the research program of this laboratory, as a starting material for the development of ferroelectrics and semiconductors.¹⁾ Rutile single crystals, grown as boules by the flame-fusion technique, have become available and an extensive study of their electrical and optical properties was made in this laboratory²⁾ a

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- 1) A. von Hippel, R. G. Breckenridge, F. G. Chesley, and L. Tisza, Ind. Eng. Chem, 38, 1097 (1946).
2) D. C. Cronmeyer, Phys. Rev. 87, 876 (1952).

number of years ago. The crystals are still far from ideal; they are badly strained and contain impurities. However, much can be learned about the motion of electrons and holes from this medium of high dielectric constant and strong anisotropy (κ' , ca. 165 $\parallel$ and 79 $\perp$ to the optic axis).

The purpose of the present investigation, using rutile single crystals, was to study the trapping of electrons and holes. It is known that in rutile each Ti^{+4} ion is surrounded by six O^{-2} ions situated at the corners of an octahedron, and that each O^{-2} ion has three Ti^{+4} ions, located at the apices of an equilateral triangle, as its nearest neighbors (Fig. 1). This description does not mean that rutile is completely heteropolar. There is a strongly covalent contribution to the binding energy, as is known from electrical and optical measurements, and the character-

Fig. 1. Crystal structure of rutile. The small circles represent metal ions and the larger ones oxygen ions.

istic TiO_6 octahedron configuration can be explained by the radius ratio or s-p-d hybridization. The optical spectra of a normal and of a slightly reduced specimen, at room temperature,²⁾ are shown in Fig. 2. The eigenabsorption begins at ca. 4000Å; reduction creates a broad absorption band centered at 1.8 μ . Photoelectric response results from light absorption in the tail of the eigenabsorption region and, for the slightly reduced rutile, extends to at least 2 μ .

Experimental Procedures

Sample Preparation

Crystal plates, cut with the smallest dimension either parallel or perpendicular to the optic axis, were prepared by orienting the rutile boules* with the Laue-pattern back-reflection technique (CuK α radiation) and cut with an accuracy of $\pm 1^\circ$ using a diamond saw and water cooling. They were then ground by hand with carborundum powder and polished by machine with alumina suspension in soap solution. To avoid rounding the edges the crystal plates were protected by a guard ring of stainless steel. After cleaning with KOH solution and washing them with distilled water, the samples were heated for several hours at ca. 150°C.

Samples ca. 3x2x2 mm in size proved to be the most convenient; larger samples tended to crack on quenching and smaller ones were not suitable for accurate dielectric measurements.

Before use the crystal plates were checked under scattered light (stereoscopic microscope, 80X) for uniformity of surface and freedom from cracks and irregularities. Dielectric constant and loss angle were measured from 100 cps to 100 kc and the optical absorption characteristics for the ultraviolet and infrared region were obtained.

* Made by the National Lead Company (Boules A) and the Linde Air Products Company (Boules B).

Fig. 2. Absorbance vs. wavelength for normal and slightly reduced rutile.

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Production of Absorption Centers

(a) By thermal quenching. The sample was placed in a Vycor or alundum boat or in an evacuated Vycor ampoule inserted in a Vycor tube and heated to the selected temperature between 330° and 900°C . A slow current of oxygen, air (dried or undried), nitrogen or helium was passed over the sample during the heating period. After heating for the desired length of time, the sample was then quenched in liquid nitrogen. Later, an apparatus was developed (Fig. 3) in which both the heating and a very rapid quenching of the sample could be accomplished without removal from the system. A slow current of dry oxygen was passed through the apparatus during the heating period. The basket containing the sample was then dropped into liquid oxygen, which had been condensed by liquid nitrogen.

(b) By optical irradiation. Optical absorption characteristics were obtained by Cronmeyer²⁾ at different temperatures and from ca. 2000Å to several microns. Our measurements agreed with these previous results. The absorption edge in the visible ultraviolet region at room temperature extends roughly from 4100 to 4300Å (Fig. 4). The optical irradiation of samples was confined to bands 1 to 6 (Fig. 4). These regions were made as narrow as the required high light intensity permitted. The time of irradiation was varied 1 to 18 h.

The light source was a xenon arc which gives a continuous spectrum in this wavelength region and proved stable after once started. The infrared was filtered out by a jacket of circulating water with quartz windows. A multilayer interference filter* of suitable constants provided the narrow

* The filter layer was of the dielectric type to avoid spurious radiations and was obtained from Baird Atomic Company, Cambridge, Mass.

Fig. 3. Thermal quenching apparatus.

Fig. 4. Absorbance characteristics of (a) filters used for irradiation (solid lines); (b) rutile at its absorption edge (dashed line).

transmission regions selected. A thin slice of clear polished rutile inserted behind the filter sharpened the cutoff in the ultraviolet. In order to shift the wavelength of the peak transmission, the filter needed only to be rotated about a vertical axis. Rotation of the filter by 20° shifted the wavelength of peak transmission from 4194 to $4088 \pm 2\text{\AA}$. The intensity of the radiation, checked photoelectrically, varied less than 5 percent.

Restoration of the Initial State by Annealing

The samples were always annealed by reheating the quenched samples and then slowly cooled to wipe out effects of previous experiments. The effect of this treatment was studied by heating the samples in air to between 100° and 500°C for various periods of time; 3 h. at 300° proved to be the most appropriate.

It was observed that absorption centers could be destroyed also by placing the quenched samples in intense sunlight for several hours. However, if the sunlight was filtered through a thick glass plate, the annealing was insignificant.

Detection and Study of Absorption Centers

The presence of absorption centers was detected by dielectric spectroscopy. Dielectric constant and loss characteristics were taken before and after the production of absorption centers at temperatures from liquid nitrogen to 278°C. At higher temperatures the samples showed signs of annealing, hence measurements were not taken. Optical absorption curves in the visible and infrared regions were checked but did not show any change. The dielectric measurements ranged from 100 cps to 100 Mc; the equipment used is listed in Table 1. For measuring capacitances less than 4 μ f, the crystal holder was connected in parallel with a linear micrometer capacitor.

Table 1. Equipment used for dielectric measurements.

Frequency range	Bridges General Radio Type	Oscillators General Radio Type	Detector
100 cps to 40 kc	716-C	713-B	{ Designed ³⁾ and built in this laboratory.
40 kc to 500 kc	716-C	805	
500 kc to 18 Mc	916-A	805	
28 Mc to 100 Mc	1601-A	805 and 1208-A	National HFS receiver with BC-348-N re- ceiver.

3) J. L. Upham, Rev. Sci. Instr. 22, 659 (1951).

After cleaning the samples, conducting silver paint was applied as electrodes for the room- and low-temperature measurements; control experiments had shown that this method gave the same results as evaporated electrodes in this range. The whole electrode area was checked for continuity and then covered by tin foil. For high-temperature work, electrodes of evaporated gold were used with thin gold foil pressed over them. The crystal plate was then inserted into a spring-loaded, shielded holder filled with dry nitrogen (Fig. 5). The oscillator output was held below 2 to 3 v.

Introduction of Impurities

In the crystals received during the later part of the work absorption centers could not be produced by quenching or optical irradiation. Spectral analysis* showed that the earlier samples contained slightly more (0.01%) silver and copper. Attempts were made to introduce silver and copper in the later samples by thermal diffusion after the initial measurements.

To add silver, fine filings of pure silver were placed on the rutile samples in an alundum boat heated in a Vycor glass tube to about 800°C for more than 6 h. in a stream of oxygen. Silver oxides are unstable at this temperature and metallic silver slowly diffused into the rutile, as established by the distinct development of a yellow tinge throughout the volume and a shift of the absorption edge toward longer wavelengths.

For the introduction of copper a higher temperature was used (1370°C). Since cuprous oxide is stable even at this temperature, the sample was placed with finely divided pure copper filings in a quartz tube, which was evacuated, sealed and heated for 14 h. Copper diffused, but the samples assumed a dark color (almost opaque) because of oxygen loss. The sample

* New England Laboratories for Industrial Research and Development, Ipswich, Mass.

Fig. 5. Crystal holders used for dielectric measurements: (a) for low temperature immersion; (b) for high temperatures; (c) for high frequencies (36 to 100 Mc); (d) for room temperature.

was reoxidized at 700°C and it resumed its characteristic color, but the presence of copper was indicated only by the increased dielectric loss at low frequencies.

Results

Low-Frequency Dispersion Obtained by Thermal Quenching

The variation of dielectric constant and loss tangent with frequency at room temperature for a typical quenched-in dispersion, with the field applied parallel and perpendicular to the optic axis, is shown in Fig. 6. A peak at 88 kc appears in the $\tan \delta$ curve only when the field is parallel to the optic axis. This peak can be annealed out and recreated. Measurements of this dispersion at various temperatures show a thermal shift (Fig. 7). The temperature of measurement from -79° to 278°C changed the peak amplitude (Fig. 8) and frequency (Fig. 9). At -180°C the peak was decreased by a factor of 100.

The time dependence of the growth of the absorption centers was also investigated as function of the heating temperature before quenching; the peak values of $\tan \delta$ at room temperature are given in Fig. 10. No centers could be produced by heating at 400°C for 12 h.; less than one hour sufficed to produce the saturation at 860°C .

In the measurements reported thus far, the samples were heated in oxygen before quenching. Figure 11 and Table 2 show the profound influence of the atmosphere on the absorbance. While He causes only a slight shift, vacuum blots out the absorption and nitrogen creates a different one at higher frequencies.

Optical measurements made before and after quenching showed no change. However, a sharp infrared band at 3μ (Fig. 12) should be noted,

Fig. 6. Dielectric constant (solid lines) and loss (dashed lines) vs. frequency for quenched rutile sample, parallel (circles) and perpendicular (triangles) to the optic axis at room temperature.

Fig. 7. Thermal shift of the quenched-in dielectric dispersion in rutile.

Fig. 8. Characteristic for rutile of $(\tan \delta)_{\max}$ vs. temperature.

which has been identified as an OH absorption, as will be shown in detail in a subsequent report by B. H. Soffer.

Annealing

The effect of heating temperature and time for the annealing of centers was investigated. After heating for 16 h. at 300°C, $\tan \delta$ did not show any peak and thus the centers were annealed out. Exposure to sunlight partially annealed out the centers (18 percent in 3 h.). Sunlight filtered through thick glass proved ineffective even after 6 h.

Optical Irradiation

Optical irradiation of samples from Boules A at $4200 \pm 100\text{\AA}$ produced

Fig. 9. Frequency of the absorption peak as a function of temperature.

Table 2. Effect of various ambient atmospheres
on the $\tan \delta$ dispersion peaks.

Ambient atmosphere	Samples from Boules A	Samples from Boules B
(1) Oxygen	$\left\{ \begin{array}{l} \text{Dispersion peak at 88 kc.} \\ \text{Temperature dependence exists.} \\ \text{Activation energy} = 0.18 \text{ ev.} \\ f_o = 3.98 \times 10^{12} \text{ sec.}^{-1} \end{array} \right.$	$\left\{ \begin{array}{l} \text{Dispersion peak at 12 Mc.} \\ \text{No temperature dependence exists.} \\ \text{At } 400^\circ\text{C dispersion is annealed out.} \end{array} \right.$
(2) Nitrogen	$\left\{ \begin{array}{l} \text{Dispersion peak at 14 Mc.} \\ \text{No temperature dependence exists.} \\ \text{Dispersion anneals out at } 400^\circ\text{C.} \end{array} \right.$	Same as for (1).
(3) Undried air	No dispersion.	No dispersion.
(4) Dried air	Same as for (1).	Same as for (1).
(5) Helium	$\left\{ \begin{array}{l} \text{Dispersion peak at 110 kc.} \\ \text{Temperature dependence exists.} \\ \text{Activation energy} = 0.10 \text{ ev.} \\ f_o = 3.9 \times 10^{12} \text{ sec.}^{-1} \end{array} \right.$	Same as for (1).
(6) Vacuum	$\left\{ \begin{array}{l} \text{No dispersion.} \\ \epsilon' \text{ increases greatly, particularly at low frequencies.} \end{array} \right.$	

two peaks at 10 and 88 kc (Fig. 13), Narrower bands in the absorption edge were then used for irradiation (cf. Fig. 4) and showed that filter curves 3 and 4 produced the dispersion peaks (Fig. 14). Under irradiation corresponding to curve 3, $\tan \delta$ showed a broad dispersion peak only at 10 kc, while that produced by irradiation corresponding to curve 4 gave both dispersion peaks at 10 and 88 kc. The 10-kc peak is larger in amplitude than that corresponding to curve 3. For irradiation corresponding to curve 4, the 88 kc

Fig. 10. Effect of temperature and time on the formation of absorption centers as shown by $(\tan \delta)_{\max}$.

peak is smaller by a factor of 2 than the 10-kc peak.

The time of irradiation using $4200 \pm 100\text{Å}$ was then varied (Fig. 15). It was observed that in 3-h. exposure no dispersion peak could be produced; after 6-h. exposure the $\tan \delta$ peak value reached a maximum of 0.48 and there was no further rise even at 15 h.

Effect of Silver and Copper

Boules A received at a later date gave no dielectric absorption spectra.

Fig. 11. Dielectric constant and loss vs. frequency for rutile samples heated to 820°C in different atmospheres before quenching at -180°C.

Fig. 12. Infrared absorption band for untreated rutile.

Fig. 13. Dielectric loss characteristic for rutile after long exposure to irradiation at $4200 \pm 100 \text{ \AA}$.

As mentioned, earlier Boules A contained a 0.01 percent excess of both silver and copper. The introduction of silver colors the crystal slightly yellow and shifts its optical absorption curve (Fig. 16) by about 120 Å toward the longer wavelength. The values of $\tan \delta$ and κ' show a marked increase but no maximum (Fig. 17).

Copper causes no color change. Quenching from 820°C produces a marked increase in the $\tan \delta$, especially at lower frequencies, but no maximum (Fig. 18).

Fig. 14. Dielectric constant (solid lines) and loss (dashed lines) characteristics for rutile after long exposure to irradiation at $4140 \pm 23A$ (open circles) and $4155 \pm 23A$ (solid circles).

Fig. 15. Variation for rutile of $(\tan \delta)_{\max}$ vs. time of irradiation at $4200 \pm 100A$.

Fig. 16. Absorbance characteristic of untreated rutile before and after introducing silver.

Fig. 17. Dielectric constant (solid lines) and loss (dashed lines) characteristics of rutile with introduced silver before (open circles) and after (solid circles) quenching.

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Fig. 18. Dielectric constant (solid lines) and loss (dashed lines) characteristics of rutile with introduced copper before (open circles) and after (solid circles) quenching.

Discussion and Conclusions

There are three characteristic frequencies corresponding to the absorption centers (10 kc, 88 kc, and 14 Mc). They are observed only with the electric field parallel to the optic axis and are accompanied by an increase in low-frequency conductivity. This may mask lower frequency centers if high frequency dispersion is present. The 14-Mc centers are produced only by heating in nitrogen, while the 88-kc centers can be created by either thermal quenching or optical irradiation. The $\tan \delta$ peak shifts with temperature according to an activation-energy equation $f = f_0 e^{-U/kT}$, where f is the frequency of $(\tan \delta)_{\max}$. The activation energy U of 0.18 ev may correspond to the infrared absorption of 3.45μ , observed by Cronmeyer.²⁾ Curves of κ' and κ'' for thermal quenching have been re-plotted in Fig. 19 from Fig. 7. The separation of κ'' in both conduction losses and dispersion peak is shown for the room temperature measurements. The nature of the absorption centers has to be more accurately clarified by further experiments. Obviously, some kind of double-well model applies. The strong anisotropy of the centers is understandable from the crystal structure (Fig. 1): Along the optic axis the Ti ions and also the oxygen ions form rows of like atoms, while perpendicular to the axis sequences of cations and of anions interfere with each other.

In the literature we find low-frequency absorptions reported for lithium fluoride⁴⁾ and the alkali halides,^{5, 6)} where the vacancy mechanism is effective. They have also been reported for rutile⁷⁾ when several mols

4) J. S. Dryden and Daas Narayana Rao, J. Chem. Phys. 25, 222 (1956).

5) R. G. Breckenridge, J. Chem. Phys. 16, 959 (1948).

6) R. G. Breckenridge, *inid.* 18, 913 (1950).

7) G. I. Skanavi and A. I. Demeshina, Zhur. Eksptl. i Teoret. Fiz. 19, 3 (1949).

Fig. 19. Characteristics of κ' and κ'' for quenched rutile at various temperatures and of conductivity and relaxation contribution to κ'' at room temperature.

of calcium, strontium or magnesium oxides per 100 mols TiO_2 were added to the melt from which the crystals were grown.

Acknowledgments

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