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Electrical and Optical Investigation of Absorption Centers in Rutile Single Crystals*

K. G. SRIVASTAVA†
Laboratory for Insulation Research, Massachusetts Institute of Technology, Cambridge, Massachusetts

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Absorption centers in single crystals of rutile, causing relaxation spectra in the low-frequency range, can be produced by thermal quenching or optical irradiation at the edge of the characteristic absorption region (4200 A). They are only observed when the ac field is applied parallel to the optic axis. The temperature dependence of the main dispersion peak indicates an activation energy of 0.18 ev. Introduction of silver or copper by thermal diffusion did not produce low-frequency absorption maxima.

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] Once rutile single crystals, grown as boules by the flame-fusion technique, became available, an extensive study of their electrical and optical properties was initiated a number of years ago,[2] and has since been continued in various laboratories.[3] The purpose of the present investigation was to study the formation of absorption centers in the electrical frequency range.

EXPERIMENTAL PROCEDURES

Crystal plates (ca 3×2×2 mm) were cut from boules[4] with the smallest dimension either parallel or perpendicular to the optic axis (accuracy of ±1°), polished, cleaned, and annealed for several hours in oxygen.

For the production of absorption centers two methods were used:

(*a*) *Thermal quenching*. The sample was placed in a Vycor or alundum boat, inserted in a Vycor tube, and heated to selected temperatures between 330° and 900°C. A slow current of oxygen, air (dried or undried), nitrogen, or helium was passed over the sample. After heating for the desired length of time, the sample was removed and quenched in liquid nitrogen. In later experiments, heating and rapid quenching of the sample could be accomplished without removal from the system (Fig. 1). The basket containing the sample was dropped into liquid oxygen, condensed by liquid nitrogen.

(*b*) *Optical irradiation*. The optical irradiation of samples was confined to narrow bands (1 to 6, Fig. 2) in the tail of the ultraviolet characteristic absorption. A xenon arc which provides a continuum in this wavelength region served as light source; infrared was filtered out by a water jacket with quartz windows. A multilayer dielectric interference filter (Baird Atomic Company) of suitable constants provided the narrow transmission regions by rotation about a vertical axis. (Rotation by 20 degrees shifted the wavelength of peak transmission from 4194 to 4088±2 A.) The intensity of the radiation, checked photoelectrically, varied less than 5%.

The initial state of the samples could be restored by heating followed by slow cooling. The absorption centers in quenched samples could also be destroyed by exposure to intense sunlight for several hours. Sunlight,

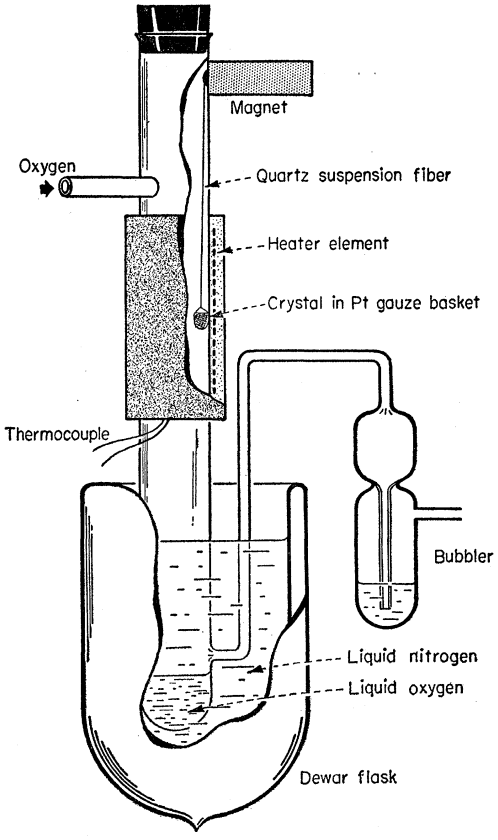

FIG. 1. Apparatus for thermal quenching.

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† Present address: Allahabad University, Allahabad, India.

[1] A. von Hippel, R. G. Breckenridge, F. G. Chesley, and L. Tisza, Ind. Eng. Chem. **38**, 1097 (1946).

[2] D. C. Cronemeyer, Phys. Rev. **87**, 876 (1952).

[3] See the recent survey by F. A. Grant, Revs. Modern Phys. **31**, 646 (1959).

[4] Made by the National Lead Company (Boules A) and the Line Air Products Company (Boules B).

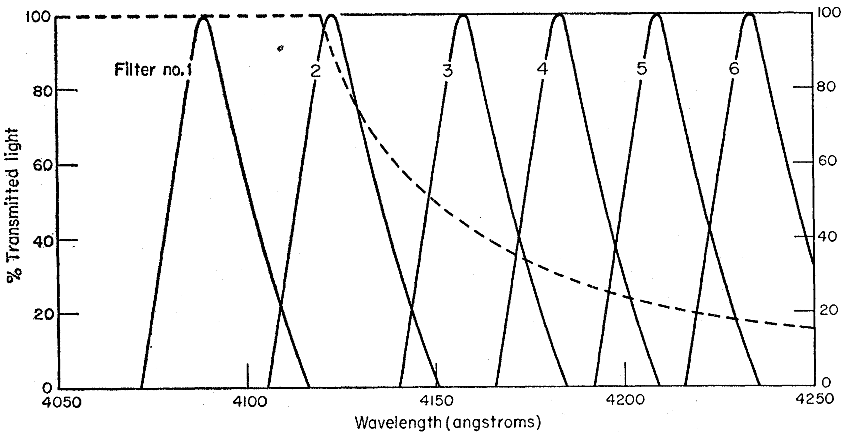

FIG. 2. Transmission characteristics on interference filters used for irradiation (solid lines) in reference to eigenabsorption edge of rutile (dashed line, right-hand scale).

when filtered through a thick glass plate, proved ineffective.

The presence of absorption centers was detected by dielectric constant and loss characteristics. The optical absorption curves in the visible and infrared regions did not show any change. Dielectric measurements ranged from 100 cps to 100 Mc/sec (Table I). For measuring capacitances $<4\ \mu\mu\text{f}$, the crystal holder was connected in parallel with a linear micrometer capacitor.

Conducting silver paint served as electrodes for room- and low-temperature measurements after control experiments had shown that in this range the results were the same as with evaporated electrodes. The 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. Figure 3 shows the various sample holders; the oscillator output was held below 2 to 3 volts.

EFFECT OF SILVER OR COPPER IMPURITIES

In crystals received during the latter part of the work, absorption centers could not be produced by quenching or optical irradiation. Spectral analysis[5] showed that the earlier samples contained slightly more (0.01%) silver and copper. Attempts were therefore made to introduce silver and copper in the newer samples by thermal diffusion.

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

For the introduction of copper a temperature of 1370°C was used. Since cuprous oxide is stable even at this temperature, the sample together with finely divided pure copper filings was placed in a quartz tube, which was then evacuated, sealed, and heated for 14 hours. Copper diffused in, but the samples assumed a dark color (almost opaque) because of oxygen loss. After reoxidation at 700°C they resumed their characteristic color, and the presence of copper could only be detected by increased dielectric loss at low frequencies. Hence, silver or copper do not produce the characteristic absorption peaks observed in the original crystals.

RESULTS

Low-Frequency Dispersion Obtained by Thermal Quenching

The variation of the loss tangent with frequency at room temperature for a typical quenched-in dispersion (field applied parallel and perpendicular to the optic axis) is shown in Fig. 4. The peak at 88 kc/sec appears only when the field is parallel to the optic axis; it can be annealed out and recreated. Measurements as function of temperature show a systematic shift (Fig. 5). The thermal change of $(\tan\delta)_{\max}$ in amplitude and frequency is given in Fig. 6. At −180°C the peak decreased by a factor of 100. The formation of the absorption was also investigated as function of heating time and temperature prior to quenching (Fig. 7). No centers could be produced by heating at 400°C for 12 hours; less than one hour sufficed to produce saturation at 860°C.

In the measurements reported thus far, the samples were heated in oxygen before quenching. Figure 8

TABLE I. Equipment used for dielectric measurements.

Frequency range	Bridges General Radio type	Oscillators General Radio type	Detector
100 cps to 40 kc/sec	716-C	713-B	Designed[a] and built in this laboratory.
40 kc/sec to 500 kc/sec	716-C	805	
500 kc/sec to 18 Mc/sec	916-A	805	Wells Gardner BC-348-N receiver.
28 Mc/sec to 100 Mc/sec	1601-A	805 and 1208-A	National hfs receiver with BC-348-N receiver.

[a] J. L. Upham, Rev. Sci. Instr. 22, 659 (1951).

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[5] New England Laboratories for Industrial Research and Development, Ipswich, Massachusetts.

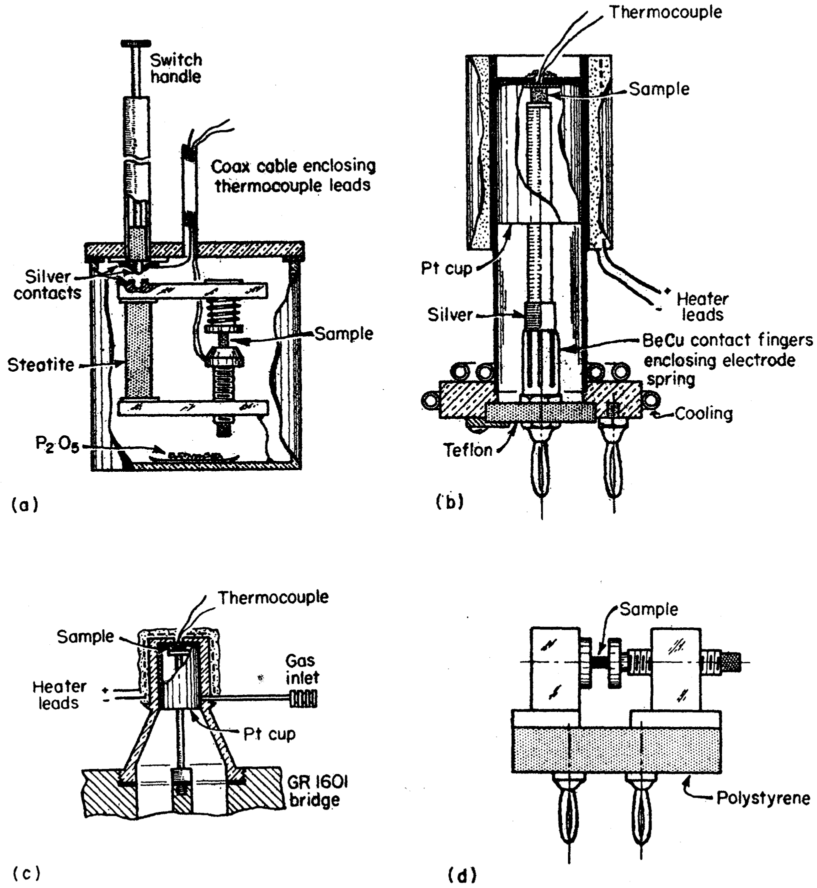

FIG. 3. Crystal holders used in the dielectric measurements (a) for low-temperature immersion; (b) for high temperatures; (c) for high frequencies (36 to 100 Mc/sec); (d) for room temperature.

illustrates the profound influence of the type of atmosphere used during heating at 820°C followed by quenching at −180°C. While helium causes only a slight shift, vacuum eliminates the absorption, and nitrogen creates a different one at higher frequencies.

Optical Irradiation

Optical irradiation of samples from Boules A at 4200±100 A produced two peaks at 10 and 88 kc/sec (Fig. 9, curve a). Narrower bands in the absorption edge were then used for irradiation (see Fig. 2) and showed that radiation at 4155±23 A produced only the one peak (Fig. 9, curve c) at 10 kc/sec, while radiation at 4140±23 A produced both dispersion peaks (Fig. 9, curve b). The buildup of the absorption peak at 10 kc/sec by irradiation with 4200±100 A is illustrated in Fig. 10.

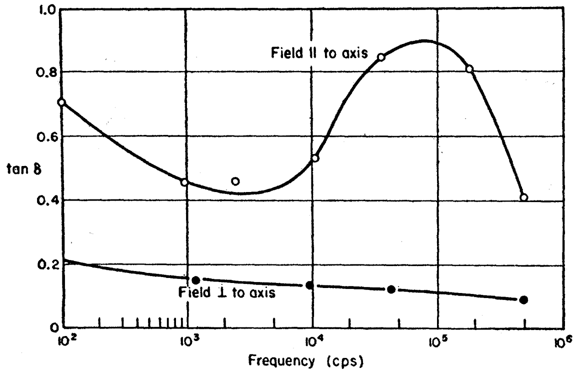

FIG. 4. Loss tangent vs frequency for quenched rutile sample at room temperature.

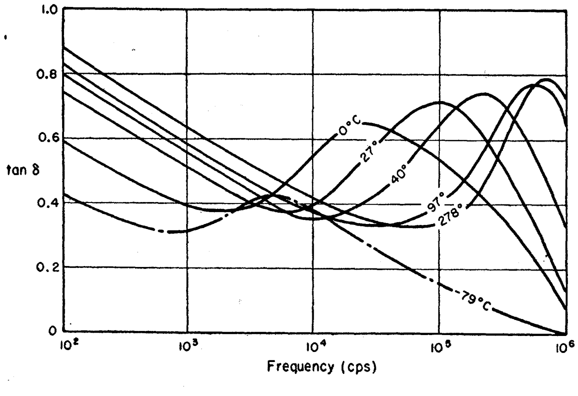

FIG. 5. Thermal shift of the quenched-in absorption of rutile.

DISCUSSION

Three characteristic frequencies corresponding to absorption centers (10 kc/sec, 88 kc/sec, and 14 Mc/sec) have been observed when the electric field is parallel to the optic axis. An increase in the low-frequency conductivity, caused by the quenching treatment, may mask additional absorption peaks. The 14-Mc/sec centers are produced only by heating in nitrogen, while the 88-kc/sec centers can be created by either thermal quenching or optical irradiation. The $\tan\delta$ peak shifts with temperature according to an activation-energy equation $\nu=\nu_0 e^{-U/kT}$, where ν is the frequency for $(\tan\delta)_{\max}$. The activation energy U of 0.18 ev may correspond to the infrared absorption of 3.45 μ, observed by Cronemeyer.[2] The nature of these absorption centers, which occur only in specific crystals, has to be clarified by further experiments.

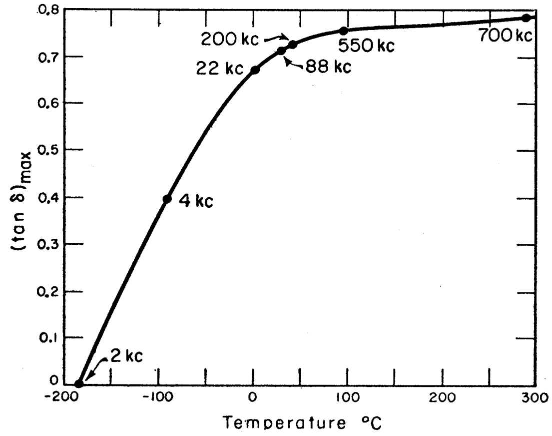

FIG. 6. Variation of loss peak with temperature of quenched-in absorption.

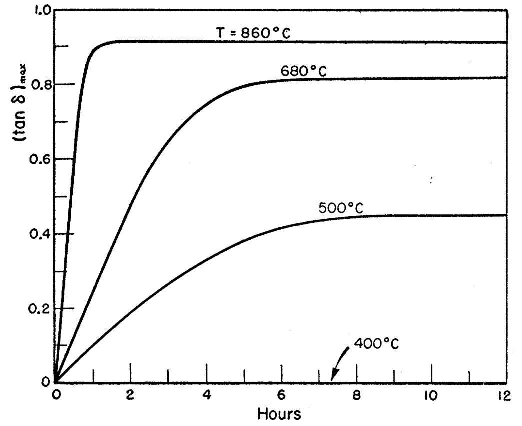

FIG. 7. Effect of temperature and time before quenching on build-up of absorption.

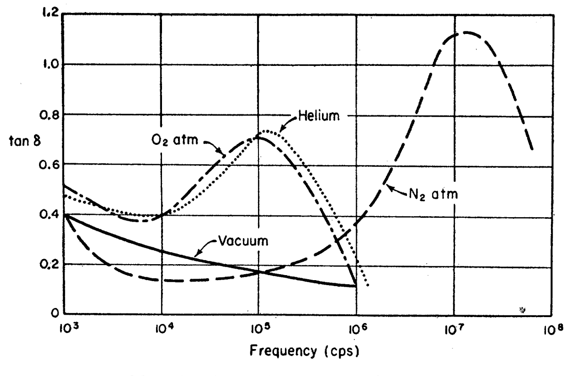

FIG. 8. Effect of heating in various atmospheres before quenching.

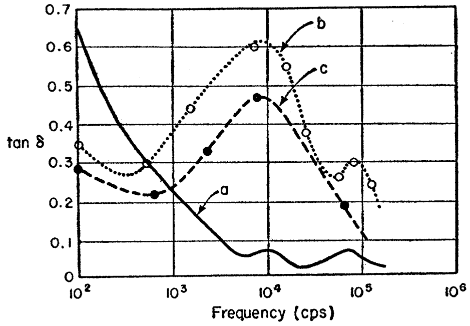

FIG. 9. Dielectric absorption spectra produced in rutile sample by optical irradiation.

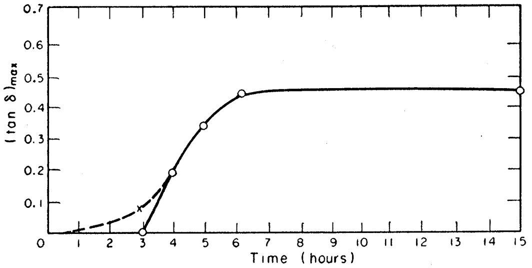

FIG. 10. Build-up of dielectric absorption maxima as function of time of irradiation at 4200±100 A.

Low-frequency absorptions were primarily found in the alkali halides, starting with a study by Breckenridge in this laboratory.[6] Absorptions have been seen in rutile[7] when several mole percent of calcium, strontium, or magnesium oxides were added to TiO_2 melts. The creation of such absorption centers by the quenching of rutile single crystals and by optical excitation apparently has not been reported; preliminary measurements were made by Sandler and Westphal[8] in the Laboratory for Insulation Research, and some characteristic absorption obtained by quenching or substitution.

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[6] R. G. Breckenridge, J. Chem. Phys. **16**, 959 (1948); **18**, 913 (1950).

[7] G. I. Skanavi and A. I. Demeshina, Zhur. Eksp. i Teoret. Fiz. **19**, 3 (1949).

[8] Y. L. Sandler and W. B. Westphal (unpublished, 1954).

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Transfer of Electric Charges through Rutile Single Crystals*

K. G. Srivastava†
Laboratory for Insulation Research, Massachusetts Institute of Technology, Cambridge, Massachusetts

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Electron transfer and onset of field emission has been investigated in TiO_2 single crystals with dc current-time characteristics parallel and perpendicular to the optic axis as function of voltage, temperature, electrode material, and light absorption. The currents are much larger and field emission sets in at lower voltage when the field is parallel to the optic axis. Higher temperature favors the current transfer by increasing the carrier mobility. The effect of different electrode materials proved minor, except in the case of Ti, which as cathode raised the current by about one order of magnitude. Photoelectric measurements showed that, in the critical voltage region of incipient field emission, light absorption can apparently force the current reversibly into the field-emitting stage.

THE PROBLEM

THE transfer of electrons through alkali halide crystals has been studied in the Laboratory for Insulation Research in some detail by a novel use of *F*-center discoloration.[1,2] Additively colored crystals can be described as electrons frozen into a positive matrix. The electrons may be mobilized by light absorption and moved toward the anode in a dc field. If they are discharged at the anode but not replaced from the cathode, a cathode fall builds up in an adjustable manner. When the field gradient at the cathode becomes high enough to enforce field emission, permanent currents can be drawn as long as the incident light keeps the electrons mobilized throughout the crystal. By observing these electronic currents as function of time, with voltage, temperature, and crystal treatment as adjustable parameters, much can be learned about field emission into dielectrics.

This work can be extended to crystals in which the electron transfer does not require optical activation. In TiO_2, for example, electrons move relatively freely, once mobilized by reduction or light absorption.[3] At the same time rutile offers strong anisotropy and high dielectric constant, two features of great interest for field-emission studies. The present investigation reports on the dc current transfer through rutile single crystals

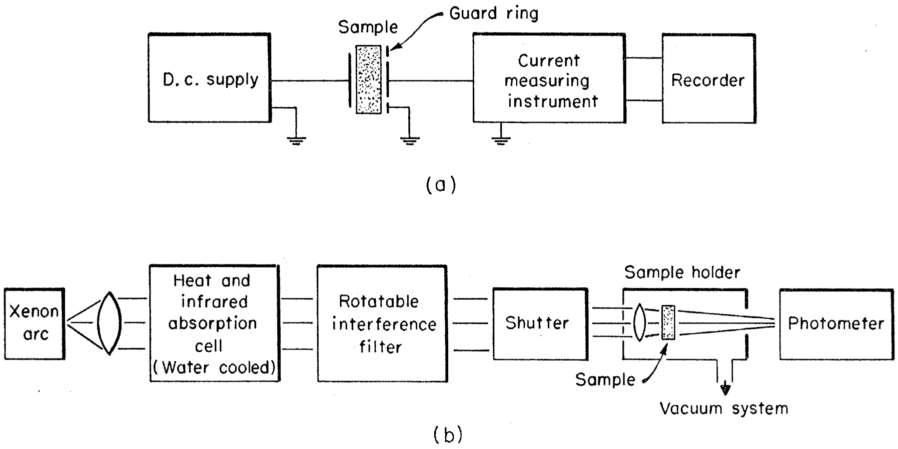

FIG. 1. Schematic diagram of measuring equipment: (a) electrical system; (b) optical system.

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* This research was supported by the U. S. Atomic Energy Commission.

† Present address: Allahabad University, Allahabad, India.

[1] A. von Hippel, E. P. Gross, J. G. Jelatis, and M. Geller, Phys. Rev. **91**, 568 (1953).

[2] M. Geller, Phys. Rev. **101**, 1685 (1956).

[3] D. C. Cronemeyer, Phys. Rev. **87**, 876 (1952).