are unfilled states of 3*d* character in the alloys used in the present measurements. It is apparent that rigid-band interpretations of properties of binary alloy systems should be used with extreme care if at all. It is doubtful if low-temperature heat-capacity measurements of binary alloy systems can be used to construct density-of-states curves for pure metals.

## ACKNOWLEDGMENTS

The author wishes to thank Dr. L. J. Dijkstra for his helpful discussions of the metallurgical problems associated with these measurements, and also for his measurement of the lattice spacing of one of the alloys and his help in microscopic examinations. Thanks are due Mr. Arthur Mosen for the chemical analysis, Mr. George Schmitt for his help in polishing metallurgical specimens, and Mr. Raymond Bartold for his help in setting up the experiments. Finally, the author wishes to thank Dr. P. H. Miller, Jr., for his interest in the work and for his helpful comments and discussions of the measurement techniques.

---

PHYSICAL REVIEW VOLUME 113, NUMBER 3 FEBRUARY 1, 1959

# Optical Transmission of Heat-Treated Strontium Titanate†

H. W. Gandy
*Electronics Laboratory, General Electric Company, Syracuse, New York*

(Received June 18, 1958)

The room-temperature optical transmission spectra of pure and doped $SrTiO_3$ crystals have been studied after heating them in oxygen and vacuum; spectral measurements were made in the quantum energy range from 0.1 to 3.4 ev.

A blue color, with strong attendant absorption in the infrared, can be induced in the pure crystals by heating them in vacuum with absorption maxima occurring at 0.9 and 2.9 ev. This induced absorption can be removed by heating the crystals in oxygen. Prolonged heatings of the pure, stoichiometric crystals in oxygen have failed to induce any measurable change in the transmission spectra in the aforementioned energy range.

Optical absorption can be induced in iron- and cobalt-doped $SrTiO_3$ crystal samples by heating them in oxygen; this absorption can be removed by heating the crystals in vacuum. The induced absorption occurs primarily at high quantum energies in the spectra of these doped crystals, with maxima occurring at 2.75 and 2.2 ev in the iron-doped samples, and at 3.0 and 2.6 ev in the cobalt-doped samples. It is suggested that the induced absorption observed in the doped crystals involves a controlled change in the valence states of these impurities.

## INTRODUCTION

INVESTIGATIONS of the optical properties of single crystals of pure strontium titanate have been reported several times in recent years. These crystals are grown by the flame-fusion method using an oxygen-hydrogen flame in a Verneuil-type furnace at a temperature of about 2100°C; the purity of the $SrTiO_3$ furnace feed material and the details of the crystal-growing process may be found elsewhere.[1,2] The structure of $SrTiO_3$ is that of a cubic perovskite, with one molecule per unit cell; strontium ions are located at the corners of the unit cell, oxygen ions at the centers of the cell faces, and a titanium ion at the center of the unit cell. These $SrTiO_3$ crystals have a high index of refraction (2.407 at 5893 A), a low-frequency room-temperature dielectric constant at 310, and a dielectric loss tangent of 0.00025 when they are in the stoichiometric condition.[2,3] The onset of fundamental electronic absorption occurs at a quantum energy of about 3.2 ev,[4] and the optical absorption coefficient rises to about $10^4$ $cm^{-1}$ at an energy of 3.5 ev as estimated from diffuse reflectance measurements made in this laboratory. The absorption coefficient of these crystals in the stoichiometric condition is less than $10^{-1}$ $cm^{-1}$ over the energy range from 0.25 to 3.1 ev.[2,4] Strong absorption occurs for energies less than 0.20 ev, the maximum being located at 0.075 ev.[5]

For the most part, the previous investigations of the pure $SrTiO_3$ crystals were performed on them in the stoichiometric state. The present work is concerned primarily with the transmission spectra of both pure and doped $SrTiO_3$ crystals which are not in the stoichiometric condition.

## EXPERIMENTAL PROCEDURES

The pure and doped crystal samples used in this work were sawed from the boule form into slabs, ground to the desired thicknesses, while maintaining parallel faces, and then polished on a rotating wax lap using a

---

† This work was supported by the U. S. Atomic Energy Commission.

[1] L. Merker, Mining Eng. **7**, 645 (1955).

[2] Levin, Field, Plock, and Merker, J. Opt. Soc. Am. **45**, 737 (1955).

[3] A. Linz, Phys. Rev. **91**, 753 (1953).

[4] J. A. Noland, Phys. Rev. **94**, 724 (1954).

[5] J. T. Last, Phys. Rev. **105**, 1740 (1957).

slurry of Linde Type A-5175 aluminum oxide in distilled water as the polishing agent.

The room-temperature transmission spectra were obtained using a sample-in, sample-out method. The measurements were made using a Perkin-Elmer Model 12C Spectrophotometer using both fused silica and rock salt optical components. A tungsten ribbon filament lamp and a Globar served as the radiation sources; a 1P28 photomultiplier tube, a lead sulfide cell, and a radiation thermocouple were used as the detectors. With different combinations of these components, transmission measurements could be made over the quantum energy range from 0.085 to 3.6 ev. Transmission measurements could be reproduced to ±0.5% in this energy interval.

The vacuum heatings given the samples were carried out in either a Kanthal-wound or a platinum-wound resistance furnace of the tube type with which either Mullite or vitrified alumina tubes were used as the vacuum envelopes. The samples were contained in platinum boats during the heatings, with only the edges of the samples in contact with the boats. The sample temperatures during the heatings were monitored by a Pt-Pt, 10% Rh thermocouple placed close to the sample inside the vacuum chamber. The kinetic pressure inside the furnace tubes during the vacuum heatings was $5\times10^{-4}$ mm Hg or less; these furnaces were also used for heating the samples in flowing oxygen at atmospheric pressure. The crystal samples were lightly polished after each treatment. In all the crystal samples investigated, it was found that the induced absorption was distributed throughout the thicknesses of the slab-shaped samples, and not merely near their surfaces.

## EXPERIMENTAL RESULTS

### Pure Crystals

The transmission spectra of a representative pure $SrTiO_3$ crystal sample after having been given various heatings are given in Fig. 1. The theoretical transmission spectrum of a nonabsorbing dielectric slab is given by curve 1; the relation $T=2n/(n^2+1)$ is used, where $T$ is the transmission of the slab, and $n$ is the index of refraction. The solid part of this curve was obtained by using published values of $n$, and the dashed portion of the curve was determined by using values of $n$ obtained by making a Cauchy extrapolation of the published values of $n$ into the near infrared.[2] The sharp decrease in the transmission for energies greater than 3.15 ev is ascribed to the onset of fundamental electronic absorption, whereas the rapid decrease in transmission for energies less than 0.2 ev is presumed to be due to lattice excitation. It is seen that curve 2, the sample in the untreated condition, lies just below the theoretical curve over most of the transparent region of the stoichiometric crystal, i.e., 0.2 to 3.1 ev. The vacuum heating of the pure crystals does induce some absorption in the visible which gives rise to a blue color in them, but inspection of curves 3, 5, and 6 indicates that the induced absorption is greatest in the infrared. The vacuum heating has induced transmission minima at 0.9 and 2.9 ev with the transmission decreasing for quantum energies less than 0.4 ev. Comparison of curves 2 and 4 in the vicinity of 1 ev would seem to indicate that the untreated crystal was slightly oxygen deficient.

Heating this sample in the stoichiometric state at a temperature of 860°C for two hours in vacuum failed to induce measurable absorption. (It is therefore thought that the "freezing-in" temperature for the diffusion of oxygen in $SrTiO_3$ is somewhere around 850°C.) It should be mentioned here, that for all the sample heatings reported in this work, it took no more than twenty minutes after the end of a heating run for the sample temperature to drop to 850°C.

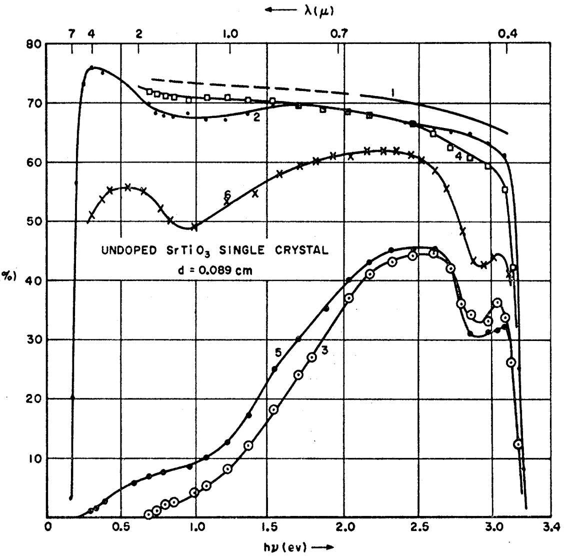

FIG. 1. Transmission spectra of heat-treated pure $SrTiO_3$ crystal. (1) Plot of $T=2n/(n^2+1)$; (2) untreated crystal; (3) 3 hours at 1040°C in vacuum; (4) $5\frac{1}{4}$hours at 1250°C in oxygen; (5) 2 hours at 1040°C in vacuum; crystal brought back to stoichiometry by oxygen heating, then (6) 2 hours at 960°C in vacuum.

The induced absorption spectra caused by the vacuum heating of the pure crystal sample are given in Fig. 2. Curves 1, 2, and 3 of Fig. 2 were derived by subtracting curves 3, 5, and 6 from curve 2 in Fig. 1. The induced absorption extends over a rather broad spectral region; however, two absorption maxima occur at energies of 0.9 ev and 2.9 ev. It is estimated that the diffusion coefficient for the induced absorption at 0.9 ev in these spectra is about $5\times10^{-8}$ cm$^2$/sec at a temperature of 1040°C. It should be noted that the oxygen heatings used to remove the vacuum-induced absorption did not induce any measurable change in the transmission spectra from that of the stoichiometric case, even though the heating times and temperatures were respectively longer and higher than those used in the vacuum heatings. Several other untreated pure samples were heated in oxygen at 1150°C for two hours and heated again for $5\frac{1}{4}$ hours at 1250°C. The transmission spectrum for each of these samples was measured after each oxygen heating; no significant changes (greater than 1%) from the untreated-sample spectra were noted in any of these spectra. It would appear therefore that prolonged oxygen heating of the pure crystals in the stoichiometric condition causes no induced absorption in the energy range from 0.13 to 3.2 ev.

## Doped Crystals

The transmission spectra obtained from a $SrTiO_3$ single-crystal sample containing iron as a deliberately added foreign impurity (0.02% $Fe_2O_3$ by weight added to the furnace feed material) after having been given several heat treatments are shown in Fig. 3. It first should be noticed that none of the treatments given the crystal engendered any significant changes in its transmission spectra for quantum energies less than 1.5 ev (the region where the absorption induced by vacuum heating of the pure crystals is the greatest). The untreated crystal was a light yellowish-brown color, and its spectrum is given by curve 2. Heating the sample in oxygen caused it to turn a dark brown color; the spectrum is given by curve 3. Two subsequent oxygen heatings of the sample failed to induce any further optical absorption in the crystal; hence it would appear that there is a "saturation effect" occurring. The crystal was then heated in vacuum causing it to become almost colorless; the spectrum of the crystal in this state is given by curve 4. It is noteworthy that this spectrum approaches that of a pure crystal in the stoichiometric condition. Heating the crystal in oxygen again caused it to turn a dark brown color, and the corresponding spectrum is shown by curve 5. These phenomena have been observed with several other iron-doped crystal samples.

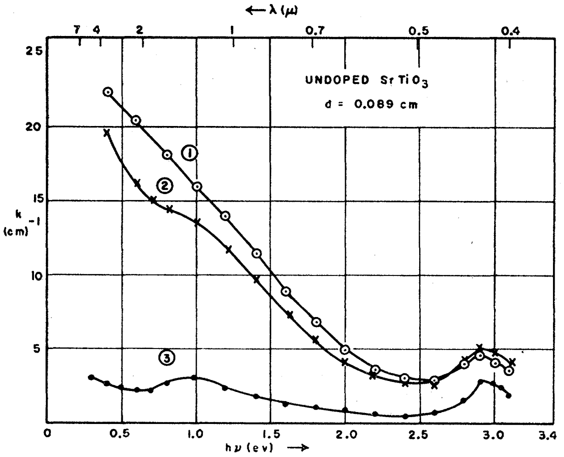

FIG. 2. Induced absorption in a pure $SrTiO_3$ crystal caused by vacuum heating. (The induced absorption coefficient, $k$, has been calculated correcting for both reflection losses and multiple passages of light through the sample.) (1) 3 hours at 1040°C; (2) 2 hours at 1040°C; (3) 2 hours at 960°C.

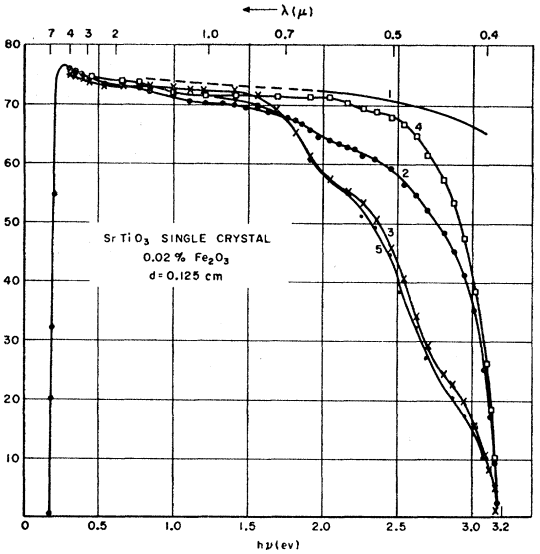

FIG. 3. Transmission spectra of heat-treated iron-doped $SrTiO_3$ crystal. (1) Plot of $T=2n/(n^2+1)$; (2) untreated crystal; (3) $5\frac{1}{2}$ hours at 1200°C in oxygen. Crystal heated for 5 hours at 1215°C in oxygen, and then for 2 hours at 1325°C in oxygen. No measurable change in the spectra could be detected after each heating from that given by curve 3; then (4) $2\frac{1}{2}$ hours at 1300°C in vacuum; (5) 3 hours at 1360°C in oxygen.

The induced absorption spectra in the iron-doped $SrTiO_3$ crystal caused by the oxygen heat treatments are shown in Fig. 4(A). Curves 1, 2, and 3 in Fig. 4(A) were derived by subtracting curves 3 and 4, 2 from 4, and 4 from 1, respectively, in Fig. 3. Curves 1 and 2 in Fig. 4(A) represent the optical absorption induced in the iron-doped samples by heating it in oxygen; curve 3 measures the difference in absorption of the iron-doped crystal in the "almost colorless" state from that of a pure crystal in the stoichiometric condition. The spectra in Fig. 4(A) indicate that two absorption bands centered about quantum energies of 2.2 and 2.75 ev are induced by heating the iron-containing $SrTiO_3$ crystal in oxygen. It is expected that curve 3 should go through a maximum at higher energies and then go to zero at a quantum energy of about 3.25 or 3.3 ev.

The spectra obtained from a cobalt-doped $SrTiO_3$ crystal sample (0.02% $Co_2O_3$ by weight added to the furnace feed material) after having been given various heat treatments are shown in Fig. 5. The untreated crystal was orange in color, and its spectrum is given by curve 2. Heating the sample in oxygen caused it to turn a darker orange color and the spectrum of the crystal in this state is shown by curve 3. A subsequent vacuum heating of the crystal rendered it almost color-

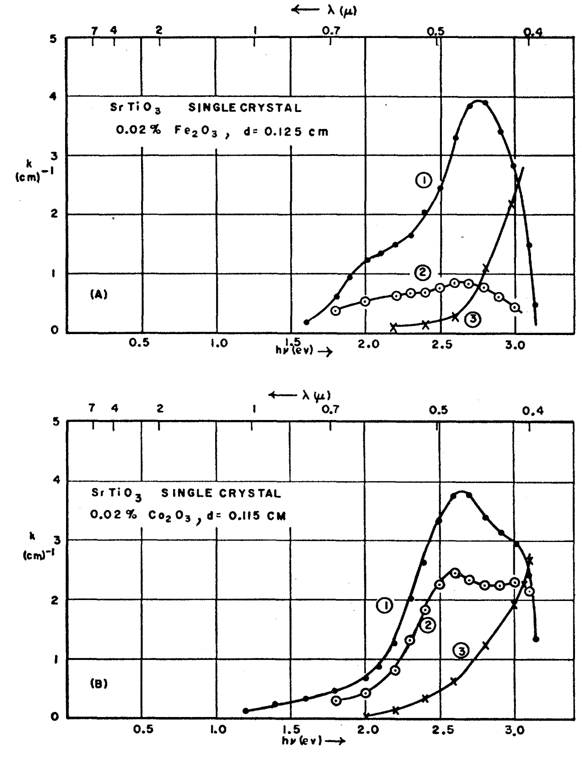

FIG. 4. (A) Induced absorption spectra of iron-doped $SrTiO_3$ crystal caused by oxygen heating. (See text for explanation.) $k$ was calculated as in Fig. 2. (B) Induced absorption spectra of cobalt-doped $SrTiO_3$ crystal caused by oxygen heating. (See text for explanation.) $k$ was calculated as in Fig. 2.

less and its spectrum in this condition is given by curve 4. Heating the crystal in oxygen again caused it to turn a bright orange color, and then curve 5 was measured. Similar results were obtained with other cobalt-doped $SrTiO_3$ crystal samples.

The optical absorption induced in the cobalt-doped $SrTiO_3$ crystal by heating it in oxygen are shown by curves 1 and 2 in Fig. 4(B). Curves 1, 2, and 3 in Fig. 4(B) were derived by subtracting curves 5 from 4, 2 from 4, and 4 from 1, respectively, in Fig. 5. Curves 1 and 2 represent the optical absorption induced in the cobalt-doped crystal by heating it in oxygen, whereas curve 3 is a measure of the difference in the optical absorption of the cobalt-doped $SrTiO_3$ crystal in the "almost colorless" condition from that of pure $SrTiO_3$ in the stoichiometric state. There appear to be two induced absorption bands in these spectra located at 2.6 and 3.0 ev.

In examining the results given in Figs. 4(A) and (B), it is evident that the primary effect of the oxygen heat treatments is to induce optical absorption at high quantum energies; the gross features of the induced spectra in the two figures are rather similar; however, there are differences in their details. It should also be noticed that this phenomenon is a reversible and easily measured effect in these crystals. By applying Smakula's equation to the 2.75-ev band of curve 1 of Fig. 4(A) (saturation case in the iron-doped $SrTiO_3$ sample), one obtains a value of $(Nf)=1.2\times10^{16}$ per cc, where $N$ is the concentration of absorbing centers and $f$ is the oscillator strength for this optical transition.[6]

The absorption spectra for $SrTiO_3$ and $BaTiO_3$ crystals for quantum energies less than 0.2 ev are given in Fig. 6. Curve 1 gives the absorption spectra of a pure, untreated $SrTiO_3$ crystal sample before and after heating in oxygen. The absorption spectra of an iron-doped crystal before and after heat treatment in oxygen are given by curve 2. The position of the absorption maxima at 0.163 ev is not measurably affected by either the presence of iron as a foreign impurity in the $SrTiO_3$ or by heating the pure or iron-doped crystals in oxygen; preliminary measurements have been made on $SrTiO_3$ crystals doped with chromium, nickel, and manganese, and similar results have been obtained.

The absorption spectrum of a Harshaw polydomain $BaTiO_3$ crystal is given by curve 3; an absorption maximum at 0.153 ev is apparent. The 0.163-ev band in pure $SrTiO_3$ crystals in the stoichiometric condition has been previously reported by Noland[4] and Levin *et al.*,[2] and the 0.153-ev band in $BaTiO_3$ has been observed by Hilsum[7]; it is possible that these two bands are satellites of the strong 0.076-ev and 0.062-ev lattice absorption bands observed in $SrTiO_3$ and $BaTiO_3$ by Last.[5] It seems probable that these satellite bands are caused by lattice excitation in the perovskite structure of these

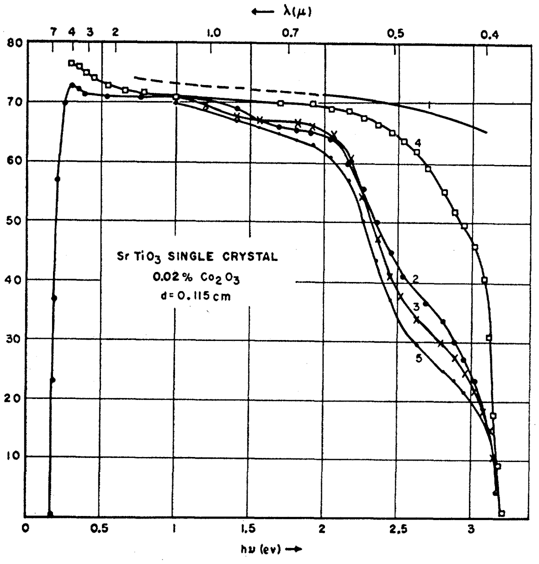

FIG. 5. Transmission spectra of heat treated cobalt doped $SrTiO_3$ crystal. (1) Plot of $T=2n/(n^2+1)$; (2) untreated crystal; (3) 5 hours at 1190°C in oxygen. Crystal heated for 2 hours at 1325°C in oxygen; no measurable change in spectrum after this treatment from that given by curve 3; then (4) 2½ hours at 1300°C in vacuum; (5) 3 hours at 1260°C in oxygen.

---

[6] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 664.

[7] C. Hilsum, J. Opt. Soc. Am. **45**, 771 (1955).

titanate because their occurrence does not seem to be measurably affected by the presence of some foreign impurities or by oxygen heating. Preliminary vacuum heating experiments indicate that optical absorption is induced in the pure $SrTiO_3$ crystals which extends to the low-energy side of the 0.163-ev band.

## DISCUSSION OF RESULTS

The optical absorption spectra obtained for the pure $SrTiO_3$ crystal samples in the stoichiometric condition in this work are in substantial agreement with those obtained by Noland[4] and Levin *et al.*,[2] on these crystals. The vacuum and oxygen heating experiments carried out with the pure crystals show that the induced absorption is a reversible effect and the amount of induced absorption can be controlled experimentally. It seems likely that the vacuum heating of these crystals has a reducing effect upon them causing a loss of oxygen from their perovskite lattice; part of the observed induced absorption is probably caused by the excitation of electrons trapped at oxygen ion vacancies in the defect lattice. It is noteworthy that the induced absorption extends over a large energy range and probably extends into the low-energy region where it is believed that lattice excitation is the dominant mechanism for optical absorption.

### Doped Crystals

The gross appearance of the optical absorption induced in both the iron- and cobalt-doped $SrTiO_3$ crystals by heating them in oxygen is rather similar, although, as was mentioned before, there are some detailed differences between the two spectra. It is thought that there is a common mechanism giving rise to the observed high-energy absorption induced in both the iron- and cobalt-doped crystals. In contemplating possible origins of this induced absorption, one should take under consideration at least the following experimental observations.

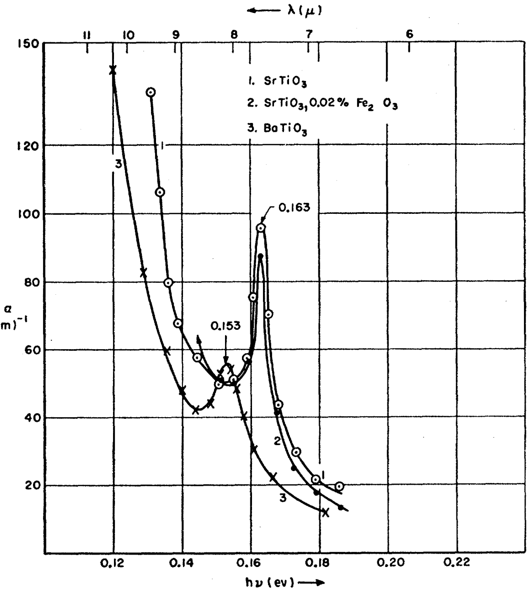

FIG. 6. Low-energy absorption spectra of $BaTiO_3$ and $SrTiO_3$. (See text for explanation.) Absorption coefficient, α, has been calculated, correcting for reflection losses.

(1) It has not been possible to induce measurable optical absorption in the pure, stoichiometric $SrTiO_3$ crystal samples by heating them for prolonged periods of time at high temperatures in flowing oxygen, whereas it is possible to induce absorption (primarily at low energies) by heating them in vacuum for shorter times at considerably lower temperatures. In the latter effect, the amount of absorption induced can be controlled by varying the time and/or the temperature of vacuum heating; furthermore, the absorption thus induced can be removed either partially or completely by heating the crystals in oxygen.

(2) It is possible to induce optical absorption at primarily high energies in the iron- and cobalt-doped $SrTiO_3$ crystals by heating them in oxygen. This induced absorption can be removed by subsequently heating the crystals in vacuum. The spectra of the crystals then approach that of a pure crystal in the stoichiometric condition.

(3) There appears to be a "saturation effect" in the amount of optical absorption which can be induced in either the iron- or cobalt-doped $SrTiO_3$ crystals after extended heating times in oxygen at high temperatures.

(4) Since the optical absorption induced in the doped $SrTiO_3$ crystals by heating them in oxygen occurs primarily at large quantum energies, the induced absorption probably results from electronic rather than lattice excitation. The preferred chemical valence states of both iron and cobalt are known to be $+2$ and $+3$.

It seems clear from the above that the presence of iron or cobalt in the lattice as well as the presence of an oxygen atmosphere during high temperature heating are necessary for the production of the high-energy absorption in the doped $SrTiO_3$ crystals. The reversible nature of induced absorption and the "saturation effect" observed in the doped crystals suggests that the valence states of the iron and cobalt impurity ions in the lattice are changed by the different heat treatments given these crystals. It seems reasonable to assume that both the iron and cobalt ions are oxidized to the $+3$ valence state by the high-temperature oxygen heating.

One is tempted to assume that iron and cobalt ions substitutionally replace strontium ions in the $SrTiO_3$ lattice because it was possible to get both the iron- and cobalt-doped crystals into the "almost colorless" state. When the doped crystals are in this state, it is assumed that the iron and cobalt are in the $+2$ valence state giving rise to a transmission spectrum which approaches that of a pure crystal in the stoichiometric state. If the iron and cobalt ions existed in either the $+2$ or $+3$ valence state while being situated in either titanium or interstitial positions in the lattice, the methods used in the coloring and the bleaching of these crystals and the requirement of local electric charge neutrality would demand that either electrons or holes be trapped in their vicinity, and should give rise to optical absorption; hence it should not be possible to get these crystals into the "almost colorless" state. Since this does not agree with experiment, it seems reasonable that the iron and cobalt ions do not occupy these positions in the lattice. However, even if all the iron (or cobalt) in the crystal were in the $+2$ valence state substituting for the strontium ions, it should be expected that their presence in the crystal will slightly increase the optical absorption in the low-energy tail of the fundamental electronic optical absorption band. This effect is probably contributing to part of the absorption given by curves 3 of Figs. 4(A) and 4(B); certainly the oxygen-induced absorption is also contributing to this curve since no serious attempt was made to maximize the transmission spectra by successive heat treatments of the doped crystals in vacuum or oxygen.

These strontium titanate crystals are grown under reducing conditions at a temperature arouns 2100°C. Even though $Fe_2O_3$ (or $Co_2O_3$) is added to the furnace feed material, it seems reasonable that iron (or cobalt) in the $+2$ valence state exists in the molten cap of the boule under these conditions, and hence it is probable that these impurities replace $Sr^{+2}$ in the growing crystal. (It is interesting to note that if all the iron added to the furnace feed material remained in the finished crystal and contributed to the induced absorption, an iron concentration in the order of $10^{18}$ per cc would be expected, whereas the iron concentration as calculated previously from the saturated 2.75-ev band is in the order of $10^{16}$ per cc if all the iron remaining in the crystal contributes to the intensity of this band. Considering the relatively high volatility of iron at the temperature of crystal growth, such a possible large concentration difference is not unexpected.)

During the course of this work, it was found that x-ray irradiation of the doped crystals in the "almost colorless" state at room temperature caused the iron-doped crystal to become brown colored and the cobalt-doped crystal to become orange colored; similar x-ray irradiations of pure $SrTiO_3$ crystals in the stoichiometric condition failed to induce any measurable optical absorption. The x-ray-induced color is not stable in either of the doped crystals at room temperature, but fades in the presence of room light (this is not true of the color induced by oxygen heating). A similar irradiation effect has been observed by Soshea, Dekker, and Sturtz in MgO crystals containing iron.[8] They attribute the induced absorption in the MgO to an x-ray-induced change in the valence state of the iron ions. It is probable that a similar explanation is in order for the x-ray-induced color in the iron- and cobalt-doped $SrTiO_3$ crystals investigated in this work.

It is of interest to speculate about possible color center models which give rise to the optical absorption induced by oxygen-heating the iron- and cobalt-doped $SrTiO_3$ crystals assuming that these ions substitute for $Sr^{+2}$ in the $SrTiO_3$ lattice. The model which seems most attractive at present is similar to the one suggested by Wertz and Auzins for substitutional impurity ions in the $+3$ valence state in MgO.[9] Their suggestion as applied to doped $SrTiO_3$ in the colored condition would be $Fe^{3+}$ or $Co^{3+}$ substituting for $Sr^{2+}$ with one of the six nearest neighbor strontium ions absent; local charge neutrality requires that a hole be trapped at this vacancy. If the use of this model for doped $SrTiO_3$ is valid, then the induced absorption is probably due to optical excitation of this hole.

Experiments similar to the ones described here have been carried out with $SrTiO_3$ crystals doped with chromium, manganese, and nickel; oxygen and vacuum heatings of these crystals cause large changes in their transmission spectra, but these results do not fall into the simple pattern followed by the iron- and cobalt-doped crystals.

## ACKNOWLEDGMENTS

The author is indebted to M. D. Beals of the National Lead Company for supplying the crystals used in this work. He is also grateful to N. Schwartz and H. C. Rothenberg of this laboratory for helpful discussions concerning this work.

---

[8] Soshea, Dekker, and Sturtz, J. Phys. Chem. Solids **5**, 23 (1958).

[9] J. E. Wertz and P. Auzins, Phys. Rev. **106**, 484 (1957).