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# Refractive Index of Strontium Oxide*

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The refractive index of single crystals of strontium oxide has been measured for 6 wavelengths in the visible spectrum. The crystals were grown from the melt in a graphite resistance furnace by the method of Ohmic heating. They were ground and polished into prisms, and the refractive index was determined by the method of minimum deviation. The absolute refractive index for the best crystal varied from $1.86245 \pm 3 \times 10^{-5}$ at the wavelength 6562.82 Å to $1.92585 \pm 3 \times 10^{-5}$ at the wavelength 4046.56 Å.

## I. INTRODUCTION

INVESTIGATION of the alkaline-earth oxides has progressed at a relatively slow rate, primarily because of the difficulty of obtaining suitable single crystals of these materials. Recently, certain properties of single crystals of barium oxide have been investigated by Sproull and co-workers,[1] and some of the properties of single crystals of magnesium oxide have been investigated by Reiling and Hensley[2] and Wertz and co-workers.[3] Kemp and Neeley[4,5] have studied the optical properties of calcium oxide, and Ward and Hensley[6] have reported experiments on color centers in single crystals of this material. Information concerning experiments with single crystals of strontium oxide is even more fragmentary.[7]

Experimental study of these materials is of great interest not only because of their inherent properties but also because they afford an opportunity for investigation of divalent ionic bonding. Most of the present knowledge of ionic bonding has been gained through studies of the alkali halides. Since the alkaline-earth oxides are the divalent analogs of the alkali halides, they offer possibilities for further investigation of defect properties in this important class of solids.

It is the purpose of this article to describe a method we have developed by which single crystals of strontium oxide were grown and to report the results of precise measurement of the refractive index of single crystals of this material.

## II. EXPERIMENTAL

### A. Crystal Growth

The primary problems to be overcome in preparing single crystals of strontium oxide were the very high melting point (2430°C)[8] and the extreme chemical reactivity of this material at elevated temperatures. In spite of the problems associated with growth from the melt, this method was selected as the most promising because of the relatively high growth rates and large crystal size attainable. The general growth technique used was controlled cooling of molten strontium oxide contained in a solid cylindrical shell of strontium oxide to prevent contamination of the melt by impurities. The graphite resistance furnace, specimen, and associated equipment are shown schematically in Fig. 1. A cylindrical sample of sintered strontium oxide, which is a fairly good insulator at room temperature, was placed in the graphite resistance furnace between two graphite rods and heated until it would conduct an appreciable current which occurred at about 1600°C. A current of 25 to 45 A was passed through the sample and controlled in a manner such that the inside of the cylinder melted while the outside surface remained solid, and hence served as a crucible for the melt. During the time current passed through the strontium oxide cylinder, the graphite resistance furnace was turned off to reduce the probability of contamination of the specimen with carbon.

The cylindrical slugs of strontium oxide, $2\frac{1}{2}$ in. in

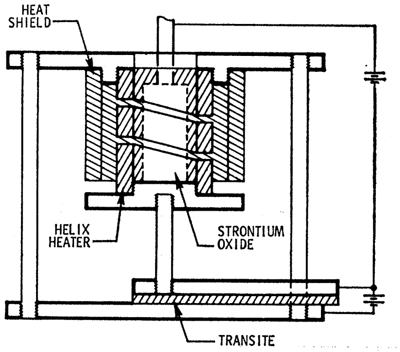

FIG. 1. The carbon resistance furnace with a SrO sample in place.

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[1] R. L. Sproull *et al.*, Rev. Sci. Instr. **22**, 410 (1951).

[2] G. H. Reiling and E. B. Hensley, Phys. Rev. **112**, 1106 (1958).

[3] J. E. Wertz *et al.*, Bull. Am. Phys. Soc. **9**, 706 (1964).

[4] J. C. Kemp and V. I. Neeley, J. Phys. Chem. Solids **24**, 332 (1963).

[5] V. I. Neeley and J. C. Kemp, J. Phys. Chem. Solids **24**, 1301 (1963).

[6] W. C. Ward and E. B. Hensley, Bull. Am. Phys. Soc. **10**, 307 (1965).

[7] L. V. Holroyd and J. L. Kolopus, Bull. Am. Phys. Soc. **10**, 374 (1965).

[8] *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, Cleveland, Ohio, 1958), 40th ed., p. 663.

TABLE I. The absolute refractive index $n$ of single crystals of strontium oxide determined by the method of minimum deviation for six wavelengths ($\lambda$ in Ångstrom units) in the visible spectrum. $\mathrm{PE}_n$ is the sum of the probable errors due to measurement of the refractive angle $A$ and the angle of minimum deviation $D$.

| $\lambda$ (Å)<br>Source | Prism No. | Refractive index | $10^5\,\mathrm{PE}_n$ | No. of measurements | $T$ (°C) | $P$ (mmHg) |
|---|---|---|---|---|---|---|
| 6562.82 | 1 | 1.86284 | 4 | 2 | 24 | 694 |
| H | 2 | 1.86245 | 3 | 6 | 23 | 701 |
| 5892.93 | 1 | 1.87091 | 7 | 2 | 24 | 694 |
| Na | 2 | 1.87084 | 3 | 6 | 23 | 701 |
| 5460.74 | 1 | 1.87826 | 4 | 4 | 23 | 696 |
| Hg | 2 | 1.87814 | 3 | 6 | 23 | 700 |
| 4916.04 | 1 | 1.89104 | 7 | 2 | 23 | 694 |
| Hg | 2 | 1.89091 | 3 | 6 | 22 | 702 |
| 4358.35 | 1 | 1.91056 | 4 | 2 | 24 | 694 |
| Hg | 2 | 1.91036 | 4 | 6 | 23 | 700 |
| 4046.56 | 1 | 1.92621 | 5 | 2 | 24 | 694 |
| Hg | 2 | 1.92585 | 3 | 6 | 22 | 670 |

diameter and 2 in. long, were prepared from anhydrous strontium oxide[9] by a dry-casting procedure. Attempts to slip cast the strontium oxide by the procedure described for calcium oxide by Cowan, Stoddard, and Nuckolls[10] were unsuccessful because of the great affinity of this material for the slightest trace of water.

In the dry casting method, a mixture of 5% strontium hydroxide and 95% strontium oxide by weight was lightly compressed in a graphite mold and heated to 500°C for 30 to 45 min. The strontium hydroxide melted at 375°C and bonded the strontium oxide powder together. The strontium oxide slug was then removed from the mold and sintered for 12 h at 1300°C. Sintering at this temperature, in addition to producing a mechanically strong slug whose density was approximately 70% of theoretical, decomposed any strontium hydroxide or carbonate which may have been present. Immediately after sintering, the cylinders were placed in the graphite furnace and the interior fused as described above. The method was not entirely satisfactory, but suitable crystals of good optical quality at least 1 mm×1 mm ×1 mm were obtained in about 10% of the attempts.

### B. Refractivity

Six of the crystals grown as described above were ground and polished into prisms, and from these two of the best were selected for the refractive index measurements. The measurements were made with a Gaertner spectrometer equipped with two verniers capable of direct reading to 20 sec of arc. To prevent the formation of strontium hydroxide on the faces of the prism during the course of the measurements, the prism was bathed in carefully dried air. A block diagram of the apparatus used to dry the air is shown in Fig. 2. Air was dried by first passing through a flask immersed in solid carbon dioxide and acetone. The air then flowed through a second flask equipped with a nichrome heater where the temperature of the air was raised to within 1°C of room temperature. The air then flowed through two steel cylinders, each of which contained 1 lb. of anhydrous calcium sulfate, after which the air was piped to a position $\frac{1}{4}$ in. above the prism and allowed to exit. The polished prism faces were examined periodically to detect the possible formation of strontium hydroxide, but none was found during exposure times as long as 20 h.

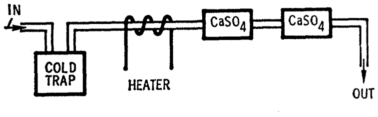

FIG. 2. Flow diagram of the air-drying system used to prevent the formation of SrOH on the prism faces.

The refractive index was computed from the usual relationship,

$$n=\frac{\sin\frac{1}{2}(A+D)}{\sin\frac{1}{2}A}, \tag{1}$$

where $A$ is the refractive angle of the prism and $D$ is the angle of minimum deviation. All angular measurements were made by the procedure described by Tilton,[11] which eliminates periodic and accidental positional errors of the scale marks. Each angular determination consisted of a series of measurements with the scale rotated through a segment of arc between measurements. The scale was rotated an amount selected to cause each scale mark used to appear twice in the series of measurements, once on each side of the angle. Any positional error of the scale mark affected the result twice but with unlike signs and was therefore eliminated from the average. The air temperature and barometric pressure were measured to the nearest degree centigrade and millimeter of mercury, respectively, to refer the measured refractive index to vacuum.

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[9] Purified anhydrous SrO supplied by the Fisher Scientific Company, Fair Lawn, New Jersey.

[10] R. E. Cowan *et al.*, Am. Ceram. Soc. Bull. **41**, 102 (1962).

[11] L. W. Tilton, J. Res. Natl. Bur. Std. (U. S.) **2**, 909 (1929).

## III. RESULTS AND DISCUSSION

The absolute refractive index of strontium oxide for six wavelengths in the visible spectrum is given in Table I. The refractive index of air as given by Born and Wolf,[12] corrected to laboratory temperature and pressure, was used to refer the measured refractive index to vacuum. The probable error $PE_n$ of $n$ is the sum of the probable errors due to measurement of the refractive angle $A$ and the angle of minimum deviation $D$. The differences in the refractive index of the two prisms are attributed to differences in crystal quality. Optical examination with a petrographic microscope revealed prism 2 to be of very high quality without strain. Prism 1 contained two distinct dislocations and appeared to be moderately strained. A spectroscopic analysis of the prisms was made to check the purity of the crystals. The following results were obtained: $SiO_2$, 0.03%; CaO, 0.5%; MgO, 0.1%; BaO, 0.5%; $Al_2O_3$, 0.1%; $Fe_2O_3$, 0.04%; $MoO_3$, 0.06%; MnO, 0.007%; NiO, 0.008%; CuO, 0.002%; $Ag_2O$, 0.0005%; and $Cr_2O_3$, 0.0001%. Analysis for carbon in the form of strontium carbide failed to reveal a trace (less than 1 part per million). The refractive index from 6600 to 4000 Å is shown in Fig. 3.

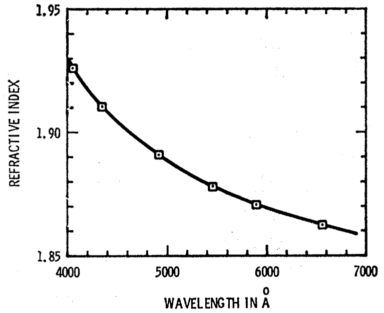

FIG. 3. The refractive index of single-crystal SrO in the visible spectrum.

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[12] M. Born and E. Wolf, *Principles of Optics* (Pergamon Press Ltd., London, 1959), p. 95.

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# cw Measurement of the Optical Nonlinearity of Ammonium Dihydrogen Phosphate

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We have measured the value of the element $d_{36}$ of the nonlinear dielectric tensor of ammonium dihydrogen phosphate for the doubling of the 6328-Å line of the He-Ne laser. Two measurements were made. The first used a collimated single-transverse-mode laser beam (focal spot radius$\approx$0.2 cm) containing several longitudinal modes. The second used a weakly focused single-mode and single-frequency laser (focal spot radius $\approx$0.03 cm). In both experiments the crystal was slowly rotated through the index-matching angle. The value of $d_{36}$ obtained by either method is $1.36\times10^{-9}(\pm12\%)$ in cgs esu. The experiments also verify the factor $(2n\text{-}1)/n$ for the enhancement of second-harmonic generation when $n$ independent longitudinal modes are present.

## INTRODUCTION

EARLY measurements[1,2] of optical nonlinearities were made by means of pulsed solid-state lasers. The limited transverse and longitudinal coherence of such lasers made the accurate interpretation of these experiments difficult. Ashkin *et al.*[3] first made a cw measurement in which the second harmonic[4] of the 1.15-$\mu$ line of a He-Ne laser was generated in a crystal of potassium dihydrogen phosphate (KDP). In their letter reporting this measurement, the authors mentioned the fact that the presence of several longitudinal modes with independent phases in the laser output enhances the harmonic generating efficiency of the laser beam by a factor $(2n-1)/n$ where $n$ is the number of independently oscillating modes.[5] These authors further specify that the result of their measurement was not corrected for this effect because the number of longitudinal modes and the power distribution among them were not known. A cw measurement of the element $d_{36}$ of the nonlinear dielectric tensor of ammonium dihydrogen phosphate (ADP) at 6328 Å was made by McMahon and Franklin.[6] Assuming the mode factor $(2n-1)/n$ to be approximately equal to two (for $n$ large) they obtained the results: $d_{36}=2.0\pm0.5\times10^{-9}$ cgs esu. This is in fair agreement with the value $d_{36}=(3\pm1)\times10^{-9}$ cgs esu reported by Ashkin *et al.*, since this latter result was not corrected for laser multimoding.

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[1] D. A. Kleinman, Phys. Rev. **128**, 1761 (1962).

[2] R. W. Terhune, P. D. Maker, and C. M. Savage, Appl. Phys. Letters **2**, 54 (1963).

[3] A. Ashkin, G. D. Boyd, and J. M. Dziedzic, Phys. Rev. Letters **11**, 14 (1963).

[4] Terminology introduced by P. A. Franken and J. F. Ward, Rev. Mod. Phys. **35**, 23 (1963), for the frequency which equals twice the fundamental frequency.

[5] N. Bloembergen, in *Symposium on Optical Masers. Microwave Research Institute*, edited by Jerome Fox (Interscience Publishers, Inc., New York, 1963).

[6] D. H. McMahon and A. R. Franklin, Appl. Phys. Letters **6**, 14 (1965).