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Additive Coloration of Calcium Oxide*

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Single crystals of CaO have been additively colored by heating them at 1700°C in calcium vapor at pressures from 0.33 to 40 Torr. An asymmetric optical absorption band which peaks at 3.1 eV is observed to grow in proportion to the increase in calcium-vapor density and is ascribed to the formation of F' centers. A second band, which peaks at 3.6 eV and saturates with increasing calcium-vapor density, is ascribed to the formation of F centers.

I. INTRODUCTION

THE results of a preliminary investigation of the color centers induced in calcium-oxide single crystals by additive coloration are reported in this paper. Related publications on CaO include brief reports on the optical-absorption spectra of nonirradiated[1] and neutron-irradiated[2] CaO crystals and on the photoconversion of $F \leftrightarrow F'$ centers (anion vacancies containing one and two electrons, respectively) using crystals colored in this investigation.[3] An optical absorption near 3.6 eV in neutron-irradiated crystals has been reported to be associated with the electron spin resonance (ESR)[2,4] and Faraday rotation[5] of the F center. The production of F centers by plastic deformation has also been reported.[6] The lowest-energy exciton absorption in CaO has been observed to occur at 7.0 eV.[7]

II. EXPERIMENTAL DETAILS

The crystals used in this investigation were cleaved from a clear crystal approximately 3×5×10 mm in size obtained from Semi Elements, Inc., Saxonburg, Pa., and from melts produced by fusing CaO powder in a carbon arc.[8] The specimens selected for coloring were about 2 mm square and a fraction of a millimeter thick. Prior to coloring, the crystals were annealed at 1500°C for about 1 h and the faces were then polished to a good optical finish.

Procedures for the additive coloration of the alkaline-earth oxides were described in the preceding paper.[9] However, since this investigation of CaO occurred early in the development of these procedures, the techniques actually used represent the rather crude early stages of their development. A single-section coloring furnace was used to control the temperature of the crystal which was held in a molybdenum wire basket in the top of the tantalum coloring bomb. The temperature of the calcium metal in the bottom of the bomb was controlled by changes in the length of the bomb and in the distance it extended out of the furnace. The temperature of the lower end of the bomb was measured with a Pt–Pt-10% Rh thermocouple and the temperature of the upper end of the bomb was measured with an optical pyrometer. Corrections for spectral emissivity and losses in the window were made by observing the melting of a platinum strip welded to the top of the bomb.

The optical absorption measurements were made using a locally constructed double-beam, ratio-recording spectrophotometer based on a Perkin-Elmer model 83 quartz-prism monochrometer coupled with a grating unit to reduce the stray light. Some of the absorption curves were rerun on a Cary model 14 spectrophotometer acquired after this investigation was completed and good agreement was found between the two instruments. The conventionally constructed cryogenic crystal holder had two 1-mm apertures which could alternately be positioned in the incident beam. The crystal was clamped over one of these for the absorption measurements and the other was used for a no-sample reference scan. A similar 1-mm aperture was placed in the reference beam of the spectrophotometer.

III. RESULTS AND DISCUSSION

The absorption spectra for five crystals colored at about 1700°C in calcium vapor pressures from 0.33 to 40 Torr are shown in Fig. 1. An approximate correction for reflectivity has been applied to these spectra but no correction was applied for the initial absorption of the uncolored crystals. This was because the initial absorption was observed to be altered by the additive coloring process, especially at the high-energy end of the spectra, leading in some cases to an apparent negative-induced

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

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[4] A. J. Tench and R. L. Nelson, Proc. Phys. Soc. (London) **92**, 1055 (1967).

[5] J. C. Kemp, W. M. Ziniker, and J. A. Glaze, Proc. Brit. Ceram. Soc. **9**, 109 (1967).

[6] R. G. Bessent and P. Feltham, Phys. Status Solidi **25**, K107 (1968).

[7] H. H. Glascock and E. B. Hensley, Phys. Rev. **131**, 649 (1963).

[8] The maximum impurities found by spectrographic analysis in samples from the crystals used were: Mg<1000 ppm; Fe, Si<30 ppm; Al, V<20 ppm; Mn<10 ppm; and Cu<1 ppm.

[9] E. B. Hensley, W. C. Ward, B. P. Johnson, and R. L. Kroes, preceding paper, Phys. Rev. **175**, 1227 (1968).

absorption. A typical before-coloring absorption spectrum is shown in Fig. 1 for crystal 34. The absorption coefficient was obtained using the expression $K=[\ln(I_0/I)+\ln(1-R)^2]d^{-1}$, where I and I_0 are the transmitted and incident intensities, d is the thickness of the crystal in centimeters, and R is the reflection coefficient. The expression used for the reflection term was $\ln(1-R)^2=-0.1191-0.0244E$, where E is the photon energy in electron volts. This expression was calculated using an extrapolation of the values for the index of refraction for CaO obtained by Liu and Sieckmann.[10]

Three absorption bands are discernible in the curves in Fig. 1. Evidence will be presented identifying the band at 3.1 eV with F' centers and the 3.6-eV band with F centers. The band at 4.8 eV is probably due to a metallic impurity.

By analogy with the alkali halides, the additive coloring process may be expected to introduce anion vacancies into a CaO crystal. For pure, divalent compounds, charge neutrality requires that each of these vacancies contain two electrons, forming F' centers. However, when impurities are present, the possibility exists for one of these electrons being lost to an impurity state, leaving an anion vacancy with one electron or an F center. Thus for low colorations, the F band would be expected to dominate as is seen for crystals 41 and 44 in Fig. 1. However, for heavier colorations, the impurity states would become saturated with the excess electrons so that the F' band would grow with little further increase in the F band.

Crystal 40 was too densily colored for normal operation of the spectrophotometer, even when the crystal had been reduced in thickness to 0.153 mm. Instead, point-by-point measurements were made of the photomultiplier current using a Keithley electrometer. Even with this procedure, it was not possible to measure the maximum absorption in the band. In order to obtain an estimate of the peak absorption, these data points were scaled to provide the best fit to the 3.1-eV peak for crystal 42, as is shown in Fig. 1. The peak absorption was thus estimated to be 980 cm^{-1}.

Two additional crystal were colored to even higher densities by heating them at 1658°C in calcium vapor at a pressure of about 200 Torr. One of these crystals was ground and polished to a thickness of 0.168 mm for optical-absorption measurements. As was expected, the absorption was much greater than for crystal 40 so that meaningful measurements were not possible. The second crystal, which was 0.838 mm thick, was used for ESR measurement.[11] Weak resonances were observed for Mn^{2+} and the F center but no resonances were observed with anywhere near sufficient strength to be correlated with the strong 3.1-eV optical absorption, indicating that this center is not paramagnetic.

The curve for crystal 40 in Fig. 1 is believed to be a good representation of the shape of the F' band, since the relative contributions due to F centers and impurities are a minimum. The effect of temperature on the peak positions and half-widths of F and F' bands can be estimated by comparing the two curves for crystal 34 taken at room temperature and at liquid-nitrogen temperature. The rather small dependence on temperature observed is understandable since the Debye temperature for CaO is about 600°K.[12]

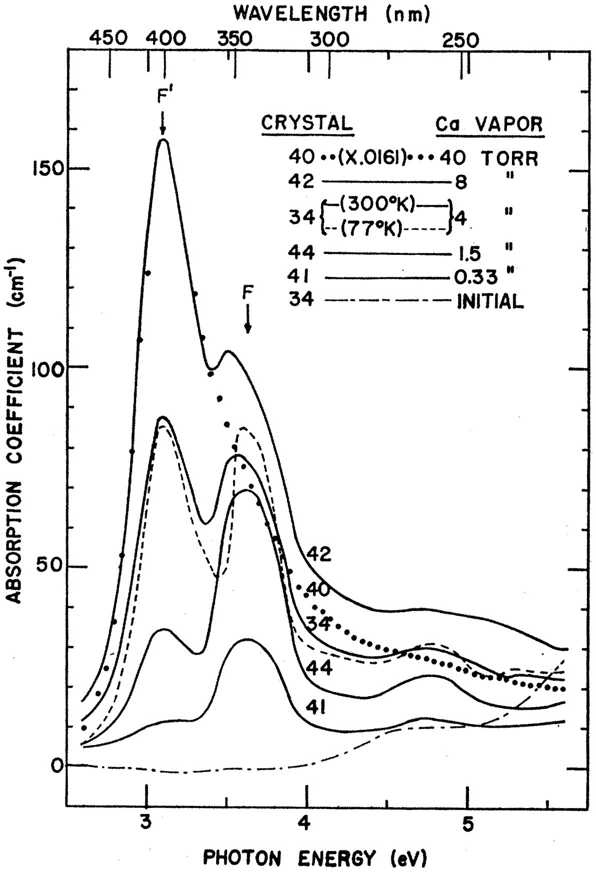

FIG. 1. Absorption spectra of additively colored crystals of CaO. The actual coloring temperatures, temperatures of calcium metal, and thicknesses, respectively, for each crystal were 41: 1685°C, 750°C, 0.574 mm; 44: 1692°C, 830°C, 0.351 mm; 34: 1693°C, 900°C, 0.272 mm; 42: 1715°C, 950°C, 0.318 mm; 40: 1700°C, 1100°C, 0.315 mm reduced to 0.153 mm for measurement. Also shown is the initial absorption of crystal 34 and the absorption spectra of the colored crystal 34 at liquid-nitrogen temperatures; all other spectra are for room temperature. All curves have been corrected for reflectivity as described in the text.

In Fig. 2, the densities of F and F' centers and their sum have been plotted as a function of the density of atoms in the calcium vapor. The pressure of the calcium vapor was first determined using the calcium vapor-pressure data of Honig.[13] The density of calcium atoms at the temperature of the crystal was then computed using the ideal gas law. The density of the color centers was calculated using Dexter's formula relating the

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[10] C. J. Liu and E. F. Sieckmann, J. Appl. Phys. 37, 2450 (1966).

[11] ESR measurements were made by James L. Kolopus.

[12] T. O. Baldwin and C. W. Tompson, J. Chem. Phys. 41, 1420 (1964).

[13] R. E. Honig, RCA Rev. 23, 567 (1962).

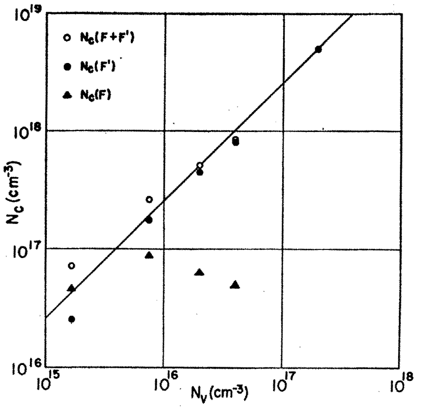

FIG. 2. The densities of color centers, N_c, plotted as a function of the density of calcium atoms in the vapor, N_v. The 45° line represents the equation $N_c=25N_v$.

color-center density to the area under the absorption curve.[14] The F' band was assumed to have the shape depicted by the curve for crystal 40 in Fig. 1, and the area of the F band was determined as being superimposed on the high-energy tail of the F' band. A value of 1 was used for the oscillator strength of both F and F'.

The density of F centers is observed to remain constant within a factor of 2 with changes in the density of atoms in the vapor. This is consistent with the hypothesis that their density is limited to the density of impurities capable of trapping electrons from F' centers. The variation observed is probably due to differences in the impurity concentrations in the various individual crystals.

In a pure crystal, the equilibrium density of F' centers would be expected to be directly proportional to the density of atoms in the vapor for a given temperature. In a crystal containing impurities such that F centers are produced, the total density of the anion vacancies, that is, the sum of the F- and F'-center densities, should probably be used. In this case, possible differences in the oscillator strengths for the F and F' centers could affect the measurements of this relationship, and also it is possible that the presence of F centers could result in a perturbation of the equilibrium density. In Fig. 2, both the densities of F' centers and the sum of the densities of the F and F' centers are shown plotted as a function of the densities of atoms in the vapor. It is believed that the present data are adequate to verify the direct proportionality between the anion vacancies and the atoms in the vapor; however, they are not believed to be of sufficient accuracy for any discussion of the refinements to this relationship suggested above.

IV. CONCLUSIONS

Two optical absorption bands peaking at 3.6 and 3.1 eV were induced in CaO crystals by the additive-coloring process. The arguments justifying the identification of these bands as arising from anion vacancies containing one and two electrons, respectively, that is, F and F' centers, will be summarized here.

The possibility of the 3.1-eV band being due to an impurity was ruled out by producing it to a density in excess of any of the detected impurities in the crystal with the possible exception of magnesium. Magnesium would not be expected to produce an absorption band in CaO. For a given temperature, the densities of these centers were observed to be directly proportional to the densities of the atoms in the vapor, as would be expected for anion vacancies. No ESR of comparable magnitude was observed, verifying that these centers were not paramagnetic.

The 3.6-eV band has previously been associated with the F center on the bases of ESR[2,4] and Faraday-rotation[5] measurements. The fact that the densities of these centers saturate at a level comparable with the impurities in the crystals is a behavior one would expect from the assumed model. Finally, the photoconversion of F centers to F' centers by red light and the reverse process induced by blue light[3] is believed to add further support to the identifications of both of these centers.[15]

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[14] O. L. Dexter, Phys. Rev. **101**, 48 (1956).

[15] An investigation is currently in progress in this laboratory by D. L. Packwood in which CaO crystals are being doped with various known impurities and then additively colored to verify that the 3.6-eV peak is independent of the particular impurity involved and to study the effects of both the F centers and temperature on the equilibrium density. Possible mechanisms for the photoconversion process are also being investigated.

Erratum

Photoemission Study of the Electronic Structure of Wurtzite CdSe and CdS, J. L. SHAY AND W. E. SPICER [Phys. Rev. **169**, 650 (1968)]. Figures 16 and 38 should be interchanged. In Sec. IV A, the quoted yield should be changed from 7 to 4%. In Table IV, the yield quoted for CdSe should be changed from 7.1 to 4.0%, and for CdS it should be changed from 9.2 to 5.2%.