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Cathodochromism in Photochromic Materials

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Photobleachable electron-beam-induced coloration has been observed in certain photochromic materials. This behavior is explained in the case of $CaTiO_3$:Fe-Mo by the trapping of electrons and holes at Mo^{6+} and Fe^{3+} ions, respectively, producing the colored state of the material. The material is restored to its uncolored state by the photo-induced transfer of an electron from Mo^{5+} to Fe^{4+}.

I. INTRODUCTION

IN this paper we report the coloration of certain photochromic materials by an electron beam. Once colored, these materials, called "cathodochromic" materials, can be bleached by light of suitable wavelengths. The absorption characteristics, coloration efficiency, and cathodochromic mechanism of Fe-Mo-doped $CaTiO_3$ will be presented in some detail.

$CaTiO_3$ is a transparent insulator with a uv absorption edge around 3900 Å. When Ni or Fe and Mo are incorporated into this host, single-crystal specimens have a slight yellow color, arising from weak absorption near the uv absorption edge. When light of wavelengths shorter than 4500 Å is absorbed by the crystal, it becomes heavily colored by photochromic absorption extending from about 4000 Å to beyond 1 μ. Light of wavelengths longer than 4500 Å causes the disappearance of this absorption and the crystal returns to its original nearly transparent state. The photochromic coloration can also bleach out in the dark by thermal deactivation processes. The thermally induced bleaching time is about 30 min at room temperature. The photochromic behavior of Fe-Mo-doped $CaTiO_3$ is similar to that observed for $SrTiO_3$,[1] with the only difference being the shorter thermal lifetime of the latter (about 10 min at 300°K). Faughnan and Kiss[2] have identified the photochromic absorption of $SrTiO_3$: Fe-Mo in the 4500 Å region with Fe^{4+} ions, and in the 6500 Å region with Mo^{5+} ions. The same may be presumed to hold in the case of $CaTiO_3$.

II. EXPERIMENTAL RESULTS

Figure 1 shows the change in reflectance induced in powdered $CaTiO_3$:Fe-Mo by light of $\lambda < 4500$ Å, and by exposure to an electron beam. These spectra were taken on a Cary-14 spectrophotometer using an integrating sphere attachment. The samples were in the form of thin powdered screens having reflective backings. The ordinate of Fig. 1 is $D_{\text{induced}} = \log_{10}(1/R) - \log_{10}(1/R_0)$ where R and R_0 are, respectively, the reflectance of the colored and uncolored material. The uncolored powdered samples are white. Light of $\lambda < 4500$ Å produces photochromic absorption filling the visible region of the spectrum as shown by the dashed curve. This absorption is similar to the absorption of single-crystal $SrTiO_3$ and $CaTiO_3$, with the exception that individual features are less well resolved. It also has some resemblance to previously published reflectance data for $CaTiO_3$ powders.[3] The coloration of the powdered screens decays thermally in about 30 min or can be bleached with light of $\lambda > 4500$ Å as in the case of single crystals.

When the same powder is exposed to a 25-keV–electron-beam cathodochromic coloration is induced as shown by the solid curve of Fig. 1. The shapes of the two curves are nearly identical; the density of the electron-beam induced coloration is 50% greater than that of the photochromic band. The electron-beam-induced coloration decays thermally and can be erased optically the same way as the photo-induced coloration. Hence we conclude that the role of the electron-beam excitation is the same as that of the uv light ($\lambda < 4500$ Å).

III. DISCUSSION

The probable cathodochromic mechanism is illustrated on Fig. 2. Fe is incorporated in the host in the trivalent state, while Mo goes in hexavalent.[2] Neither Fe^{3+} nor Mo^{6+} has appreciable absorption in the visible region of the spectrum. Both in the cathodochromic and photochromic process an electron is transferred from the Fe to the Mo leading to the following pairs:

$$\begin{pmatrix} Fe^{3+} \\ Mo^{6+} \end{pmatrix} \xrightarrow[\text{excitation}]{\text{electron-beam}} \begin{pmatrix} Fe^{4+} \\ Mo^{5+} \end{pmatrix}.$$

The coloration shown in both curves of Fig. 1 arises from contributions of Mo^{5+} and Fe^{4+} as in photochromic $SrTiO_3$. Cathodochromic excitation, as in the case of photoexcitation of phosphors, is accomplished by the generation of electron-hole pairs across the bandgap of $CaTiO_3$. The electrons and holes are then trapped at Mo^{6+} and Fe^{3+} sites, respectively, producing the colored state of the material. Light of wavelengths longer than 4500 Å excites electrons from the Mo^{5+} to the conduction band, reversing the excitation process.

From the known electron beam exposure (2μC/cm^2) leading to $D_{\text{induced}} = 0.25$ at 6500 Å (where the absorp-

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[2] B. W. Faughnan and Z. J. Kiss, J. Quantum Electron. (to be published).

[3] W. M. MacNevin and P. R. Ogle, J. Am. Chem. Soc. **76**, 3846 (1954).

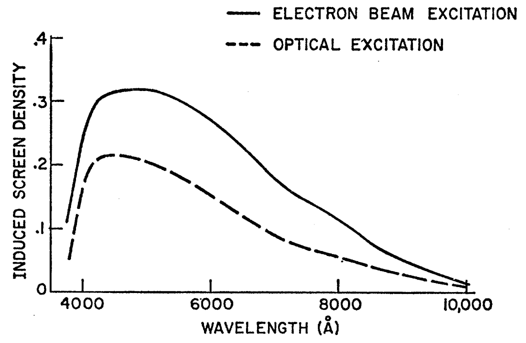

Fig. 1. Photo-induced and cathode-ray-induced coloration of $CaTiO_3$:Fe-Mo-powdered screen.

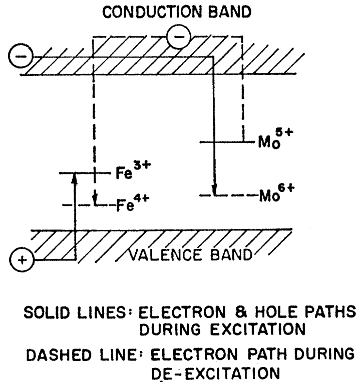

Fig. 2. Proposed schematic model for cathodochromic behavior of $CaTiO_3$:Fe-Mo.

tion is due largely to Mo^{5+}), the number of excited photochromic centers per incident electron can be calculated. For this purpose, one employs the Smakula equation modified for a Gaussian line shape,[4] and makes the approximation $R/R_0 = e^{-k\delta}$ where k is the induced absorption coefficient for the material and δ is the effective optical path length of light through the sample. Using an oscillator strength of about 0.3, and a width for the Mo^{5+} absorption centered about 6500 Å of 6000 cm^{-1}, in agreement with previously reported optical data,[1] one finds that each 25-keV electron excites about 200 photochromic centers. This implies that the power efficiency for filling ~ 2.5 eV deep traps is of the order of 2%. Thus the efficiency of cathodochromic excitation is comparable to the cathodoluminiscent efficiencies of phosphors.

We have observed cathodochromism in several photochromic materials, although not all photochromic materials are also cathodochromic. The phenomenon is similar to the electron-beam-induced color changes that occur in KCl; however, the photobleaching of KCl is a strongly temperature-dependent process that is rather inefficient at room temperature.[5] Large coloration has been observed in Fe-Mo-doped $SrTiO_3$ and in several varieties of photochromic sodalite.[6] Cathodochromic materials may be of significant interest in reflective display devices where storage is also required.

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[6] William Phillips and Zoltan J. Kiss, Proc. IEEE. **56**, 2072 (1968).