Color Centers in Alkaline Earth Fluorides

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Several experiments are presented dealing with color centers in alkaline earth fluorides. Evidence for simple color centers is not observed. Color centers previously reported in CaF_2 are due to the contamination of fluorite with Y. The optical and electron paramagnetic resonance spectra of $Y^{2+}(4d^1)$ are discussed.

LASER action has been observed[1–3] in alkaline earth fluorides containing either rare earth or actinide ions. A method has been reported[4] whereby the valence of Sm^{3+} can be partially reduced by ionizing radiation in order to obtain a $CaF_2(Sm^{2+})$ laser. During that study, it was observed that irradiated $CaF_2(Sm^{3+})$ did not exhibit the four bands (see Fig. 1) which have been associated with color centers,[5] i.e., electrons or holes trapped at lattice defects. This paper briefly reports additional experiments wherein we will conclude that contrary to the literature[5] (1) subtractive color centers[6] in CaF_2, SrF_2, and BaF_2 are not observed and (2) the usual coloration of CaF_2, is due to a trace impurity, Y^{2+}.

Materials to be described in this paper are single crystals grown in a modified[7] Bridgman furnace under a vacuum $<10^{-6}$ mm Hg. The samples that have been irradiated were exposed at 20°C to 5×10^6 rad of 2.5 MeV electrons from a Van de Graaff generator.[8] Optical spectra (200 mμ–10μ) were measured[9] at 20°C using several double-beam spectrometers. Measurements in the uv were made with a single-beam, vacuum instrument.

Several doped crystals were grown from Harshaw CaF_2. Mass and emission spectroscopy[10] indicate that this material contains 5×10^{-4}% Y, 5×10^{-2}% Al and Fe, and trace quantities of several other impurities. Impurity levels are given in mole percent. In this work, crystals of CaF_2 containing 5×10^{-4}% SmF_3, 0.2% SmF_3, 0.2% UF_4, 0.2% YF_3 plus 0.2% SmF_3, 0.2% AlF_3, and 0.2% FeF_3 have been grown. Since Scouler and Smakula[11] have shown that YF_3 enhances the coloration of CaF_2, the dopants 0.2% Y, 0.2% YF_3, 0.2%Y_2O_3, and 0.2% $NaYF_4$ were also studied. Our observations after irradiation are: (1) The addition of Y^{3+}, independent of its charge compensator, enhances coloration, (2) small quantities of Sm^{3+} completely suppress coloration, and (3) impurities with stable valence (i.e., Al^{3+}) have no effect on the coloration process. These data suggest that the coloration normally seen in CaF_2 is due to the reduction of Y^{3+} and that this reaction is suppressed by the presence of electron traps such as Sm^{3+}.

To substantiate this view we have tried to investigate Y-free CaF_2. An attempt to remove Y from CaF_2 by zone purification was not successful, because the distribution coefficient is unity.[7] Crystals containing less Y than Harshaw fluorite were grown from Baker, reagent grade CaF_2 and CaF_2 synthesized from pure $CaCO_3$. These crystals as well as Harshaw CaF_2 were irradiated and are compared in Fig. 1. The absorptions become negligibly small as the Y contamination is reduced.

These studies were extended to SrF_2 and BaF_2, recrystalized from commercial single crystals.[12] Contrary to the literature,[13] no coloration was observed in either SrF_2 or BaF_2. When these materials, doped with

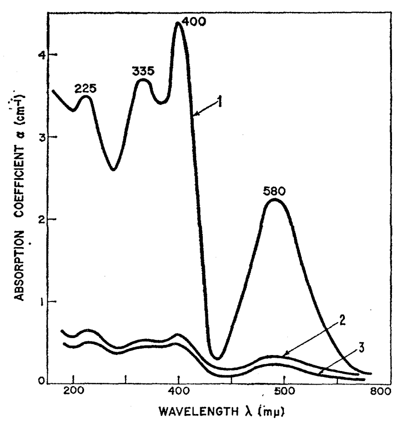

FIG. 1. Absorption of irradiated (5×10^6 rad) materials: (1) Harshaw CaF_2 (5×10^{-4}%Y); (2) a crystal grown from Baker, reagent grade CaF_2; (3) a crystal grown from CaF_2, synthesized from pure $CaCO_3$ by Dr. A. Wold, Lincoln Laboratory. The Y contamination of crystals (2) and (3) is less than 1 part per million.

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[6] Subtractive color centers are produced by ionizing radiation.
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[8] The authors gratefully acknowledge the help of Dr. K. A. Wright at MIT.
[9] For infrared and vacuum uv measurements, the authors are indebted to Dr. D. F. Edwards and Dr. W. J. Scouler.
[10] E. B. Owens (to be published).
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[12] These materials were kindly supplied by W. Hargreaves, Optovac, Inc.
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0.2% YF_3, are irradiated, a four-band spectra (Fig. 2) is observed. The coloration of BaF_2(Y) is unstable. The rate of thermal bleaching of SrF_2(Y) is greater than CaF_2(Y) but much less than BaF_2(Y). Photochemical bleaching is not observed.

Impurities such as $Y^{2+}(4d^1)$ and $Sm^{2+}(4f^6)$ behave as electron traps in CaF_2. During irradiation, electron-hole pairs are formed. Depending upon the electron capture cross section, the valence of the impurity may be reduced. Assuming a crude hydrogenic model, the binding energy ΔE of the trap is given by $\sim R/\epsilon^2$. For $BaF_2(Y^{2+})$ this energy is approximately equal to $\sim$ 1 eV at 20°C. More stability is expected for CaF_2 and SrF_2 because ΔE increases rapidly as the dielectric constant ϵ is reduced. For Sm^{2+}, ΔE is larger than kT due to the shielding of $4f$ electrons by $5s$, $5p$ shells; and consequently, no thermal bleaching occurs at room temperature. This model also shows we can expect two saturation effects. For a given radiation level, a law of mass action exists between the concentrations of holes, electrons, and Y^{2+}. This leads to a saturation of Y^{2+} independent of the concentration of Y^{3+}. At higher radiation levels the concentration of Y^{2+} will increase and then saturate because of lattice heating, thermal spikes, etc. These saturations have been observed.

The optical and electron paramagnetic resonance (EPR) spectra of Y^{2+} are of considerable interest. In an octahedral field the ground state Γ_5 is an orbital triplet. The excited state Γ_3 is an orbital doublet. Spin-orbit coupling, $\lambda\mathbf{L}\cdot\mathbf{S}$, splits the ground state into a lower quartet Γ_8 and a higher doublet Γ_7. An axial field[14] splits both the Γ_3 and Γ_8 so that the resultant level diagram consists of five Kramers doublets. In a strong crystal field the levels are separated so that four of the doublets remain in a group separated by a large energy Δ from a low-lying t orbital. Four optical transitions should be observed. The four-band spectra (Figs. 1 and 2) are interpreted as $4d^1$ transitions. Similar spectra have been observed by Jørgensen[15] for $V^{4+}(4d^1)$ in an axial field. One electron resonance should be observed in the ground state, a spin doublet. The g value should be smaller than free-spin by a small orbital contribution of the order λ/Δ (i.e., $g=1.988$). Using a 23.4 kMc/sec spectrometer at 4.2°K, only one strong resonance was observed at $g=1.994\pm0.005$. For this simple model,[16] the agreement is considered good. The EPR absorption shows complex, hyperfine structure which is interpreted as interaction between the $4d^1$ electron and several fluorine nuclei. The number of fluorine nuclei has not as yet been resolved.[17]

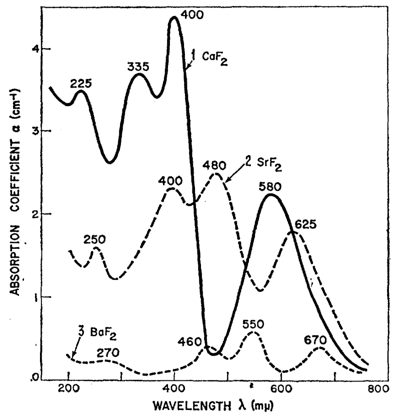

FIG. 2. Absorption of irradiated (5×10^6 rad): (1) Harshaw CaF_2 (5×10^{-4}%Y); (2) single crystal SrF_2 (0.2%Y); (3) single crystal BaF_2 (0.2%Y). These materials color as follows: CaF_2(Y)–blue; SrF_2(Y)–green; and BaF_2(Y)–red.

The model of Y^{2+} in CaF_2 resolves several problems that have been associated with the coloration process.[5] We briefly comment on the following: (1) The red, polarized luminescence reported by Feofilov[18] is due to radiative transitions between Kramers doublets in a strong axial field; (2) Thermal bleaching is due to nonradiative, electron-hole recombination from shallow acceptor levels; (3) Slight additive coloration[18,19] is due to the reduction of Y^{3+} by the diffusion of positive charges into the lattice; and (4) Photo-, thermo-, and radio-luminescence involve rare earth contaminants as well as radiative charge transfer processes associated with Y^{2+}.

Additive or subtractive coloration produce the same F center in alkali halide crystals. A large variety of absorption bands has been reported[19–21] when alkaline earth fluorides are additively colored. It is possible that none of these bands should be associated with color centers. However, if an additive color center exists, it must be closely associated with the excess positive charge that has entered the lattice. Perhaps subtractive coloration does not exist, because these centers are unstable in the absence of excess positive charge. In either case, it is clear that simple color centers, analogous to the well-defined F center in the alkali halides, were not observed in alkaline earth fluorides.

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[14] Irrespective of the method by which Y is introduced into CaF_2, strong axial fields are observed. This field is caused by local charge compensation and associated lattice distortion.

[15] C. K. Jørgensen, Acta. Chem. Scand. **11**, 73 (1957). Absorptions at and below 200 mμ are also present in these materials. These bands have been associated by Bontinck [Physica **24**, 639 (1958)] to oxygen. Oxygen enters the lattice during irradiation.

[16] A larger than expected g value for $Mo^{+5}(4d^1)$ has been reported by Griffiths [Proc. Roy. Soc. (London) **A219**, 526 (1953)]. The EPR that is observed cannot be associated with an F center because of the F^{-1} ($I=1/2$), hyperfine structure. More complex centers (e.g., V, M, etc.) would have a g value >2.02. The resonance can only be explained on the basis of a $4d^1$ electron at a cation site. The fact that the g value is somewhat large indicates the crystal field model is not sufficient to give a complete description of magnetic properties.

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