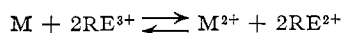


combination to occur, and the phosphorescent lifetimes increase.

Divalent Rare Earths.—The case for RE^{2+} ions in CdF_2 hosts has been discussed previously.¹⁰ Since Cd^{2+} is rather easily reduced and Ca^{2+} is not, RE^{2+} ions can be obtained in CaF_2 but not CdF_2 . Any agent strong enough to reduce RE^{3+} to RE^{2+} can reduce the CdF_2 host more easily. Hence, Ca vapor firings produce RE^{2+} ions in CaF_2 while Cd vapor does not produce RE^{2+} ions (except Eu^{2+}) in CdF_2 .

A qualitative estimate of the stability of various oxidation states in these highly ionic solids can be obtained from the values of the oxidation potentials for the appropriate reactions. From the appropriate potentials it can be seen that in the reaction



the products are favored for Ca plus CaF_2 while the reactants are favored with Cd plus CdF_2 .

In the CaF_2 - CdF_2 solid solution region the RE^{2+} concentrations obtained by the above reaction will change. Consider the equilibrium constant for Cd firing $\text{Cd}_{1-x}\text{Ca}_x\text{F}_2:\text{RE}^{3+}$ crystals. As x increases, the Cd^{2+} concentration decreases. Since P_{Cd} and the RE^{3+} concentration remain essentially constant, the

RE^{2+} content increases. This is precisely what is observed experimentally. Divalent ytterbium is detected optically at 7% CaF_2 as is shown in Figure 3. Divalent samarium, being considerably less stable than Yb^{2+} , was not observed until the CdF_2 content was very low.

Then the occurrence of various RE^{2+} ions at different compositions in the CaF_2 - CdF_2 solid solution region upon Cd firing at 500° can be explained on the basis of the relative stability of the RE^{2+} and Cd^{2+} oxidation states as indicated by their oxidation potentials. The concentration of RE^{2+} ions in the solid solutions can be increased by decreasing the Cd^{2+} concentration. However, except for Eu^{2+} and Yb^{2+} , no RE^{2+} can be obtained in the solid solutions except at very low CdF_2 contents. The presence of optically detectable RE^{2+} , then, does not necessarily correspond with the conductivity, infrared absorption, and phosphorescent lifetime changes that occur in the 1 to 10% CaF_2 region of the CdF_2 - CaF_2 solid solutions.

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CONTRIBUTION FROM THE IBM WATSON RESEARCH CENTER,
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Semiconductivity in $\text{Cd}_{1-x}\text{Ca}_x\text{F}_2:\text{In}^{3+}$ Single Crystals

By PAUL F. WELLER¹

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Bridgman-grown $\text{Cd}_{1-x}\text{Ca}_x\text{F}_2$ single crystals were doped with 0.1 mole % In_2O_3 , Ga_2O_3 , and Tl_2O_3 . Heat treating the crystals in a Cd atmosphere at 500° had no effect on the resistivity (about 10^7 ohm-cm) of the Ga- and Tl-doped crystals. However, with In-doped crystals Cd firing turned the colorless insulators into dark red, n-type semiconductors. The 300°K resistivity, carrier concentration, and mobility were about 10 ohm-cm, 10^{17} e⁻/cm³, and 10 cm²/v-sec, respectively. At 77°K the crystals had high resistivity (about 10^8 ohm-cm). Two activation energies for conduction of 0.15 and 0.20 eV appeared to be present. The dark red crystal color, associated with the conductivity, was caused by the combination of strong infrared and visible absorptions. Yellow-green phosphorescent and thermoluminescent emissions in untreated, In-doped crystals were excited with 2537-Å radiation. All of the above properties were strongly dependent on the CaF_2 content of the doped $\text{Cd}_{1-x}\text{Ca}_x\text{F}_2$ crystals. Between 0 and 1% CaF_2 there was little change in the properties. Between 1 and 10% CaF_2 the resistivity increased from 10 to 10^8 ohm-cm, the carrier concentration and mobility became unmeasurable, the crystal color changed from dark red to colorless, and the phosphorescent lifetimes increased from seconds to minutes. Since the properties exhibited by the In-doped $\text{Cd}_{1-x}\text{Ca}_x\text{F}_2$ crystals are quite similar to those previously found for RE-doped crystals, it appears that the same conductivity model previously proposed for $\text{CdF}_2:\text{RE}^{3+}$ crystals is also applicable for In^{3+} doping. The stability of the lower oxidation states of In can account for the differences between In and RE doping.

Introduction

When CdF_2 crystals are doped with rare earth elements (except La, Ce, Pr, and Eu), yttrium, or scandium and fired in Cd vapor at 500° , they switch from electrical insulators (resistivity about 10^7 ohm-cm at 300°K) to n-type semiconductors (resistivity about 1 ohm-cm at 300°K).²⁻⁴ Simultaneously, the crystals

become deep blue. The temperature dependence of the the resistivity, Hall coefficient, and Hall mobility indicate impurity conduction.^{4,5} In CdF_2 - CaF_2 mixed crystals doped with rare earths, the properties obtained by Cd firing are strongly dependent on the CaF_2 content.⁶ Between 1 and 10% CaF_2 the crystals change from blue conductors to colorless insulators.

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TABLE I

VALUES OF RESISTIVITY, HALL COEFFICIENT, CARRIER CONCENTRATION, AND HALL MOBILITY FOR SEVERAL Cd-FIRED In_2O_3 -DOPED $\text{Cd}_{1-x}\text{Ca}_x\text{F}_2$ CRYSTALS (SAMPLE NUMBERS ARE GIVEN AT THE LEFT IN THE DOPANT COLUMN)

Dopant	Resistivity, ρ , ohm-cm		Hall coefficient, $-R_H$, cm ² / coulomb	Carrier concn, n , e ⁻ /cm ³	Hall mobility, μ_H , cm ² /v-sec
	300°K	77°K	300°K	300°K	300°K
105 0.01% In_2O_3	10.7	...	104	6.0×10^{16}	9.7
72 0.1% In_2O_3	9.26	3.0×10^7	64	9.8×10^{16}	6.9
106 0.1% In_2O_3 + 0.01% CaF_2	7.86	2.9×10^7	64	9.8×10^{16}	8.1
107 0.1% In_2O_3 + 0.1% CaF_2	8.20	2.8×10^7	57	1.0×10^{17}	7.0
108 0.1% In_2O_3 + 1.0% CaF_2	17.0	...	123	5.1×10^{16}	7.2
115 0.1% In_2O_3 + 3.0% CaF_2	161	2.4×10^8	700	9×10^{15}	4.4
116 0.1% In_2O_3 + 7.0% CaF_2	$\sim 3 \times 10^4$	Ionic conduction
109 0.1% In_2O_3 + 10.0% CaF_2	$\sim 10^7$

This study was undertaken to see if any non rare earth like dopants would give rise to conducting CdF_2 crystals and whether the changes in observed properties with CaF_2 additions would be similar to those found for rare earth doping.

Dopants were added to Bridgman-grown crystals generally at the 0.1 mole % level as In_2O_3 , Ga_2O_3 , and Tl_2O_3 . Optical absorption data were taken on selected crystals before and after Cd firing, and the visible phosphorescence and thermoluminescence under 2537- and 3660-Å. excitation were observed visually. The electrical resistivity and Hall effect were studied as a function of temperature on the conducting $\text{CdF}_2:\text{In}^{3+}$ crystals.

Experimental Section

Crystal Growth and Treatment.—Optically clear single crystals of CaF_2 were powdered and used as host starting material. The preparation of the CdF_2 starting material from reagent grade CdCO_3 and aqueous HF^4 and the Bridgman single-crystal growth using graphite crucibles⁷ were described previously. Reagent grade In_2O_3 , Ga_2O_3 , and Tl_2O_3 (all of the cubic $\alpha\text{-Mn}_2\text{O}_3$ structure which is closely related to the cubic CdF_2 structure) were added as dopants at 0.1 mole % concentrations unless stated otherwise. Some segregation of the In and Ga (segregation coefficients less than 1) was observed along the length of the crystal in the optical measurements reported below. Tl doping appeared to be quite homogeneous. Some segregation of CdF_2 and CaF_2 as well as crystal strain and cracking were noted in the mixed crystals.⁸ Crystals were heat treated in a Cd atmosphere at 500° as reported previously.⁴

Conductivity and Hall Effect.—All of the doped $\text{Cd}_{1-x}\text{Ca}_x\text{F}_2$ crystals were fired in Cd at 500°. Resistivities for the treated Ga- and Tl-doped crystals were greater than 10^7 ohm-cm, approximately that of the untreated crystals or of undoped CdF_2 . However, in the case of 0.01 or 0.1 mole % In_2O_3 doping, the crystals showed n-type electronic conductivity and were very dark red. A darker red color indicated higher conductivity. Typical room-temperature resistivity, carrier concentration, and Hall mobility values for 0.1% doping and CaF_2 concentrations between 0 and 1% were about 10 ohm-cm, 10^{17} e⁻/cm³, and 10 cm²/v-sec, respectively. Other values are given in Table I.

The conductivity and Hall Effect were measured using standard direct current techniques and apparatus between 77 and 600°K as described previously.⁴ Experimental problems were encountered in the measurements above 300°K. A running vacuum of about 10^{-3} mm was used in the crystal holder. After completing a measuring run (from 77 to 600°K) on Cd-fired $\text{Cd}_{1-x}\text{Ca}_x\text{F}_2:\text{In}^{3+}$ crystals, a surface film was always present, and the crystal bulk was changed as evidenced by a lightening or

disappearance of the deep red color. These results were interesting since the In-doped crystals after the measuring run gave some indications of being p type. It is not known whether this was a surface or bulk effect. A pressure of less than 10^{-5} mm or a very pure inert atmosphere is needed to prevent film formation at the higher temperatures.

Another interesting phenomenon was observed during the electrical measurements on the In-doped sample containing 7% CaF_2 . As seen in Table I the resistivity of this crystal was rather high at room temperature. When a dc field was applied to the sample, the crystal color began to change. The dark red, conducting crystal turned into a light yellow insulator. A sharp boundary between the yellow and red regions progressed from the negative toward the positive electrode. This was undoubtedly caused by some form of ionic conduction. No study was made of the transport process involved. Since the yellow region was insulating and occurred at the negative electrode, it is possible that the corresponding electrode reaction would involve the formation of In^+ . An In^+ ion would act as an acceptor in the conducting $\text{CdF}_2:\text{In}^{3+}$ crystal and would increase the resistivity by compensating the donor centers.

It should also be noted that the In^{3+} -doped samples showed evidences of photoconductivity. For this reason all of the data presented in Table I were taken in the dark. The photoconductivity was most noticeable in the high-resistivity samples. For example, the resistivity of sample 105 was greater than 10^7 ohm-cm at 77°K in the dark while in the light it was 7.2×10^4 ohm-cm. Similar effects were observed with other samples with a difference in resistivity of one to three orders of magnitude between light and dark measurements.

Many of the electrical properties observed for In-doped crystals are very similar to those observed for RE-doped crystals. The room temperature properties for In-doped crystals listed in Table I are quite similar to those found with rare earth doping.^{4,5} The temperature dependences of the resistivity, Hall coefficient, and Hall mobility shown in Figures 1 and 2 also resemble those obtained with rare earth doping, in the temperature region 125 to 600°K.^{4,5} (The behavior of the resistivity between 77 and 125°K appears to be quite different for In-doped CdF_2 and is discussed below.)

The impurity conduction present with RE doping^{4,5} also seems to be present in the In^{3+} -doped crystals. This is indicated by the resistivity plateau (just before the second "trapping" level becomes effective) seen in Figure 1 and the apparent maximum in the mobility as shown in Figure 2.

Another similarity between RE- and In-doped crystals is the dependence of the conductivity properties produced by Cd firing on the CaF_2 concentration in $\text{Cd}_{1-x}\text{Ca}_x\text{F}_2:\text{M}^{3+}$ crystals.⁶ The resistivity, ρ , carrier concentration, n , and mobility, μ_H , are shown as a function of CaF_2 content in Figures 3 and 4. The behaviors are essentially identical with those of RE-doped crystals. Between 0 and 1% CaF_2 ρ , n , and μ_H are all constant. Between 1 and 10% CaF_2 ρ increases from about 10 to about 10^8 ohm-cm and n and μ_H become unmeasurable.

Two differences in electrical properties were found for conducting $\text{CdF}_2:\text{In}^{3+}$ crystals as compared to $\text{CdF}_2:\text{RE}^{3+}$ crystals.

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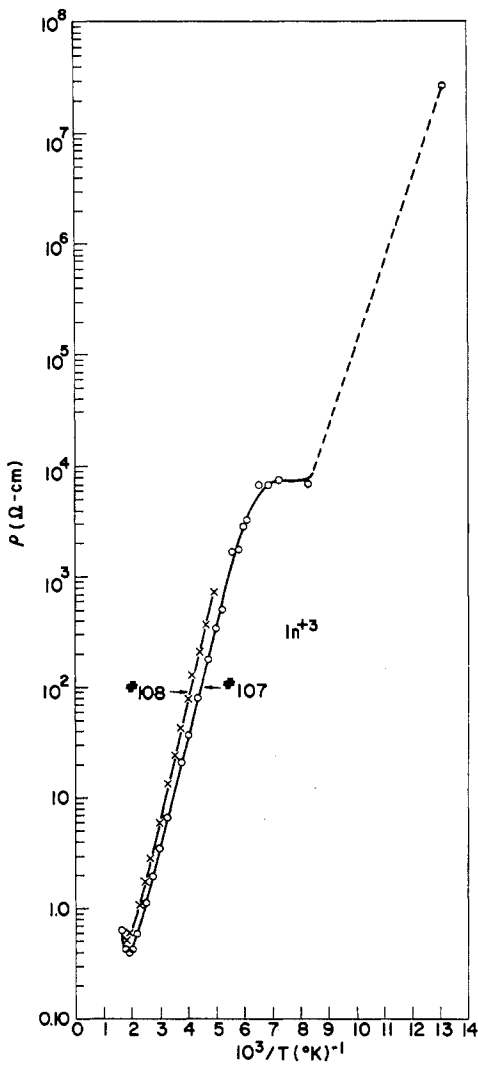


Figure 1.—Log ρ vs. $10^3/T$ for Cd-treated $Cd_{1-x}Ca_xF_2$ crystals doped with 0.1 mole % In_2O_3 . Samples 107 and 108 contained 0.01 and 0.1% CaF_2 , respectively.

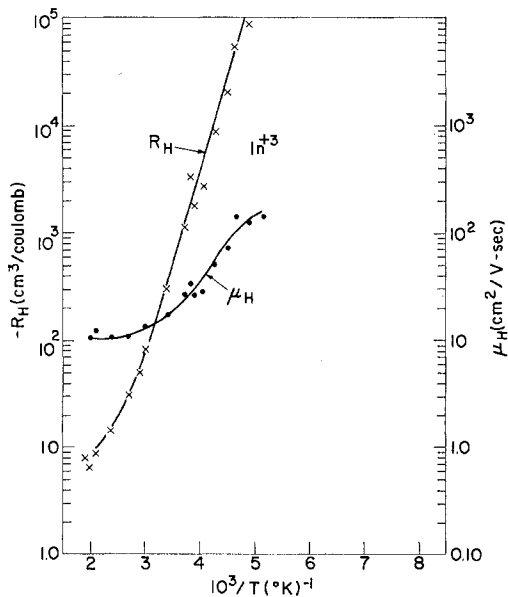


Figure 2.—Log R_H vs. $10^3/T$ and log μ_H vs. $10^3/T$ for sample 107 shown in Figure 1.

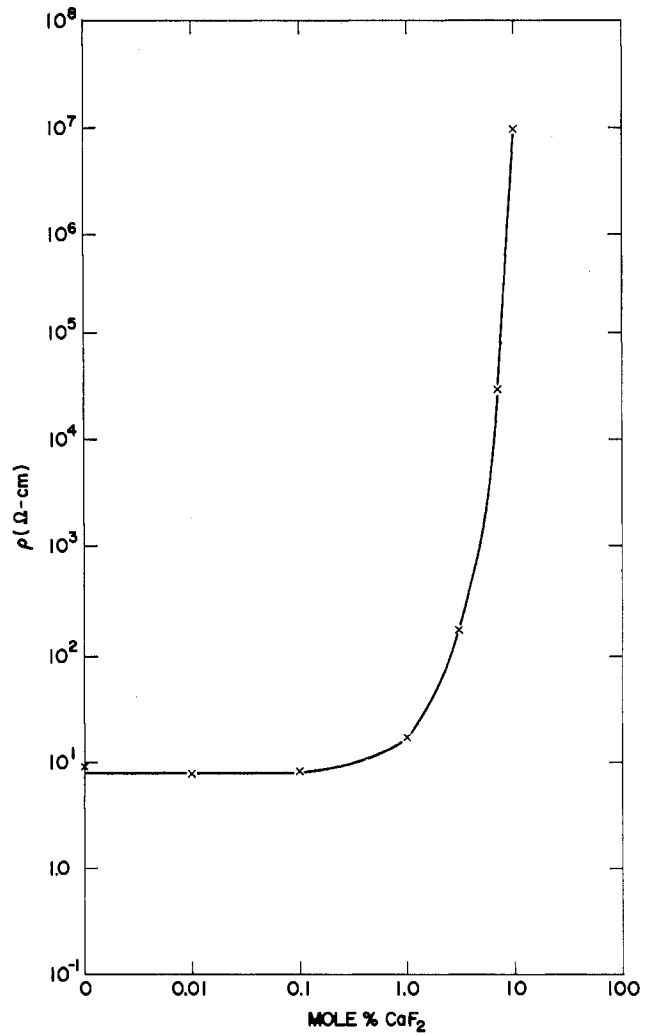


Figure 3.—Log ρ vs. log % CaF_2 for $Cd_{1-x}Ca_xF_2:0.1\%$ In_2O_3 crystals at 300°K.

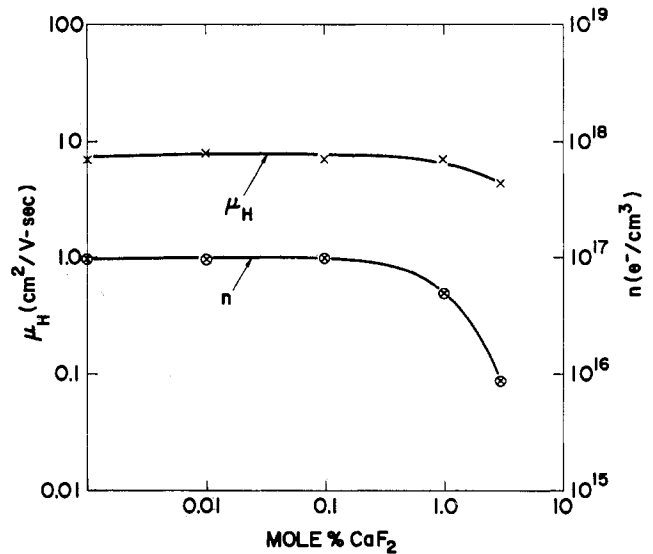


Figure 4.—Log n vs. log % CaF_2 and log μ_H vs. log % CaF_2 at 300°K for the samples shown in Figure 3.

The first is the high resistivity of the In^{3+} -doped crystals at 77°K. The second is the high-temperature activation energy for conduction, about 0.2 eV for $CdF_2:In^{3+}$ as compared to about 0.1 eV for $CdF_2:Re^{3+}$ crystals.

The rapid increase in resistivity below about 125°K for CdF₂:In³⁺ crystals is shown in Figure 2. (Since no data points were taken between 125 and 77°K, the activation energy calculated from the dashed portion of the curve is only approximate and represents a minimal value.) With RE dopants the increase in resistivity in this temperature region is generally small (impurity conduction is present).^{4,5} Two activation energies can be calculated for the In³⁺-doped Cd_{1-x}Ca_xF₂ crystals. The slopes of the log ρ vs. $1/T$ plot in Figure 2 give a low-temperature donor-activation energy $E_1 = 0.15$ eV and a high-temperature activation energy $E_2 = 0.20$ eV assuming that the concentration of donors and acceptors is not too different. In the case of RE doping, only one activation energy for the conduction process is apparent.^{4,5}

Optical Measurements.—Optical absorption spectra were run at 300, 77, and 6°K on samples before and after Cd firing using a Cary Model 14 spectrophotometer. Studies were made on CdF₂ crystals doped with Th₂O₃, Ga₂O₃, and In₂O₃ and on Cd_{1-x}Ca_xF₂ crystals doped with In₂O₃.

Thallium doping yielded yellow crystals both before and after Cd firing. No distinct absorption peaks were present, only very broad bands. The absorption decreased slightly with Cd treatment, but the band shapes did not change significantly.

The Ga-doped crystals were essentially absorption free between 0.4 and 2.5 μ both before and after Cd firing. However, 2537-A irradiation for periods of 1 or 2 min turned the crystals brown to gray. The colors were caused by increased visible absorption that decreased to essentially zero at about 8000 Å. One small peak was observed at 3460 Å. These "color centers" were bleached upon heating the crystal to about 100° but were stable at room temperature for several weeks. A probable cause for the "color centers" is the formation of divalent Ga.

In the In³⁺-doped CdF₂ crystals that were Cd fired, the infrared absorption increased with wavelength in a similar fashion to that of conducting, rare earth doped crystals.^{2,4} Figure 5 shows this behavior for 0.01 and 0.1% In₂O₃ doping at different temperatures.

The properties observed for In and RE dopants in Cd-fired Cd_{1-x}Ca_xF₂ crystals are also very similar.⁶ The absorption spectrum shown in Figure 5 was essentially unchanged by additions of CaF₂ up to 1%. At 10% CaF₂, however, the spectrum was similar to the one observed for the unfired CdF₂:In³⁺ sample in which there was a broad shoulder on the ultraviolet absorption edge with a maximum around 4000 Å but essentially no infrared absorption up to 2.5 μ .

The temperature dependence of the broad infrared absorption of the conducting crystals, however, appears to be different for In and RE doping. Figure 5 shows that the absorption increased as the temperature was lowered from 300 to 77 to 6°K for In³⁺ doping. In the case of RE dopants⁶ the broad absorption decreased as the temperature was lowered from 300 to 77°K, and between 77 and 6°K the absorption was constant.

The phosphorescent and thermoluminescent behaviors of the In-doped crystals were very similar to those observed with RE doping.⁶ The emissions were excited with the 2537-A line of a low-pressure Hg pen lamp (3660-Å excitation did not produce any visible radiation) and were observed visually at 77 and 300°K.

All of the unfired crystals with CaF₂ contents between 0 and 3% exhibited yellow-green phosphorescence at both 77 and 300°K. At 300°K the phosphorescent emissions changed from green-white to blue-white to weak blue as the CaF₂ content increased from 7 to 10 to 30%. The phosphorescent lifetimes were longer at 77 than at 300°K and increased (seconds to minutes) as the CaF₂ content varied between 1 and 10%.

The thermoluminescence, from 77 to 300°K, of the unfired crystals were bright yellow-green when the crystals contained between 0 and 3% CaF₂. The emissions changed from a green-white to blue-white to weak white as the CaF₂ content increased from 7 to 10 to 30%.

All of the phosphorescent and thermoluminescent emissions were quenched, in the conducting samples, upon firing in Cd vapor.

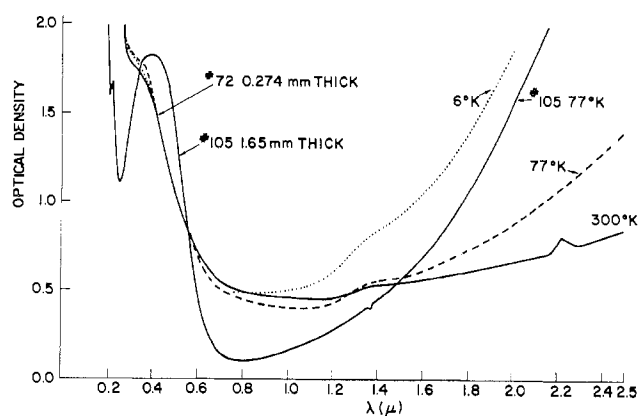


Figure 5.—The optical absorption spectra of Cd-fired In₂O₃-doped CdF₂ crystals. Sample 72, containing 0.1% In₂O₃, is shown at 300, 77, and 6°K. Sample 105, containing 0.01% In₂O₃, is shown at 77°K only.

There was one difference observed between In- and RE-doped samples. Two thermoluminescent peaks were present in the In-doped samples indicating the possible presence of two levels rather than the one formed with RE doping.

Discussion

Since there are so many similarities between In- and RE-doped Cd_{1-x}Ca_xF₂ crystals, it is proposed that the observed crystal properties with In and RE doping can be explained on the basis of the same model. All of the above results on In-doped crystals, similarities as well as differences compared to RE doping, can be considered using the conductivity model previously proposed for CdF₂:RE³⁺ crystals.⁴ This model uses a donor or "impurity" level, formed by an electron being shared by the Cd²⁺ ions nearest the substituted M³⁺ dopant thereby forming a "resonance" stabilized Cd⁺ state, to account for the conductivity. Then overlap of the wave functions of these levels can produce impurity conduction (impurity banding) as has been observed with RE doping^{4,5} and as is indicated above for In doping.

The optical absorption associated with the conductivity also seems to be consistent with this conductivity model. The absorption process can be envisioned as a charge transfer between impurity centers. In the case of In doping the electron transfer can occur, for example, from a "Cd⁺-In³⁺" to a "Cd⁺-In²⁺" center with the formation of "Cd²⁺-In³⁺" and "Cd⁺-In⁺" centers.

The proposed donor level is also consistent with the CaF₂ content dependence of the observed properties. Since the level is composed of the host Cd ions, it can be destroyed by substituting other ions such as Ca²⁺ for the cadmiums. As seen in Figure 3 for Cd_{1-x}Ca_xF₂:0.1% In₂O₃ crystals, the resistivity increases from about 10 to about 10⁷ ohm-cm when the CaF₂ content varies between 1 and 10%. Figure 4 shows the associated changes in carrier concentration and mobility. This same concentration region is also critical for the optical properties that depend on the "impurity" centers. Between 1 and 10% CaF₂ the intense optical absorption of the conducting Cd_{1-x}Ca_xF₂:In³⁺ crys-

tals vanishes, and the phosphorescent and thermoluminescent emissions of the untreated crystals change noticeably. These observations indicate that about one in every ten Cd^{2+} ions (each substituted M^{3+} ion has 12 Cd^{2+} nearest neighbors) has to be replaced in order to destroy the "resonance" stabilized state and, hence, the properties dependent upon it.

The following differences observed between $\text{Cd}_{1-x}\text{Ca}_x\text{F}_2$ crystals doped with In^{3+} and Re^{3+} ions can also be considered with the use of the proposed Cd "impurity" level model. Two other observations are valuable. One is the chemical similarity of Cd and In. The second is the relatively high stability of lower oxidation states of In, such as In^{2+} and In^+ . (Rare earths, on the other hand, are chemically dissimilar to Cd and do not generally form stable lower oxidation states.) The existence of an In^{2+} ion allows for the two activation energies for conduction with In doping and the resulting high-resistivity crystals at 77°K. The low-temperature activation energy, $E_1 = 0.15$ ev, can be identified with the ionization of an electron from an In^{2+} ion into the Cd "impurity" centers (impurity band). Then the high-temperature activation energy, $E_2 = 0.20$ ev, can be attributed to ionization from the Cd centers into the CdF_2 conduction band. This high-temperature energy, E_2 , might be larger than that with RE dopants since Cd and In are quite similar chemi-

cally. This would tend to lower the "impurity" level in energy, thereby increasing the donor energy, since In could enter into the proposed "resonance" effect.

The increase in broad infrared absorption, in the $\text{Cd}_{1-x}\text{Ca}_x\text{F}_2:\text{In}^{3+}$ -conducting crystals, with decreasing temperature is also consistent with the formation of lower In oxidation states. As the temperature is lowered, more In^{2+} (and possibly In^+) ions are formed. Charge transfer between the "impurity" centers then becomes more favorable, and the absorption increases.

The observation of two thermoluminescent peaks in untreated crystals with In doping also seems to agree with the proposed model. The thermal activation from two states at different energies to the same energy state, say the CdF_2 conduction band, with subsequent yellow to yellow-green emission to a single, terminal, fluorescent level would explain the two identically colored thermoluminescent peaks. Two peaks would be observed above 77°K since electrons would be thermally excited from two levels, the Cd "impurity" and the In^{2+} levels, at two different energies below the conduction band edge.

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CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA

The Crystal Structure of Ammonium Hexabromoantimonate, $(\text{NH}_4)_4\text{Sb}^{\text{III}}\text{Sb}^{\text{V}}\text{Br}_{12}$ ¹

BY STEPHEN L. LAWTON AND ROBERT A. JACOBSON

Received November 22, 1965

A single-crystal X-ray structure analysis of jet black octahedral crystals of ammonium hexabromoantimonate has confirmed the existence of a mixture of trivalent and pentavalent antimony in salts of the type M_2SbX_6 ($\text{M} = \text{NH}_4^+$, Rb^+ , or Cs^+ ; $\text{X} = \text{Cl}$ or Br). The crystals of the ammonium salt are tetragonal, space group $\text{I4}_1/\text{amd}$ (D_{2h}^{19}) with unit cell dimensions $a = 10.66 \pm 0.02$ Å and $c = 21.52 \pm 0.02$ Å ($c/a = 2.02$). Using three-dimensional scintillation-counter data and a full-matrix anisotropic least-squares analysis, the refinement of all atoms, except hydrogen, has yielded a final unweighted reliability index of 10.5% for 621 observed reflections. Both antimony atoms are six-coordinated and form a distorted K_2PtCl_6 structure in which the ions are arranged in an ordered array with like oxidation states of antimony repeating along the a and b directions in the unit cell but alternating along the c direction. The $\text{Sb}^{\text{III}}\text{Br}_6^{3-}$ ions are undistorted (O_h symmetry), and the $\text{Sb}^{\text{V}}\text{Br}_6^-$ ions are distorted (D_{2d} symmetry). The average $\text{Sb}(\text{III})\text{-Br}$ and $\text{Sb}(\text{V})\text{-Br}$ bond lengths, corrected for thermal motion assuming rigid-body libration, have been found to be 2.795 ± 0.006 and 2.564 ± 0.006 Å, respectively.

Introduction

Crystals of M_2SbX_6 ($\text{M} = \text{NH}_4^+$, Rb^+ , or Cs^+ ; $\text{X} = \text{Cl}$ or Br) are jet black, octahedral, and diamagnetic, and have a high specific resistance. The interest in these salts has been largely that of determining by chemical and physical methods the true oxidation state(s) of antimony. In particular, attempts have been aimed at determining whether it is tetravalent or

a mixture of trivalent and pentavalent and then attempting to explain the cause of the black color in terms of its oxidation state(s), their distribution in the crystal, and their halogen environment. Studies of these salts in hydrochloric acid solution, such as the spectroscopic studies by Whitney and Davidson² and the exchange reactions between antimony(III) and -(V) by Bonner,³

(1) This work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 1826.

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(3) N. A. Bonner, *ibid.*, **71**, 3090 (1949).