Contribution from the IBM Watson Research Center,
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Electrical and Optical Studies of Doped CdF_2–CaF_2 Crystals

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Received August 16, 1965

Bridgman-grown $Cd_{1-x}Ca_xF_2$ crystals were doped with SmF_3, YbF_3, and YF_3. X-Ray powder diffraction photographs showed complete solid solution between CaF_2 and CdF_2. The crystals were fired in a Cd atmosphere at 500°. Electrical resistivity and Hall effect studies showed that crystals doped with 0.1 mole % REF_3 and fired in Cd were n-type semiconductors with a room-temperature resistivity, carrier concentration, and mobility independent of crystal composition between 0 and 1% CaF_2. Between 1 and 10% CaF_2 the resistivity increased from about 1 to about 10^7 ohm-cm. The intense infrared absorption, which is associated with the conductivity and which causes the blue color of the crystals, followed the same pattern. Up to 1% CaF_2 the crystals were blue. With 10% CaF_2 added, the crystals were colorless. Similar sharp changes in resistivity and infrared absorption were observed with REF_3 dopant concentration variations. Optical absorption studies indicated Yb^{2+} ions in CdF_2–7% CaF_2–0.1% YbF_3 crystals after Cd firing, but no Sm^{2+} or Y^{2+} ions were observed until the CaF_2 content was very high (greater than 99.5%). The lack of correspondence between RE^{2+} formation and the cessation of conductivity are considered on the basis of chemical oxidation potentials. A model is proposed for the conductivity in which the Cd^{2+} ions nearest the RE^{3+}-substituted ion share an electron thus creating an "impurity" donor level. This model is consistent with the variations of the conductivity and of the RE^{2+} concentrations with changing CdF_2/CaF_2 ratios.

Introduction

In the last few years the optical properties of rare earths in CaF_2 have been studied extensively and many optically pumped lasers have been produced.[2] Lasers have been made using divalent rare earth dopants such as Sm^{2+}, Dy^{2+}, and Tm^{2+}.[3,4] In fact, all rare earths have been obtained in the 2+ oxidation state in CaF_2 crystals and their optical properties investigated.[5] Recently, CdF_2 crystals doped with rare earths have also shown a very interesting property. When the crystals are fired in Cd vapor at 500°, they change from electrical insulators (resistivity about 10^7 ohm-cm at 300°K) to n-type semiconductors (resistivity about 1 ohm-cm at 300°K).[6–8] Simultaneously, the crystals become deep blue in color. Although CaF_2 and CdF_2 show the above differences, they are also similar in many ways. For example, CaF_2 and CdF_2 have identical cubic structures (fluorite) with very similar lattice constants, 5.45 and 5.40 A, respectively. Also, the ionic sizes of Ca^{2+} and Cd^{2+} are very similar, 0.99 and 0.97 A, respectively. Consequently, CaF_2 and CdF_2 form a continuous series of solid solutions. This system has several interesting features. Consider the two end members. In rare earth doped CaF_2, RE^{2+} ions can be obtained by firing in Ca vapor,[9] and the crystals are highly insulating. In rare earth doped CdF_2, no RE^{2+} ions that can be detected by epr or by optical absorption (except Eu^{2+}) are produced by firing in Cd vapor. The crystals, however, exhibit electronic conducivity (except with La, Ce, Pr, and Eu doping).[10] Then the CaF_2–CdF_2 solid solution region should contain regions of transition. At one CaF_2/CdF_2 ratio RE^{2+} ions should be observable; at another ratio only RE^{3+} ions should be detected. At some CaF_2/CdF_2 ratio, conductivity should be produced by firing the crystals in Cd; at another ratio no conductivity should be obtained.

In order to investigate this CdF_2–CaF_2 solid solution region, the following experiments were conducted. Crystals were grown by a Bridgman technique and doped with SmF_3, YbF_3, and YF_3. Optical absorption spectra were taken at 300, 77, and 6°K, and the visible fluorescence, phosphorescence, and thermoluminescence under 2537- and 3660-A excitation were observed visually. The electrical resistivity and the Hall effect were studied at 300 and 77°K.

Experimental Section

Crystal Growth and Treatment.—The preparation of the CdF_2 starting material from reagent grade $CdCO_3$ and aqueous HF was described previously.[10] Powdered single-crystal sections of CaF_2 (and SrF_2, BaF_2, and PbF_2 when used) also served as host starting material. Dopants were added as SmF_3, YbF_3, and YF_3 (all 99.9% purity) generally at the 0.1 mole % level. No pretreatment was used until the CdF_2 content in the CaF_2-CdF_2 mixed crystals fell below about 1%. Then the dopants were rendered anhydrous by firing in flowing HF at about 1000° for several hours.

The Bridgman single-crystal growth using graphite crucibles was described previously.[11] The grown crystals were about 10 mm in diameter and 10 to 50 mm long. In the CaF_2-CdF_2 mixed crystals there was often considerable strain and some cracking. Segregation of CaF_2 and CdF_2 was indicated by varying ratios of CaF_2 to CdF_2 along the length of a crystal. However, very sharp patterns in X-ray powder diffraction photographs showed complete solid solution between CaF_2 and CdF_2 with Vegard's law being obeyed.

To ensure that crystal inhomogeneities did not affect the experimental measurements, slices for study were cut perpendicular to the growth direction. No variations in the CaF_2/CdF_2 ratio,

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[1] Department of Chemistry, State University College, Fredonia, N. Y.
[2] See, for example, L. F. Johnson, *J. Appl. Phys.*, **34**, 897 (1963).
[3] P. P. Sorokin and M. J. Stevenson, *IBM J. Res. Develop.*, **5**, 56 (1961).
[4] Z. J. Kiss and R. C. Duncan, Jr., *Proc. IRE*, **50**, 1531, 1532 (1962).
[5] D. S. McClure and Z. J. Kiss, *J. Chem. Phys.*, **39**, 3251 (1963).
[6] J. D. Kingsley and J. S. Prener, *Phys. Rev. Letters*, **8**, 315 (1962).
[7] J. S. Prener and J. D. Kingsley, *J. Chem. Phys.*, **38**, 667 (1963).
[8] J. S. Prener and H. H. Woodbury, Proceedings of the 7th International Conference on Semiconductor Physics, Paris, 1964, p 1231.
[9] Z. J. Kiss and P. N. Yocom, *J. Chem. Phys.*, **41**, 1511 (1964).
[10] P. F. Weller, *Inorg. Chem.*, **4**, 1545 (1965).
[11] P. F. Weller and J. E. Scardefield, *J. Electrochem. Soc.*, **111**, 1009 (1964).

TABLE I

RESISTIVITY, HALL COEFFICIENT, CARRIER CONCENTRATION, AND HALL MOBILITY FOR $Cd_{1-x}Ca_xF_2$:0.1% REF_3 AND CdF_2:x% YF_3 CRYSTALS TREATED IN Cd AT 500°

Dopant	Resistivity, ρ, ohm-cm 300°K	Resistivity, ρ, ohm-cm 77°K	Hall coefficient, $-R_H$, cm^3/coulomb 300°K	Carrier concn, n, e^-/cm^3 300°K	Hall mobility, μ_H, cm^2/v-sec 300°K
0.1% YF_3	0.178	2.18	1.4	4.4×10^{18}	7.9
0.1% YF_3 + 0.01% CaF_2	0.162	8.6	1.4	4.5×10^{18}	8.6
0.1% YF_3 + 0.1% CaF_2	0.154	2.38	1.6	4.1×10^{18}	10
0.1% YF_3 + 1.0% CaF_2	0.188	4.21	1.8	3.5×10^{18}	9.6
0.1% YF_3 + 7.0% CaF_2	2.85	2.4×10^2	12	6×10^{17}	4.2
0.1% YF_3 + 10.0% CaF_2	$\sim 10^7$				
0.1% YbF_3	0.144	4.77	1.8	3.6×10^{18}	13
0.1% YbF_3 + 3% CaF_2	87				
0.1% YbF_3 + 7% CaF_2	2.2×10^4				
0.1% YbF_3 + 10% CaF_2	$\sim 10^7$				
0.1% YF_3	0.178	2.18	1.4	4.4×10^{18}	7.9
1.0% YF_3	2.0				
10.0% YF_3	$\sim 10^7$				
20.0% YF_3	$\sim 10^7$				

greater than experimental error, were detected in the electrical, optical, or X-ray studies reported in this study.

To test whether or not conductivity was produced, all crystals were fired in Cd vapor (except CaF_2:M^{3+} which was fired in Ca). The crystal and a piece of high-purity Cd metal were heated at 500° for 1 hr in a sealed, evacuated (about 10^{-6} mm) quartz tube.

Electrical Properties.—The conductivity and Hall effect were measured using standard direct current techniques and apparatus at 300 and 77°K as described previously.[10] All of the conducting crystals measured were n type and were blue. A darker blue color indicated higher conductivity.

The electrical properties of CdF_2 crystals doped with Sm, Yb, and Y and fired in Cd at 500° were very similar. Table I lists the resistivity, ρ, Hall coefficient, R_H, carrier concentration, n, and Hall mobility, μ_H, for several crystals. The data on the Sm-doped samples are not tabulated since the measurements were less accurate. Crystals doped with Sm and fired in Cd, however, were n-type conductors, and at 300°K they behaved as is shown in Figure 1 for Y doping. In Figure 1 it is seen that the resistivity at 300 and 77°K for Cd-treated crystals with a dopant concentration of 0.1 mole % YF_3 is essentially constant from 0 to 1% CaF_2 added to CdF_2. Between 1 and 10% CaF_2, ρ goes from about 1 ohm-cm to about 10^7 ohm-cm. Similar behavior is noted with the carrier concentration and mobility as is shown in Figure 2. At 1% added CaF_2, n and μ_H are about 10^{17} e^-/cm^3 and 10 cm^2/v-sec, respectively. They both decrease as CaF_2 is added until at 10% CaF_2 they can no longer be measured. Very similar electrical results were obtained with solid solutions of CdF_2 and SrF_2 or BaF_2, whereas different results were indicated for CdF_2–PbF_2 mixtures.

Table I also shows the variation of the resistivity of Cd-fired CdF_2 crystals as a function of doping concentration. As is seen for the case of CdF_2:x% YF_3 crystals, the observed behavior is quite similar to that of adding CaF_2. Between 1 and 10% YF_3 the resistivity increases from about 2 to about 10^7 ohm-cm.

Optical Properties. Infrared Absorption.—When doped crystals are rendered conducting by firing in Cd at 500°, an associated property is the blue color of the crystals. This color is caused by strong infrared absorption; the absorption coefficient varies approximately as λ^3.[4]

Absorption spectra of selected samples before and after Cd firing were run on a Cary Model 14 spectrophotometer at 300, 77, and 6°K. Examples of these spectra are shown in Figure 3 for YbF_3 doping. From this figure and the data below on YF_3 doping it is apparent that the broad infrared absorption goes through a transition, similar to that of the conductivity, as the CaF_2/CdF_2 ratio or dopant concentration changes. Figure 3 shows the absorption of untreated and Cd-fired crystals of $Cd_{1-x}Ca_xF_2$: 0.1% YbF_3 containing 0 and 7% CaF_2. The 7% curves resemble the 0% CaF_2 untreated spectrum. There is one noticeable difference, however. The large absorption peak at 9760 A in the 0% CaF_2 curve has almost disappeared in the 7% CaF_2 sample. The reason for this single large absorption peak in YbF_3-doped CdF_2 is not fully understood, nor is its drastic reduction in intensity upon addition of CaF_2 to CdF_2.

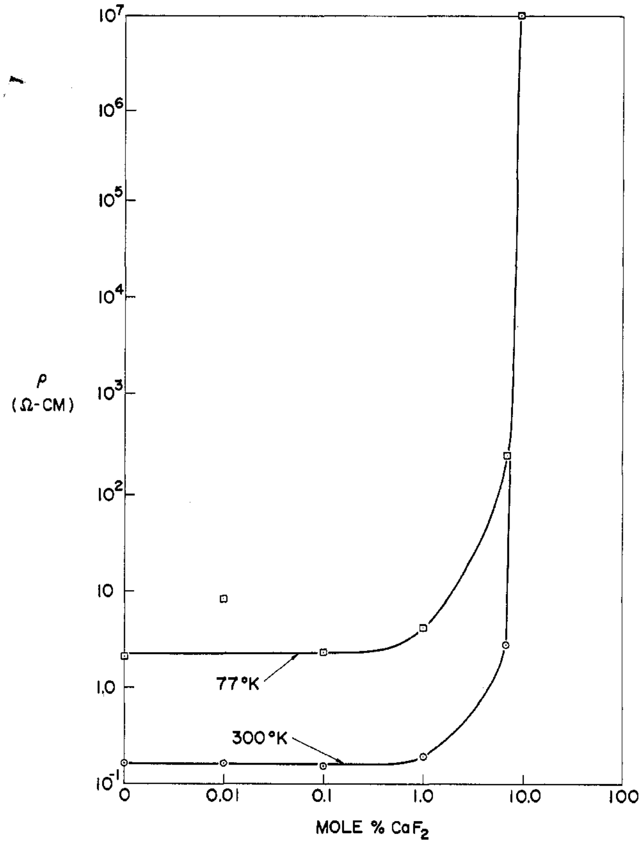

Figure 1.—Log ρ *vs.* log % CaF_2 added to CdF_2:Y^{3+} crystals at 300 and 77°K.

The behavior of the infrared absorption of Cd-fired crystals of $Cd_{1-x}Ca_xF_2$:0.1% YF_3 and CdF_2:x% YF_3 was similar to that for Yb doping. Between 1 and 10% CaF_2 or YF_3, the crystals changed from blue to colorless.

Visible Fluorescence, Phosphorescence, and Thermoluminescence.—Visible fluorescent, phosphorescent, and thermoluminescent radiations under 2537- and 3660-A excitation (low-pressure Hg pen lamps) were observed visually. Generally, the 2537-A

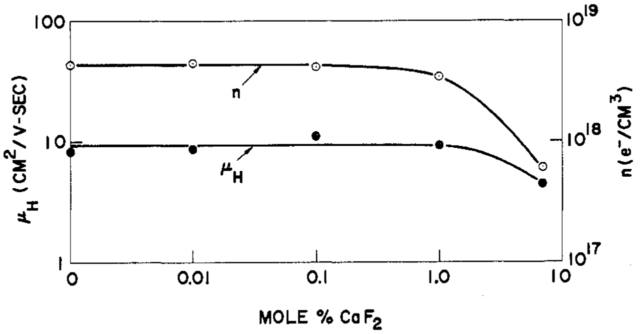

Figure 2.—Log n *vs.* log % CaF_2 and log μ_H *vs.* log % CaF_2 for the samples in Figure 1 at 300°K.

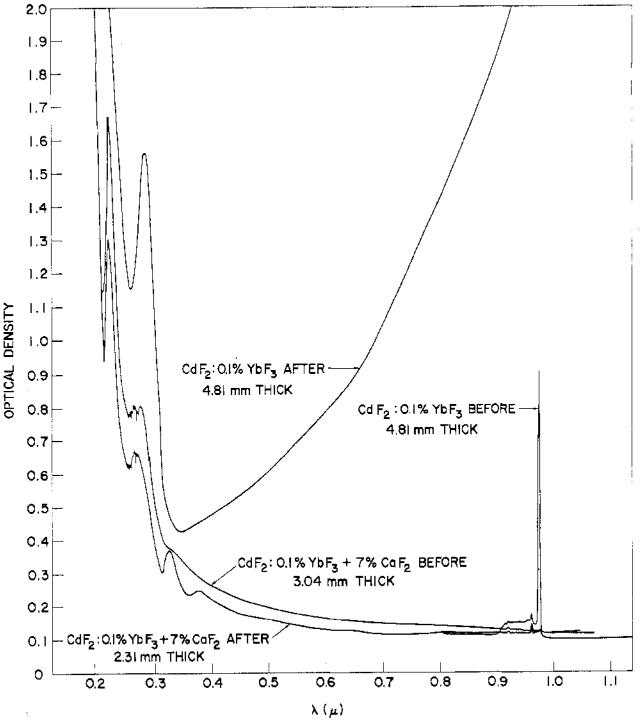

Figure 3.—Absorption spectra for $Cd_{1-x}Ca_xF_2$:1% YbF_3 crystals before and after firing in Cd at 500°.

line was the more efficient source although the 3660-A line did excite observable emissions in the CaF_2-CdF_2 mixed crystals. The thermoluminescence was observed by allowing the sample to warm naturally to room temperature after ultraviolet irradiation at 77°K.

Typical results under 2537-A excitation follow for Cd_{1-x}-Ca_xF_2:0.1% YF_3 crystals. The fluorescence of untreated crystals changed from weak pink to yellow to whitish at 1, 3, and 10% CaF_2, respectively. The fluorescent intensities were about equal at 300 and 77°K, but Cd firing quenched only the 300° emissions. The 300° phosphorescence changed from yellow to yellow-green to whitish while that at 77°K became weaker yellow-gold at 1, 3, and 10% CaF_2. The phosphorescent lifetimes of untreated crystals were much longer at 77 than at 300°K—minutes as compared to seconds—except in the 10% CaF_2 sample in which they were about equal. The lifetimes increased progressively as the CaF_2 crystal content increased from 3 to 7 to 10%. The thermoluminescence, from 77 to 300°K, was bright yellow between 0 and 7% CaF_2 and white at 10% CaF_2. At CaF_2 concentrations less than 7%, Cd firing quenched both the phosphorescence and thermoluminescence.

Divalent Ions.—Optical absorption studies on Sm-doped crystals, both untreated and Cd fired, over the entire CaF_2-CdF_2 solid solution range indicated the presence of Sm^{2+} only at very high CaF_2 concentrations. With about 0.2% total Sm, no Sm^{2+} could be obtained in the crystals unless the CaF_2 content was 99.5% or greater. Similar results were found with YF_3 doping and also with YbF_3 doping up to about 7% CaF_2. At this concentration there was some indication of Yb^{2+} ions as seen by the ultraviolet absorption bands centered around 2170, 2650, 3250, and 3750 A in Figure 3. These bands became stronger upon Cd firing. Absorption studies on Yb^{2+} in CaF_2[12] found bands centered around 2200, 2470, 2620, 2730, 3080, and 3650 A. A strong yellow fluorescence at 77°K under 2537-A excitation also appeared to be characteristic of Yb^{2+}.

Discussion

The reasons for the rapid transitions in the conductivity, the associated infrared absorption, and the phosphorescent lifetimes in a specific CaF_2 concentration region in the $Cd_{1-x}Ca_xF_2$:RE^{3+} crystals along with the production of RE^{2+} ions at varying compositions—not necessarily the 1 to 10% CaF_2 region—are considered below using the model proposed previously for CdF_2:RE^{3+} crystals.[10]

Conductivity, Infrared Absorption, and Phosphorescence.—The donor level proposed for the conducting CdF_2:RE^{3+} crystals consists of an electron being shared by the Cd^{2+} nearest neighbors to the substituted RE^{3+} dopant. The donor can be identified with a "resonance" stabilized Cd^+ oxidation state. This illustrates a significant difference between CaF_2 and CdF_2, one that allows for a shallow donor level. The 1+ oxidation state is much more stable for Cd than for Ca. Generally, Cd^+ needs to be stabilized somewhat to prevent disproportionation. This can be accomplished in the conducting CdF_2:RE^{3+} crystals by an electron being shared among several Cd^{2+} ions[12] near the substituted RE^{3+}. The stabilized Cd "impurity" state provides a natural shallow donor level (hydrogenic possibly)[8] in Cd-fired CdF_2:RE^{3+} crystals.

When the Cd "resonance" network is disrupted, the "impurity" state can no longer be formed. Consequently, there can be no conductivity. This is what happens when CaF_2 is added to the CdF_2:RE^{3+} system or the RE^{3+} dopant concentration is increased. As seen above, the resistivity, Hall mobility, carrier concentration, and broad infrared absorption all undergo sharp changes between 1 and 10% CaF_2 or RE^{3+} dopant concentration. Apparently, the impurity level giving rise to conduction and blue crystals is destroyed by replacing about one in every ten Cd^{2+} ions with another ion, such as Ca^{2+} or Re^{3+}, that cannot participate in the "resonance" effect.

The phosphorescent behavior also supports the proposed conductivity model. The phosphorescent lifetimes in the unfired crystals increase from seconds to minutes in the 1 to 10% CaF_2 concentration region. This can be explained as proposed previously.[10] The electron excited by ultraviolet radiation is trapped in the Cd "impurity" levels until recombination can occur. As the CaF_2 content increases from 1 to 10%, the number of "impurity" states decreases and their physical separation increases. It then takes longer for re-

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[12] P. P. Feofilov, *Opt. Spectry.* (U.S.S.R.), **1**, 992 (1956).

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

$$M + 2RE^{3+} \rightleftharpoons M^{2+} + 2RE^{2+}$$

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 $Cd_{1-x}Ca_xF_2$: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 then 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.

Acknowledgments.—The author wishes to thank Mr. J. E. Scardefield for help in growing the crystals and Mr. G. D. Pettit for the optical absorption measurements.

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Semiconductivity in $Cd_{1-x}Ca_xF_2$:In^{3+} Single Crystals

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Received August 16, 1965

Bridgman-grown $Cd_{1-x}Ca_xF_2$ 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^-/cm^3, and 10 cm^2/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-A radiation. All of the above properties were strongly dependent on the CaF_2 content of the doped $Cd_{1-x}Ca_xF_2$ 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 $Cd_{1-x}Ca_xF_2$ crystals are quite similar to those previously found for RE-doped crystals, it appears that the same conductivity model previously proposed for CdF_2: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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