CONDENSED-MATTER SPECTROSCOPY

Formation of H_a^- Hydrogen Centers upon Additive Coloration of Alkaline-Earth Fluoride Crystals

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Abstract—The mechanism of coloration of alkaline-earth fluoride crystals CaF_2, SrF_2, and BaF_2 in calcium vapors in an autoclave with a cold zone is studied. It was found that the pressure in the autoclave upon constant evacuation by a vacuum pump within the temperature range of 500−800°C increases due to evaporation of metal calcium. In addition to the optical-absorption bands of color centers in the additively colored undoped crystals or to the bands of divalent ions in the crystals doped with rare-earth Sm, Yb, and Tm elements, there appear intense bands in the vacuum ultraviolet region at 7.7, 7.0, and 6.025 eV in CaF_2, SrF_2, and BaF_2, respectively. These bands belong to the H_a^- hydrogen centers. The formation of hydrogen centers is also confirmed by the appearance of the EPR signal of interstitial hydrogen atoms after X-ray irradiation of the additively colored crystals. Grinding of the outer edges of the colored crystals leads to a decrease in the hydrogen absorption-band intensity with depth to complete disappearance. The rate of hydrogen penetration inside the crystal is lower than the corresponding rate of color centers (anion vacancies) by a factor of tens. The visible color density of the outer regions of the hydrogen-containing crystals is several times lower than that of the inner region due to the competition between the color centers and hydrogen centers.

INTRODUCTION

Additive coloration is an effective tool for the formation of thermally stable color centers in crystals and for the transformation of the valence state of impurity ions, which is important for development of new laser and holographic media. Extensive investigations of additive coloration of alkali halide crystals were performed as early as in the 1930s and 1940s [1, 2]. Interest in these investigations was renewed in the 1970s–1990s due to the development of laser media based on color centers in alkali halide crystals [3, 4]. Investigations of the processes occurring upon additive coloration of alkaline-earth fluoride crystals are extensively continued at present in order to find laser and photochromic media for holography [5, 6].

The additive coloration of halide crystals in metal vapors begins from binding of a metal ion to a cation site on the external plane of the crystal lattice and subsequent migration of an anion vacancy and an electron inside the lattice [1]. Heating of an sealed ampoule with the sample and metal spaced from each other was frequently used to color alkali halide crystals [2] and alkaline-earth fluoride crystals [19]. A method of controlling the color density by varying the buffer-gas pressure was developed by van Doorn [13]. Later, this method was called the "heat-pipe" method [4−6].

The complexity of additive coloration of calcium fluoride crystals was noted in work [7], which reported on the formation of hydrogen ions in fluorine sites (U centers [1] or H_a^- centers [8]). Despite the fact that the starting mechanism of additive coloration has been known for a long time [1, 2], many details of the accompanying processes remain unstudied.

In the present work, we study the mechanisms of additive coloration of alkaline-earth fluoride crystals CaF_2, SrF_2, and BaF_2 in an autoclave with a cold zone and the accompanying formation of hydrogen centers.

EXPERIMENTAL TECHNIQUE

The fluoride crystals were grown by the Stockbarger method in a three-channel graphite crucible in vacuum.[1] Several percent of CdF_2 were added to the raw material to purify it from oxygen impurity. The absence of oxygen was controlled by the absorption spectra in the vacuum ultraviolet region and by the absence of emission under excitation in the region of 200 nm by a DDS-30 deuterium lamp through a focal monochromator.

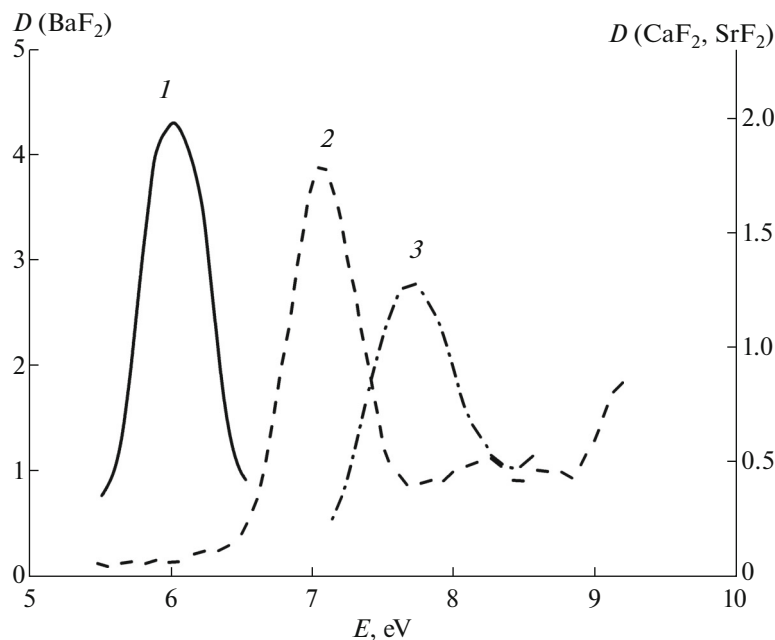[1] The crystals were grown by V.A. Kozlovskii.

Fig. 1. Absorption spectra of additively colored alkaline-earth fluoride crystals in the region of the bands of H_a^- centers. The thickness of the samples is 1 mm.

The absorption spectra in the range of 190−3000 nm were measured on a Perkin−Elmer Lambda-950 spectrophotometer,[2] and the spectra in the vacuum ultraviolet region were recorded using a laboratory setup equipped with a VMR2 monochromator (115−300 nm). An L7292 deuterium lamp (Hamamatsu) was used as a source of vacuum ultraviolet radiation, and an FEU-142 photomultiplier was used as a detector.

Additive coloration of crystals was performed in a stainless steel autoclave at temperatures of 700−850°C. The crystal samples and metal calcium pieces were placed in different containers (boats). After evacuation to $10^{-2}-10^{-3}$ Torr, the autoclave was lowered into a furnace. After heating to a required temperature, the autoclave with the samples was kept in the furnace for 0.5−3 h depending on the thickness of samples and the coloration temperature. As a result of coloration, the surface of SrF_2 and BaF_2 samples became opaque, and the samples were polished again.

The metal calcium granules were stored in oil to prevent interaction with air. After withdrawal, the calcium granules were dried with filter paper and washed in acetone to remove oil from the surface. After coloration, hollow white spheres remained in the calcium container. Obviously, metal calcium evaporated during the coloration leaving a surface oxide film.

RESULTS AND DISCUSSION

Absorption Spectra

The additive coloration of alkaline-earth CaF_2, SrF_2, and BaF_2 fluoride crystals, both pure and doped with RE^{3+} ions, forms, apart from the absorption bands of F aggregate centers in the visible region, strong absorption bands at 7.7 and 7.0 eV in CaF_2 and SrF_2 crystals (see also [9]) and a band at 6.025 eV in BaF_2 (Fig. 1). The optical density of ultraviolet bands was several times higher than the density of bands in the visible spectral region. The crystals doped with trivalent rare-earth ions exhibited, in addition to the strong bands in the vacuum ultraviolet region, bands of divalent ions or photochromic centers in the visible spectral region.

The on-site H_a^- hydrogen ions at 77 K have absorption bands with maxima at 7.65, 7.04, and 6.00 eV in CaF_2, SrF_2, and BaF_2, respectively [8]. The hydrogen centers were obtained by coloration of fluorides in contact with aluminum in a hydrogen atmosphere (tens of mm Hg) at a temperature of about 900°C [10]. The formation of IR absorption bands of H_a^- centers in CaF_2 was observed after additive coloration in calcium vapors [7]. The ultraviolet bands observed in our CaF_2, SrF_2, and BaF_2 crystals colored in calcium vapors are probably also caused by the H_a^- ions.

As is known, the H_a^- centers in alkaline-earth fluorides dissociate under the action of X-ray irradiation at
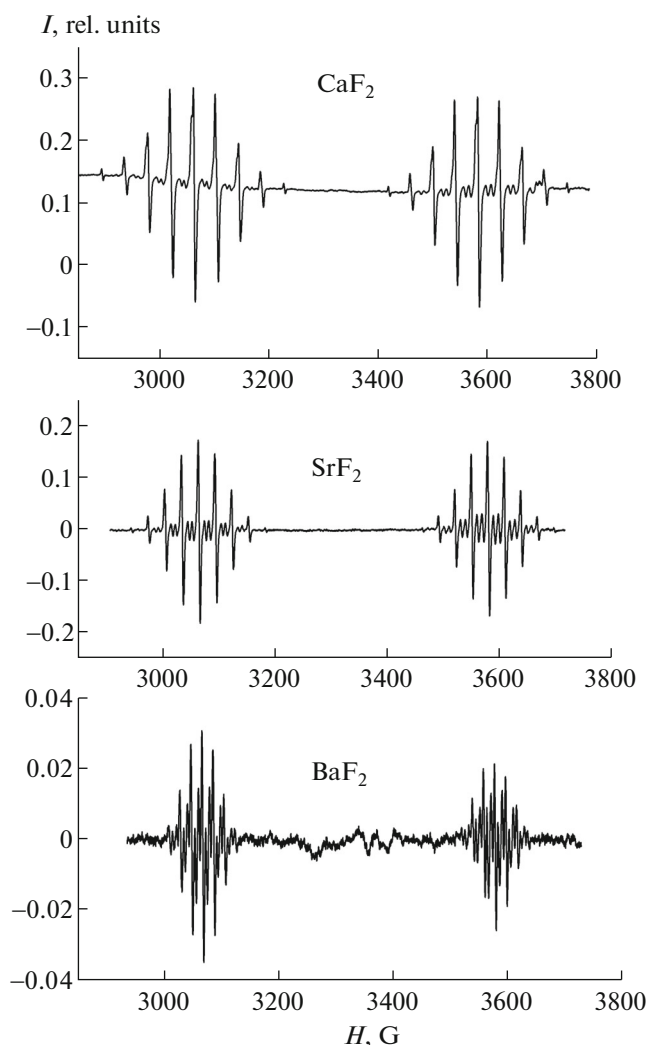
I, rel. units

Fig. 2. EPR spectra of additively colored CaF_2, SrF_2, and BaF_2 crystals after X-ray irradiation at room temperature.

room temperature with the formation of aggregate color centers (F_2^+) and interstitial hydrogen atoms H_i^0 [11]. The interstitial hydrogen atoms in alkaline-earth fluorides have no optical-absorption bands in the region of 250–2000 nm [11] and are detected by EPR spectra [10–12].

X-ray irradiation of our additively colored CaF_2, SrF_2, and BaF_2 crystals at room temperature leads to the appearance of EPR spectra of interstitial hydrogen atoms (Fig. 2) and optical-absorption bands of aggregate color centers (F, F_2^+, ...) in the visible and near-IR spectral regions.

Thus, the formation of hydrogen ions (H_a^- centers) upon additive coloration of alkaline-earth CaF_2, SrF_2, and BaF_2 fluorides can be considered proven.

The Mechanism of Additive Coloration in an Autoclave with a Cold Zone

The additive coloration is caused by "dissolving" of metal atoms, i.e., by binding of a metal ion from vapor to a cation site on the crystal face and by motion of a formed anion vacancy and an electron inside the crystal [1, 2]. When the entire ampoule is in the heater, the concentration of color centers is determined by the metal-vapor pressure. For metals with a triple point (Na, K, Rb, Cs, Zn, Cd, Hg, S, Se, Te, P), one can use coloration in an autoclave with a cold zone, in which the liquid metal condensed in the cold zone flows down to the hot zone again [13]. The metal-vapor pressure in this process is determined by the buffer gas pressure in the upper zone of the autoclave [13]. This method is inapplicable for metal calcium. A variant of the van Doorn method [13] was used to additively color CaF_2 in [5, 6], in which metal calcium in a low concentration was dissolved in a liquid alkali metal.

In our method, the coloration of alkaline-earth fluoride crystals begins from the addition of calcium atoms to the surface. Metal calcium is in another container, and Ca atoms are transferred to the crystal surface by the metal vapors. Evaporated calcium atoms drift in vacuum through the region with the crystals to the upper cold walls of the autoclave and condense there. The color center concentration is proportional to the mass of metal calcium in the container.

The flow of calcium atoms should increase the pressure in the upper region of the autoclave. We measured the pressure in the autoclave during heating at a rate of about 9°/min. The pressure was recorded by a PMT-4 thermocouple gauge lamp. A broad peak in the pressure was observed within the range of 500–800°C with a maximum at 650°C. The peak amplitude increased with increasing metal calcium mass and was $1-5 \times 10^{-3}$ Torr. As is known, the temperature dependence of calcium vapor pressure is described by the empirical formula $p(\text{Torr}) = 7.79 - 8524/T$ (where T is the absolute temperature, K) [14, 15]. The calcium vapor pressure at a temperature of 650°C is 3.7×10^{-2} Torr. The peak pressures measured by us are lower than the equilibrium calcium vapor pressure due to the continuous evacuation by a vacuum pump. We can conclude that the increase in pressure within the range of 500–800°C is caused by calcium evaporation.

The Formation Mechanism of H_a^- Centers

It is obvious that the formation of H_a^- centers is caused by the interaction of primary vacancies and electrons with hydrogen-containing impurities inside the crystal or on its surface.

One likely mechanism of formation of hydrogen centers is the dissociation of OH^- ions into hydrogen (H_a^-) and oxygen (O^- vacancy) centers upon additive coloration, which we previously observed in sodium
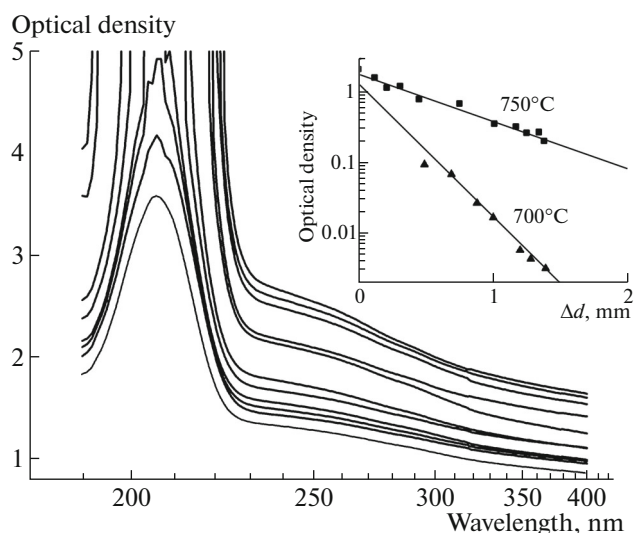
Fig. 3. Absorption spectra of BaF_2 crystals additively colored at 750°C. The sample was cut off of the colored crystal and its outer side was stepwise ground; the arrows show the sequence of steps. The inset shows the decrease in the hydrogen band optical density with decreasing thickness of BaF_2 samples colored at temperatures of 750 and 700°C. The optical density of the hydrogen band is measured at wavelengths of 215 nm (700°C) and 223 nm (750°C). The straight lines correspond to the exponents $\exp(-x/k)$ that most precisely describe the measurement data (x is the thickness of samples in mm, and $k = 0.65$ mm for 750°C and 0.23 mm for 700°C).

halide crystals [16, 17]. As was noted above, the absorption spectra of our CaF_2, SrF_2, and BaF_2 crystals contain no OH^- bands in the IR region (3640–3630 cm^{-1} [12]). Nevertheless, assuming that hydroxyl groups still exist in the crystals, we should expect that the shift of the band of hydrogen centers inside the crystal upon additive coloration will coincide with the motion of vacancies and electrons.

The color propagation was studied by cleaving the cylindrical sample into disks with subsequent stepwise polishing of their outer sides. The additively colored crystal rod about 6 mm thick was cleaved into identical parts about 2 mm thick each. The inner sample exhibited no bands of H_a^- centers, while the outer samples had strong absorption in the vacuum ultraviolet region (Fig. 1). Stepwise polishing of one of the outer samples from the external surface led to a continuous decrease in the H_a^- band density (Fig. 3). The optical

density of the H_a^- band is proportional to the number of hydrogen centers remaining in the sample. The decrease of the optical density of hydrogen centers in semilogarithmic coordinates is described by straight lines (Fig. 3, inset). To find the distribution function of hydrogen centers over the thickness, one should differentiate the thus-obtained lines. Therefore, the concentration of hydrogen centers exponentially decreases with thickness.

The rate of additive coloration of CaF_2 crystals, pure or doped with a low concentration of rare-earth ions (about 0.01 mol %), is several millimeters per hour at a temperature of 750°C. The rate of motion of hydrogen centers in the CaF_2 and SrF_2 samples at this temperature was about 0.2 mm/h. The hydrogen motion rate in the BaF_2 crystal was considerably higher, because the inner part of the sample 3 mm thick also had an absorption band of H_a^- centers.

The process of hydrogen penetration into the crystals can be clearly seen by the change in the color of undoped fluoride crystals with depth. Since the hydrogen centers penetrate into the crystal from all surfaces, we cut out the inner part of the cylindrical crystal to visualize this penetration (Fig. 4). The inner part of the sample was colored more strongly than the external surface, which is obviously caused by the competition between the color and hydrogen centers.

Thus, hydrogen centers appear on the external side of the sample subjected to coloration and move inside with a rate considerably lower than the rate of conventional additive coloration due to the motion of anion vacancies.

Hydrogen Source

The hydrogen source may be the walls of the autoclave in which the coloration occurs. It is known that steel releases hydrogen at high temperatures [18]. However, long annealing of the autoclave in vacuum did not decrease the efficiency of formation of hydrogen centers in our crystals, which allows us to exclude hydrogen release from the autoclave walls as a possible reason for the appearance of hydrogen centers upon additive coloration.

Another source of hydrogen may be the mineral oil in which metal calcium was stored or other organic impurities, which release hydrogen upon heating in vacuum. To decrease the amount of organic impurities introduced into the autoclave with metal calcium

Fig. 4. Photographs of CaF_2 (left), SrF_2 (center), and BaF_2 (right) crystals additively colored at 800°C for 30 min. The crystals are about 9 mm in diameter. Plates 1−1.5 mm thick are cut off of the central part of cylindrical crystals about 5 mm thick.

granules, the metal particles were cleaned from oil by filter paper and then washed in acetone. The access of oil vapors from the pump was cut off by a liquid nitrogen trap. In the process of heating in the autoclave, we exposed the samples for a long time at 200 and 400°C with continuous evacuation to a pressure of 5×10^{-3} Torr. This exerted no noticeable effect on the intensity of the ultraviolet bands of hydrogen centers. On the other hand, the fact that the hydrogen absorption bands become more intense with increasing amount of metal calcium, as well as the spherical shells remaining from calcium granules, indicate that organic impurities are introduced with calcium granules.

In some experiments, the oxide shells of the granules were removed by etching in hydrochloric acid—ethanol solution until a metallic luster appeared on the granules and then by washing them in ethanol and ether (see also [14]). After additive coloration, oxide shells from calcium granules remained in the boat with the metal, and the crystals exhibited the bands of hydrogen centers.

Thus, the sources of hydrogen can be either the autoclave walls or calcium granules. In additional experiments, the crystals were colored in samarium vapors and in contact with aluminum foil. Since the pressure of aluminum vapors at the coloration temperatures is four to six orders of magnitude lower that the pressure of Ca or Sm vapors [15], the crystal surface must be in contact with Al. In both cases, the absorption spectra after coloration contained the bands of color centers and H_a^- centers. The presence of hydrogen in the autoclave is independent of coloring metal (Ca, Sm, Al). Hydrogen obviously remains in the autoclave due the insufficiently high degree of evacuation (about 10^{-3} Torr). A strong increase in the absorption in the region of $E > 6$ eV after additive coloration of SrF_2 at a pressure of 10^{-3} Torr, which is probably related to the tail of the hydrogen band at 7.0 eV, was observed in [19].

CONCLUSIONS

The additive coloration of fluoride crystals in vacuum in an autoclave with a cold zone occurs due to the transfer of calcium atoms from the hot zone to the cold one. The additive coloration of alkaline-earth fluoride crystals in metal (Ca, Sm) vapors or in contact with Al at temperatures of 700−900°C in an autoclave is accompanied by the formation of a hydrogen atmosphere. Then, a hydrogen atom occupies an anion vacancy in fluoride crystals, captures an electron, and thus forms an on-site hydrogen ion H_a^-, which migrates inside the crystal lattice at a rate considerably lower than the rate of motion of anion vacancies.

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