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Role of oxygen atoms in CaF$_2$ crystals doped with Eu atom

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The optical transparency in function of wavelength of CaF$_2$ crystals doped with Eu (denoted by CaF$_2$:Eu) has been measured. The optical absorption occurs below $\lambda=400$ nm depending on the amount of Eu atoms doped. The short wavelength below 400 nm has been shifted to around $\lambda=425$ nm. As a result, the 425 nm wavelength increased and the light below 400 nm was cut through CaF$_2$:Eu crystals. This scintillating effect has been found much increased by adding oxygen atoms in crystals. This is due to the distortion of electrical and structural symmetry in crystals by adding oxygen atoms in the form of oxide materials. © 2008 American Institute of Physics. [DOI: 10.1063/1.2970155]

I. INTRODUCTION

Recently, blue light emitting devices (LEDs) have attracted many researchers’ attention.$^1$ The LEDs with short wavelengths are used in some areas such as traffic signals, cell phones, and new displays. The use of blue LED is especially increasing. The short wavelength light attacks the organic materials that are used as coating for optical devices such as LED and laser diode. The output light power decreases due to the coating materials becoming opaque with time. This tendency is detrimental for the optical devices needing high reliability. Materials for cutting shorter wavelength are strongly desired to maintain the life of the device such as traffic lights. It is also important to protect a human from potentially life threatening UV optical problem.

In addition, CaF$_2$ crystals attracted much attention due to their high transparency from UV light to IR light.$^{2,3}$ We previously reported their fundamental properties.$^{4,5}$ In addition, we have grown CaF$_2$ crystals using the vertical Bridgman technique under the vacuum condition. The Eu atoms were doped at the growth process. It has been found that the optical absorption occurs below 400 nm and the short wavelength component has been translated into 425 nm wavelength. We believe CaF$_2$:Eu crystals are the favorite material to cut shorter wavelength emitted by LED semiconductors to protect the organic materials, including human body, and enhance the output power around 425 nm. This scintillating effect has been strongly enhanced by adding oxygen atoms into CaF$_2$ crystals.

This paper describes the scintillating effect and the role of oxygen atoms in terms of optical measurements and x-ray photoelectron spectroscopy (XPS) analyses.

II. EXPERIMENT

The crystals were grown using vertical Bridgman technique under $10^{-6}$ Torr vacuum conditions. The carbon crucibles were used to grow crystals. The inner diameter and length were around 250 and 250 mm, respectively. The growth speed was varied from 2 to 20 mm/h to control the heat flow during the growth process. To remove the excess residual oxygen atoms in a starting material such as CaO, a small amount of ZnF$_2$ was added to the melt to evaporate as ZnO during the heating process. The amount of ZnF$_2$ and heating conditions influence the oxygen atom concentration in the crystals obtained. EuF$_3$ or Eu$_2$O$_3$ powder was used as a dopant into the melt. To add oxygen atoms into crystals, Eu$_2$O$_3$ was used as a doping material. The starting materials were powderlike solidified CaF$_2$. The amount of doping was calculated as Eu atom fraction in crystals. The relationship of excitation and emission was obtained by fluorescence spectroscopy (Hitachi, F-4500). The transparency was also measured by spectrophotometer. The photoluminescence was measured at room temperature excited by a 325 nm wavelength He–Cd laser. The variation in electron energy of Eu atom orbital was measured by XPS analyses.

III. RESULTS AND DISCUSSION

CaF$_2$ crystals were grown without any trouble by adding EuF$_3$ or Eu$_2$O$_3$ as a doping material. In each case, the amount was less than 1 mol % calculated as amount of Eu atoms. The variation in optical transparency is given in Fig. 1 with parameters of Eu source materials with 0.1 mol % Eu doping. The shorter optical wavelength, which is less than 400 nm, is absorbed by the CaF$_2$:Eu crystals. The amount of absorption increases by increasing the amount of doping material. It has been found that the shorter wavelength component (less than 400 nm) is cut by using CaF$_2$:Eu crystals. It should be noted that the transmittance variation in crystals doped with Eu$_2$O$_3$ is larger than those doped with EuF$_3$. It seems favorable to use these in optical device caps or in windows used to protect human safety as almost all LED fabricated with GaN related materials contain 364 nm peak emitted by the GaN itself, so the 364 nm light strongly damages the materials such as coating plastics, which will be opaque within several years of use.

Next, fluorescence spectroscopy of CaF$_2$ crystals was measured, as shown in Figs. 2(a)–2(c) [Eu doped, undoped,
and Eu with oxygen atom (Eu2O3) doped, respectively], in which the penetrated laser for measurement through the crystal is denoted at the same figures. The vertical axis means input wavelength; the horizontal axis means output wavelength. Figure 2(a) shows the result of a typical fluorescence spectroscopy of CaF2:Eu with 0.1 mol % Eu doped comparing with an undoped CaF2 as is given in Fig. 2(b). It should be noted that CaF2:Eu crystals showed a scintillating effect such as the light with less than 400 nm wavelength absorbed by the crystal. So the light emission occurred at 425 nm wavelength as shown in Fig. 2(a), whereas the undoped CaF2 did not emit any light as shown in Fig. 2(b). The result of Eu2O3 added material is given in Fig. 2(c). This result indicates that the scintillating effect is clearly shown and that the short wavelength region is also clearly cut by this crystal, while 300 and 200 nm wavelengths are not clearly absorbed. It is partially transparent. Next, the photoluminescence results show that the 425 nm luminescence clearly appeared as is given in Fig. 3. Varying the amount of Eu doping denotes the results of crystal doped with EuF3. Those doped with Eu2O3 are also shown with variation in the Eu doping amount. These results indicate that the crystals doped with Eu2O3 show stronger luminescence as shown in Fig. 3. This result indicates that the residual oxygen atoms strongly influenced the efficiency of the crystals. One of the most important points is that the oxide materials as doping materials are quite cheaper than pure metals and fluoride materials. This result means that CaF2:Eu crystals have two advantages:

1. optical components with less than 400 nm are cut to protect devices and human life safety and
2. 425 nm optical components are enhanced.

For example, we tried to measure emission spectra shifting by using UV LED with 360–380 nm peak wavelength. It has been found that the UV light shifted to 425 nm wavelength. Actually, the UV LED looked like blue LED through the CaF2:Eu crystals. This result indicated that the LED output light wavelength became stable wavelength with 425 nm through CaF2:Eu crystals, even if the LED active layer component such as In/Ga ratio fluctuated during crystal growth process.

These scintillating phenomena were strongly enhanced...
by adding Eu$_2$O$_3$ as a source of Eu atoms. In this case ZnF$_2$ is intentionally codoped to reduce the excess oxygen atoms with forming ZnO to evaporate out of the growing system. As photoluminescence results indicated that the emission around 425 nm of Eu$_2$O$_3$ added crystals is stronger than that of EuF$_3$ added crystals even if nearly the same amount of Eu atoms were doped. To elucidate the role of oxygen atoms, we have measured Eu atoms by XPS analyses. It should be noted that the 4$d$ electron energy of Eu atom shifted in the crystal doped with Eu$_2$O$_3$. The signal of the 4$d$ electron of the Eu$_2$O$_3$ added crystal is shown in Fig. 4(a) as compared to EuF$_3$ doped crystals in Fig. 4(b). The energy shift, about 2.5 eV, has been recognized in the presence of oxygen atoms around Eu atoms as shown in Fig. 4(a). Even though $E^{2+}$ emission occurs with 5$d$-4$f$ transition, the signal 5$d$ electron was not clearly divided with other energy levels in this measurement. So the 4$d$ electron level of Eu atom is shown in Fig. 4. The 5$d$ electron orbital is outer than the 4$d$ electron orbital, so 5$d$ electron orbital should be more influenced by surrounding molecules.

These results indicate that the electron energy was much influenced in the presence of oxygen atoms around Eu atoms in the crystals. Even the electrons with outer orbital were much influenced in the presence of oxygen atoms. It is possible that the incorporation of oxygen partially influences the electron energy state of Eu atoms and slightly the electron level value with variation in the transition rate. As a result, the electrical symmetry and structure symmetry were slightly distorted in Eu$_2$O$_3$ doped crystals by the presence of oxygen atoms, so it is considered the absorption-emission efficiency of Eu atoms increased. In order to elucidate the atomic ordering, a rocking curve was measured by x-ray diffraction. The typical results of the crystals doped with 0.1 mol % Eu

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**FIG. 3.** Typical examples of photoluminescence measurements of CaF$_2$ doped with Eu. The amount of doping material was calculated as amount of Eu atoms.

**FIG. 4.** XPS results of 4$d$ electron. Two peaks denote 4$d$ electron spin differences: (a) Eu$_2$O$_3$ doped (b) EuF$_3$ doped.
atoms showed that the (200) diffraction full width at half maximum (FWHM) of Eu$_2$O$_3$ doped crystal is larger than 0.22° as compared to EuF$_3$ doped crystals being 0.16°. It has been found that FWHM of Eu$_2$O$_3$ doped crystal is slightly larger than that of EuF$_3$ doped crystals. These crystals were cut from the crystals obtained without annealing process. This result supports that the oxygen atom partially distorted the crystal structure. The detail of oxygen atom concentration in crystals and the relationship between optical properties and the oxygen concentration are not yet well known and are now under investigation. The effects of other impurities for optical devices such as white LED cap and solar cell windows are also now under investigation and will be reported as soon as possible.

IV. SUMMARY

CaF$_2$:Eu crystal cuts off shorter wavelength light and emitted light around 425 nm. The CaF$_2$:Eu crystals have two advantages:

1. optical components with less than 400 nm are cut to protect devices and human life safety and
2. 425 nm optical components are enhanced.

It has been found that the crystal doped with Eu$_2$O$_3$ demonstrated stronger effect compared with crystals EuF$_3$ doping. We believe this is due to the distortion of electrical and structural symmetry in crystals by adding oxygen atoms. The detail of oxygen atom concentration in crystals and the relationship between optical properties and the oxygen concentration are not yet well known and are now under investigation. The other detail data will be reported as soon as possible.

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