HIGHLY SENSITIVE FLUORESCENCE THERMOMETER USING LONG AFTERGLOW PHOSPHOR

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Abstract: Long afterglow phosphorescent $SrAl_2O_4$ and $CaAl_2O_4$ based phosphors are found to be a useful sensor head material in the fluorescence thermometer because of extremely long fluorescence lifetime. Highly sensitive temperature sensor can be developed based on temperature dependence of afterglow intensity of long afterglow phosphor. Sensitivity of long afterglow phosphorescent $SrAl_2O_4$:Eu, Ln and $CaAl_2O_4$:Eu, Ln based phosphors are considered to be dominated by depth of the hole traps generated by doped rare-earth elements.

Keywords: fiber-optic fluorescence thermometer, sensor material, long afterglow phosphor.

1. INTRODUCTION

The fiber-optic fluorescence thermometer has attracted much attention, because it enables the temperature measurement in the extra-ordinary environments [1-8]. In the fluorescence thermometer, phosphor used as a sensor material is responsible for the accuracy and the sensitivity of the measurements. Among many phosphors used in thermo-sensors, long afterglow phosphorescent $SrAl_2O_4$ and $CaAl_2O_4$ based phosphors are found to be a highly sensitive sensor material in the fluorescence thermometer because of its extremely long fluorescence lifetime [2-8].

In this paper, composite of $SrAl_2O_4$:Eu, Ln and $CaAl_2O_4$:Eu, Ln phosphor powders have been systematically examined as a sensor material. Mechanism for highly sensitive temperature measurement is reported based on thermal excitation of trapped carriers

2. EXPERIMENTAL

Fiber-optic fluorescence thermometer is schematically illustrated in Fig. 1. The equipment consists of a excitation laser or LED, optical fiber, sensor material and detector. Sensor material, $CaAl_2O_4$:Eu, Ln, is excited by a YAG laser (λ=355 nm) or UV-LED (λ=365 nm) through an optical fiber. In $SrAl_2O_4$:Eu, Ln, blue LED is also used as an exciting source.

Fluorescence thermometer using sensor sheet is also shown in Fig. 2. In this system, fluorescence sensor sheet made from long afterglow $SrAl_2O_4$ and/or $CaAl_2O_4$ phosphors is excited by UV LED or blue LED.

The composite sensor materials are prepared as shown in Fig. 3 using a dipping or molding process [6]. Sensor head equipped with the composite of $SrAl_2O_4$:Eu, Ln and $CaAl_2O_4$:Eu, Ln phosphor powders with a silicone attached at the top of the optical fiber is used as the specimens. Sensor composite in sheet shape is also fabricated for fluorescence thermometer. Afterglow intensities were measured at temperatures from 283 K to 573 K under the

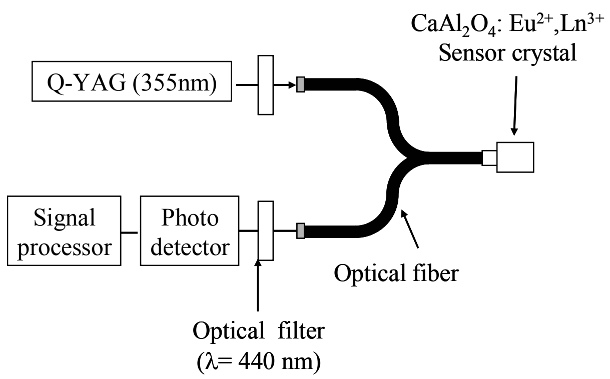

Fig. 1. Fiber-optic fluorescence thermometer equipment using $SrAl_2O_4$:Eu, Ln and $CaAl_2O_4$:Eu, Ln phosphor composite as a sensor material. Sensor material, which is formed at the end of SiO_2 fiber, is made from a composite of phosphor powders and silicone polymer.

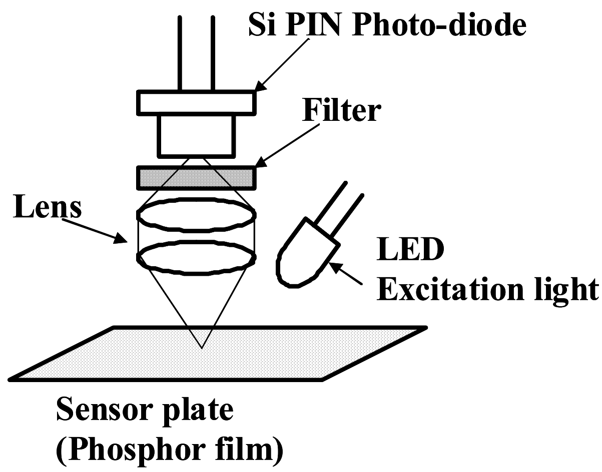

Fig. 2. Fluorescence thermometer equipment using $SrAl_2O_4$:Eu, Ln and $CaAl_2O_4$:Eu, Ln phosphor composite as a sensor material. Sensor plate is made from a composite film of phosphor powders and silicone polymer.

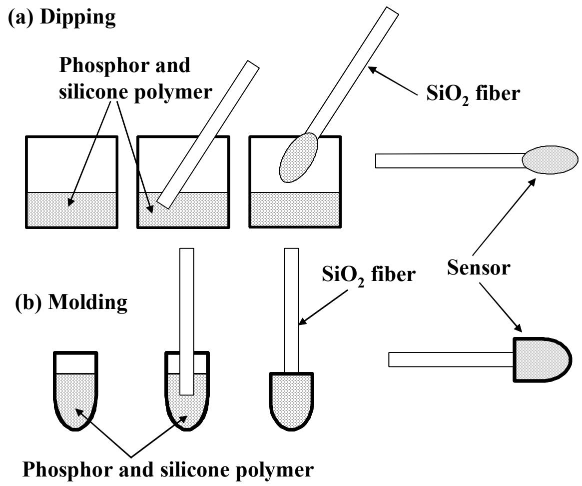

Fig. 3. Schematic diagram for the preparation of sensor composite using a dipping process (a) and a molding process (b). $CaAl_2O_4$:Eu, Ln phosphors mixed with silicone polymer is fabricated at the end part of a SiO_2 fiber

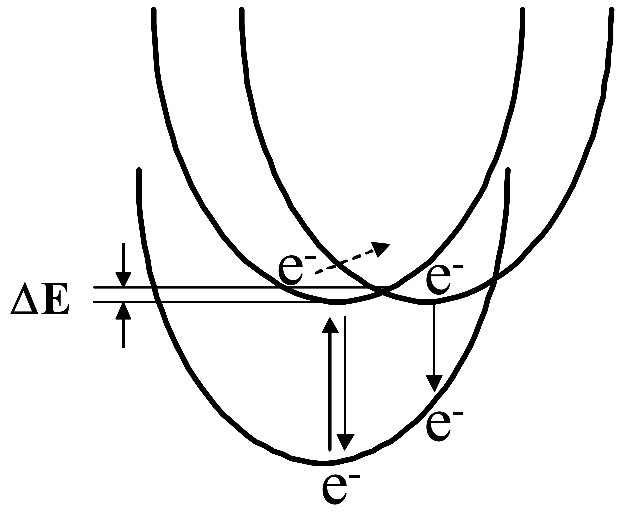

Fig. 5. Energy diagram for d-electrons in Cr^{3+} ions of a sensor materials used in fiber-optic fluorescence thermometer [1]. Mechanism using ruby sensor is reported by K. T. V. Grattan and Z. Y. Zhang [1].

excitation by third harmonic generation (λ=355 nm) from Q-switched YAG laser.

3. MECHANISM

Mechanism of a typical fluorescence thermometer is schematically illustrated in Fig. 4. Electrons at excited states are excited thermally and return to the ground state through a non-radiative process. Photoluminescence intensity, therefore, decreases with temperature. Transition

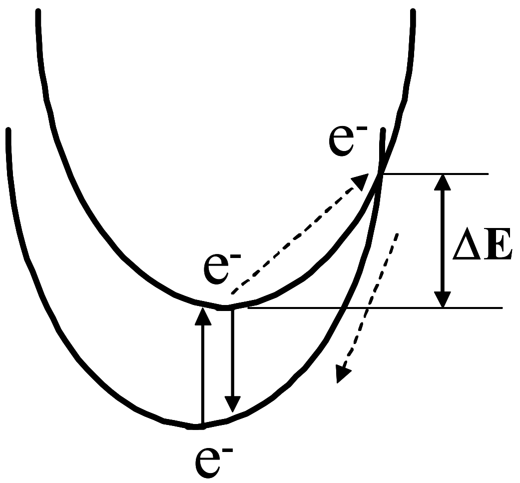

Fig. 4. Schematic illustration of a energy diagram for thermal excitation of optically excited electrons.

in the non-radiative process is generally faster than that in the radiative process. Lifetime of photoluminescence also decreases with temperature.

Temperature dependence of photoluminescence from ruby (Cr doped Al_2O_3 crystal) is explained as shown in Fig. 5. In ruby, electrons at excited states are excited thermally and return to the ground state through another radiative process and a non-radiative process. Photoluminescence intensity observed decreases with temperature. Lifetime of photoluminescence also decreases with temperature. Temperature dependences of photoluminescence intensity and lifetime are both potentially useful for fluorescence thermometry.

Figure 6 shows a schematic illustration of mechanism of temperature dependences for long afterglow phosphor and photo-stimulated luminescent phosphor. Holes generated by the excitation of Eu^{2+} ions is trapped with a hole trap level in Fig. 6 (a). The trapped holes are, then, released by thermal activation. Afterglow phosphorescence intensity, therefore, varies with temperature sensitively. Similar mechanism is considered to be occurred in $SrAl_2O_4$:Eu, Ln phosphors. Thermal excitation from electron trap is also shown in Fig. 6 (b).

4. RESULTS AND DISCUSSION

Blue colored fluorescence at wavelength of λ=442 nm is observed in $CaAl_2O_4$:Eu, Ln phosphors as shown in Fig. 7. Green colored fluorescence at wavelength of λ=520 nm is also observed in $SrAl_2O_4$:Eu, Ln phosphors. In both cases, decay curves are composed of two exponential components.

Temperature variations of afterglow phosphorescence intensity (0.1 ms after stopping the excitation beam) of $CaAl_2O_4$:Eu phosphors co-doped with Ho, Nd, Dy is shown

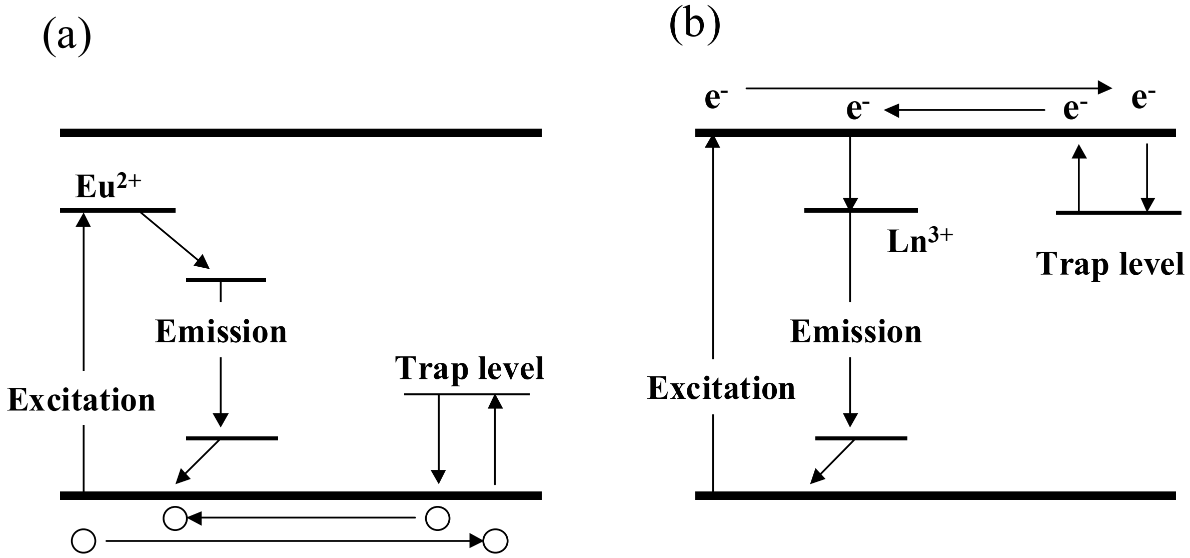

Fig. 6. Schematic illustration for afterglow mechanism of photo-stimulated luminescence. Holes generated by the excitation of Eu^{2+} ions is trapped with a hole trap level. The trapped holes are, then, released by thermal activation. Afterglow phosphorescence intensity, therefore, varies with temperature sensitively. Similar mechanism is considered to be occurred in $SrAl_2O_4$:Eu, Ln phosphors.

in Fig. 8. Both in $SrAl_2O_4$:Eu, Ln and $CaAl_2O_4$:Eu, Ln phosphors, temperature variations of afterglow intensities change dramatically with the doping elements. In other word, these are effected greatly with the hole trap depth generated by doped elements. $CaAl_2O_4$:Eu, Ho specimen shows the largest coefficient of -0.00207 in the temperature ranging from 293 to 393 K. Temperature coefficient of Ho, Nd and Dy doped $CaAl_2O_4$ sensors are also shown in Table 1. Temperature sensitivity of the long afterglow phosphors depend strongly on the trap depth.

Figure 9 shows a schematic illustration for afterglow mechanism of $CaAl_2O_4$:Eu, Ln phosphors. Similar mechanism is considered to be occurred in $SrAl_2O_4$:Eu, Ln phosphors. In Fig. 9, holes generated by the excitation of Eu^{2+} ions is trapped with a hole trap level [6-9]. The trapped holes are, then, released by thermal activation. Afterglow phosphorescence intensity, therefore, varies sensitively with temperature. Temperature coefficient varies, therefore, with the hole trap depth.

Trap depth for $CaAl_2O_4$:Eu, Ln phosphors is estimated based on thermally stimulated luminescence technique [7-9]. Traps depth of $CaAl_2O_4$:Eu, Ln phosphors varies from 0.3 to 0.85 eV depending on the rare-earth elements. Thermal excitation of holes from trap levels is shown as follows.

$$I = I_0 \exp(-\Delta E/kT) \qquad (1)$$

Where I is the thermally excited holes which dominates fluorescence intensity, I_0 is the trapped carrier, ΔE is the trap depth, k is Boltzman constant and T is temperature (K). From eq.(1), trapped holes are excited more effectively at lower temperature in the specimens with shallower trap

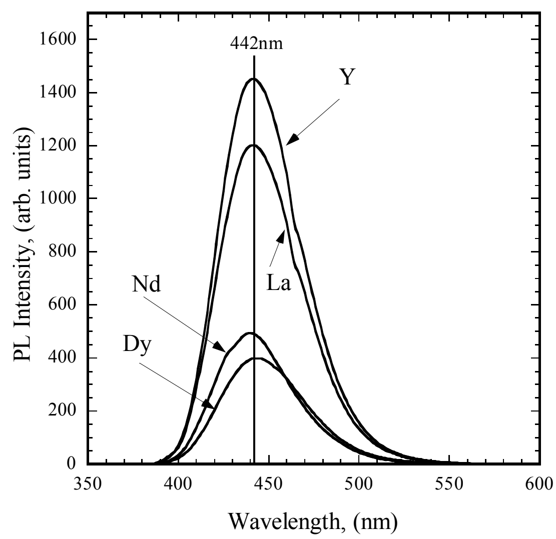

Fig. 7. Photoluminescence spectra from rare-earth element doped $CaAl_2O_4$ crystals.

Table. 1. Afterglow intensity of $CaAl_2O_4$:Eu,Ln phosphors.

Ln	Temperature	Afterglow intensity
Ho	293-343 K	0.73-0.00207 T
Nd	293-368 K	0.21-0.000583 T
Dy	283-373 K	$1.21+0.00061\ T+1.31\times10^{-5}\ T^2$

level.

5. CONCLUSION

The long afterglow phosphor is potentially useful sensor material for the highly sensitive fiber-optic fluorescence thermometer. Sensitivity of long afterglow phosphorescent $SrAl_2O_4$:Eu, Ln and $CaAl_2O_4$ based phosphors are found to be dominated by depth of the hole traps generated by doped rare-earth elements. Sensitivity and measuring range can be modified widely by controlling the trap depth with rare-earth doping.

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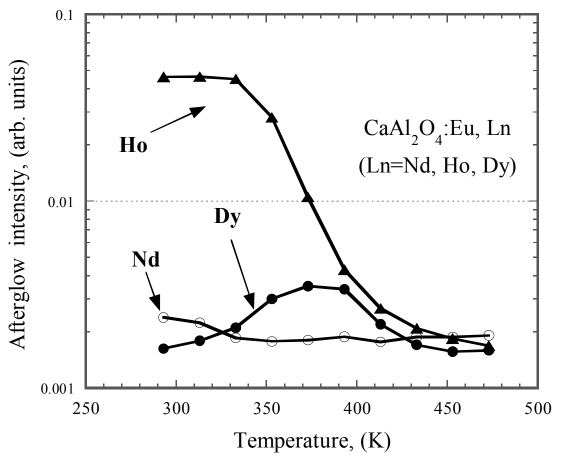

Fig. 8. Temperature variations of afterglow phosphorescence intensity (0.1 ms after stopping the excitation beam) of $CaAl_2O_4$:Eu phosphors co-doped with Ho, Nd, Dy. Similar temperature dependences can be seen in $SrAl_2O_4$:Eu phosphors doped with rare-earth elements.

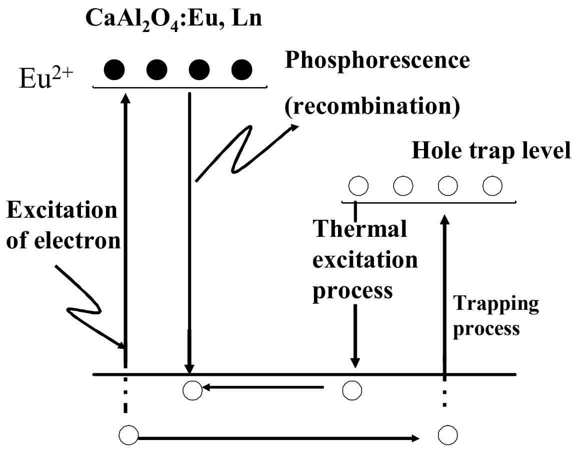

Fig. 9. Schematic illustration for afterglow mechanism of $CaAl_2O_4$:Eu, Ln phosphors. Holes generated by the excitation of Eu^{2+} ions is trapped with a hole trap level. The trapped holes are, then, released by thermal activation. Afterglow phosphorescence intensity, therefore, varies with temperature sensitively. Similar mechanism is considered to be occurred in $SrAl_2O_4$:Eu, Ln phosphors.

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