

Luminescence Study of $\text{CaF}_2.5\text{Al}_2\text{O}_3$ doped with Tb^{3+} and Pb^{2+} Activators

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Abstract --Wide-band-gap fluoride CaF_2 provide attractive hosts for those rare earth (RE) ions that are capable of producing fast and efficient emissions under ionizing irradiation. The quality of calcium difluoride (fluorite, CaF_2) as an optical material has been greatly improved over the past years following a demand for highest quality materials used as lens and window material in ultraviolet laser lithography systems. $\text{CaF}_2:\text{Eu}$ have been investigated as efficient luminescent materials with potential applications in solid state lighting, fiber amplifiers, solid state lasers, and radiation detection $\text{CaF}_2:\text{Eu}^{2+}$ is one of the earliest known thermoluminescent materials and was among the earliest used for TL dosimetry. Wet chemical synthesis and combustion synthesis were used to prepare $\text{CaF}_2.5\text{Al}_2\text{O}_3$. The X-ray diffraction pattern of the powder synthesized by combustion synthesis of aluminium nitrate and calcium fluoride in the mole ratio of 1:10:26.66. All the peaks are well indexed to $\text{CaF}_2.5\text{Al}_2\text{O}_3$ phase (Acta Cryst. 6 (1953) 363). Luminescence studies have been carried out frequently for CaF_2 but there are no data on $\text{CaF}_2.5\text{Al}_2\text{O}_3$. The excitation spectra for Tb^{3+} consists of two peaks ranging from 200 to 310 nm with a maximum at about 235 nm, corresponding to $4f^8 - 4f^7 5d^1$ transition for the prominent emission at 543nm. Similarly for Pb^{2+} the emission is around 370nm for the excitation of 254nm

Keywords: Calcium difluoride, Aluminate, X-Ray diffraction, photoluminescence, combustion synthesis.

I. INTRODUCTION

The quality of calcium difluoride (fluorite, CaF_2) as an optical material has been greatly improved over the past years following a demand for highest quality materials used as lens and window material in ultraviolet laser lithography systems[1]. Wide-band-gap fluoride CaF_2 provide attractive hosts for those rare earth (RE) ions that are capable of producing fast and efficient emissions under ionizing irradiation[2,3,4,5]. Doped phosphors such as $\text{CaF}_2:\text{Eu}$ and $\text{MgF}_2:\text{Eu}$ have been investigated as efficient luminescent materials with potential applications in solid state lighting, fiber amplifiers, solid state lasers, and radiation detection[6,7]. $\text{CaF}_2:\text{Eu}^{2+}$ is one of the earliest known thermoluminescent materials and was among the earliest used for TL dosimetry[8]. $\text{CaF}_2:\text{Eu}^{2+}$ acts as a scintillator which is frequently used in investigations for rare events such as dark matter and neutrinoless double beta decay. Recently, spectral hole burning has been reported in $\text{CaF}_2:\text{Eu}$ phosphors[9,10].

Though luminescence studies have been carried out frequently for CaF_2 but there are no data on $\text{CaF}_2.5\text{Al}_2\text{O}_3$. Only a small note on the crystal structure of $\text{CaF}_2.5\text{Al}_2\text{O}_3$ is given by Harald Perlitz and Gunnar Gunther[11]. In this paper we tried to prepare $\text{CaF}_2.5\text{Al}_2\text{O}_3$ for the first time by combustion synthesis. For the confirmation of the single phase compound prepared by combustion synthesis, XRD was taken. We have also attempted activation of this host using rare earth Tb^{3+} and transition metal Pb^{2+} for their photoluminescence studies.

II. EXPERIMENTAL

The preparation process involved wet-chemical synthesis and combustion synthesis. To prepare $\text{CaF}_2.5\text{Al}_2\text{O}_3$, Calcium fluoride (CaF_2) was first prepared by wet-chemical synthesis by using calcium nitrate dissolved in distilled water and hydrofluoric acid in Teflon beaker. Then stoichiometric composition of Calcium fluoride (CaF_2), aluminium nitrate ($\text{Al}(\text{NO}_3)_3.9\text{H}_2\text{O}$) as oxidizer and urea ($\text{NH}_2.\text{CO}.\text{NH}_2$) as a fuel, were mixed together to prepare $\text{CaF}_2.5\text{Al}_2\text{O}_3$ by combustion synthesis. Stoichiometric composition of the metal nitrates (oxidizers) and urea (fuel) was based on the total oxidizing and reducing valences of the components using the concepts of propellant chemistry.

$\text{CaF}_2:\text{Al}:\text{Urea}$ were in the ratio 1:10:26.66. Due to the presence of large crystallization water in aluminium nitrate, a thick paste was formed. A china dish containing the paste was inserted in a vertical cylindrical muffle furnace preheated at 500°C

in ambient air. No reducing atmosphere was provided. Initially the mixture boiled and underwent dehydration followed by decomposition with the evolution of large amount of gases (oxides of carbon, nitrogen and ammonia). The process being highly exothermic continued and the spontaneous ignition occurred. The solution underwent smoldering combustion with enormous swelling, producing white foamy and voluminous ash. The flame temperature, as high as 1400 -1600°C, converts the vapor phase oxides into mixed aluminates. The flame persists for 20-30 seconds. The silica crucible was immediately removed from the furnace. The foamy product can easily be milled to obtain the fine powder. The single phase formation of hexagonal structure of a compound was confirmed from the study of powder X-ray diffraction (XRD) that has been carried out at room temperature using Philips PANalytical X'pert Pro diffractometer. Photoluminescence (PL) characteristics of the doped material were studied using a Hitachi F-4000 spectrofluorimeter, at room temperature, using 1.5nm spectral slit width in the range of 200–700 nm.

III. RESULTS AND DISCUSSION

The X-ray diffraction pattern of the powder synthesized by combustion synthesis of aluminium nitrate and calcium fluoride in the mole ratio of 1:10:26.66 is shown in Fig. 1. All the peaks are well indexed to $\text{CaF}_2 \cdot 5\text{Al}_2\text{O}_3$ phase (Acta Cryst. 6 (1953) 363). The host lattice $\text{CaF}_2 \cdot 5\text{Al}_2\text{O}_3$ has a hexagonal structure with space group $D_{6h}^{16} - C6/mmm$ or $D_{6h}^{36} - C6/mcm$ and its lattice parameters are $a=5.529\text{\AA}$ and $c=21.79\text{\AA}$.

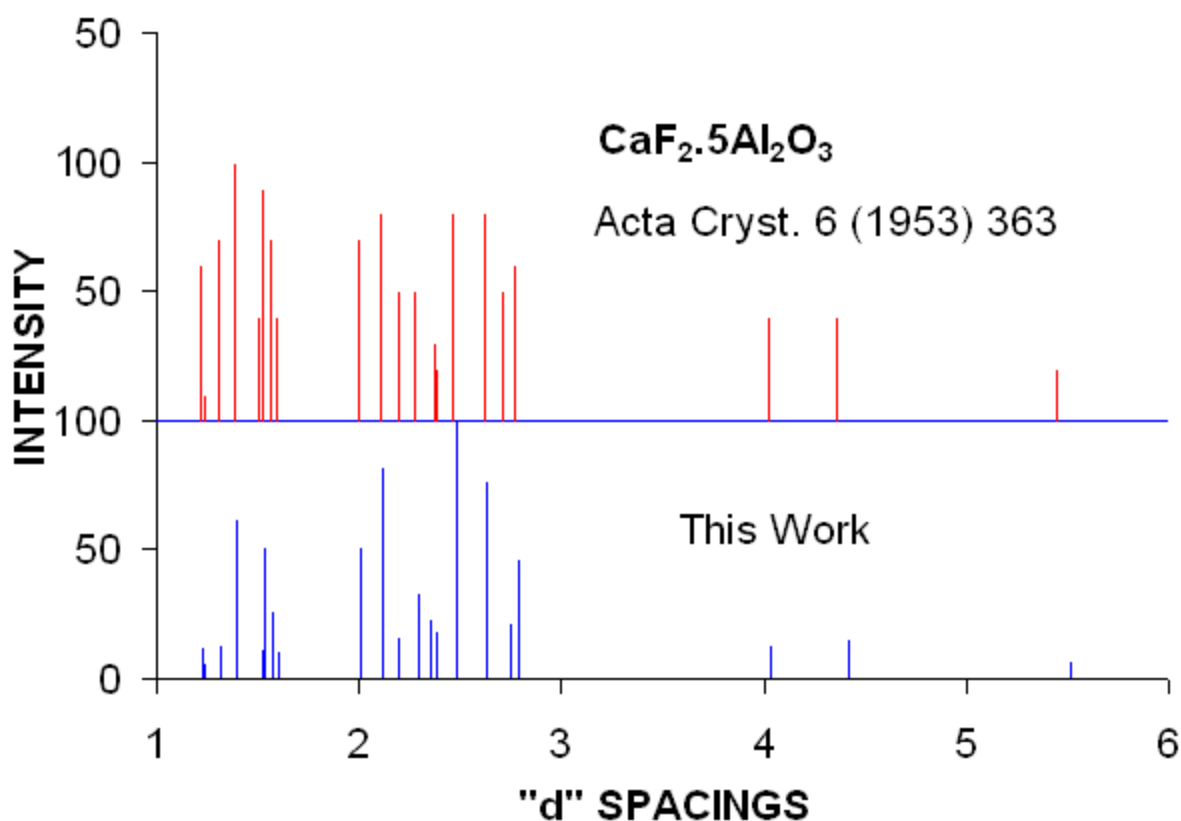


Fig. 1: XRD pattern of $\text{CaF}_2 \cdot 5\text{Al}_2\text{O}_3$

RARE EARTH ACTIVATOR

Tb^{3+}

In case of Tb^{3+} ion, the absorption is usually due to allowed f-d transition. From excited state of $4f^7 5d^1$ configuration, the electron loses energy to lattice and comes to 5D_3 . $^5D_3 \rightarrow ^7F_3$ emission is in UV and blue region while $^5D_4 \rightarrow$

7F_J emission is predominantly green. At lower concentrations, blue emission is observed, but at higher concentration, there is an energy transfer between Tb^{3+} ions, e.g. the cross relaxation-
 $Tb^{3+}(^5D_3) + Tb^{3+}(^7F_J) \rightarrow Tb^{3+}(^5D_4) + Tb^{3+}(^7F_0)$

Due to which the blue emission gets quenched increasing the green emission at the same time. The terms 'low' and 'high' are relative. In some hosts, even at the lowest concentrations only green emission is observed, while in others the blue emission may be predominant even for concentrations as high as fraction of a mol%. f-d excitation is strong when Tb^{3+} occupies site of inversion symmetry. The quantum efficiency of luminescence is high usually when the f-d absorption is at longer wavelengths (Blasse and Bril 1967).

Fig.2 (curve a and curve b) shows the excitation and emission spectra of Tb^{3+} in $CaF_2.5Al_2O_3$ phosphor prepared by combustion synthesis ($\lambda_{em} = 543$ nm). The excitation spectra consists of two peaks ranging from 200 to 310 nm with a maximum at about 235 nm, corresponding to $4f^8 - 4f^7 5d^1$ transition of the Tb^{3+} ion.

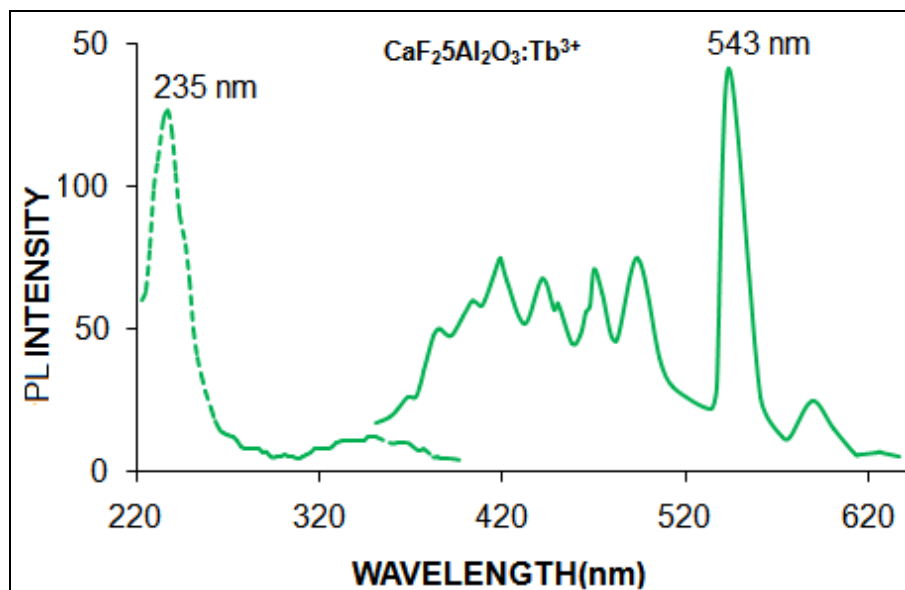


Fig.2 PL spectra of $CaF_2.5Al_2O_3:Tb^{3+}$

ns² ACTIVATOR

Pb²⁺

The Pb^{2+} luminescence center belongs to the so-called ns² ions such as Tl^{2+} , Pb^{2+} and Bi^{3+} , which have been studied for several decades and attractive luminescence properties have been found. For ns²-type impurities, the ground level is 1S_0 arising from the S^2 configuration and the lowest excited levels are 3P_0 , 3P_1 and 1P_1 derived from the excited sp configuration. The lowest excited state 3P_0 and 3P_1 are responsible for the luminescence features. The transition from the 3P_0 to the ground 1S_0 state is J-J forbidden and only weakly allowed by phonon interactions so that it is characterized by long radiative lifetime of the order of milliseconds. The transition from 3P_1 to the ground 1S_0 state is partially allowed due to the spin-orbit coupling which mixes the spin-allowed 1P_1 level with 3P_1 level, such mixing results in radiative lifetime of the order of hundreds of nanoseconds. The 3P_0 level is usually called as metastable state, while the 3P_1 level is often referred to as radiative. The 3P_1 and 3P_0 levels are close enough to obtain the thermal population of the 3P_1 level from the 3P_0 at higher temperatures. The absorption spectra of ns² ions in solids consists of three main bands labeled A, B and C in order of increasing energy corresponding to transitions $^1S_0 \rightarrow ^3P_0$, 3P_1 and 1P_1 , respectively. The C band corresponds to the allowed transition, whereas transition corresponding to A and B bands are only partly allowed by spin-orbit coupling and vibronic coupling, respectively. The A band lies in the UV range. It is markedly sensitive to the environment .

Fig.3 (curve c and d) represents the emission and excitation spectra of Pb^{2+} doped $CaF_2.5Al_2O_3$ compound. The broad emission is around 370 nm for the excitation of 254 nm. The excitation spectra is quite narrow then emission spectra.

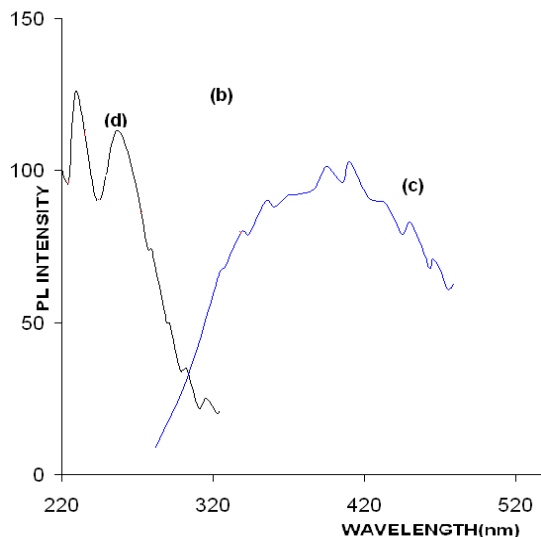


Fig. 3: PL Spectra of $\text{CaF}_2.5\text{Al}_2\text{O}_3:\text{Pb}^{2+}$

IV. CONCLUSION

We have investigated luminescence in $\text{CaF}_2.5\text{Al}_2\text{O}_3$ for the first time. The method used is combustion synthesis which is found to be a more simple, low cost and feasible method. Tb^{3+} and Pb^{2+} doped phosphors were successfully prepared and characteristic luminescence was observed.

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