

DEVELOPMENT OF HALOSULPHATE BASED PHOSPHORS AND IT'S APPLICATIONS

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Abstract-Synthesis and characterization of halosulphate-based phosphors is important for thermoluminescence dosimetry (TLD), radiophotoluminescence dosimetry (RPL) and scintillator materials. The enhancement of luminescence output in halosulphate-based phosphors and it may be useful for lamp, solid-state lamp and radiation. Dosimetry by activator as well as sensitizer are well known properties. The combustion technique is not applicable for the synthesis of TLD phosphors due to very fine particles, which show less TL intensity, while sol-gel, solid-state diffusion, melt method and precipitation methods are applicable for TLD phosphors. Two halosulphates namely $\text{Na}_{21}(\text{SO}_4)_7\text{F}_6\text{Cl}$ and $2\text{K}_3\text{Ca}_2(\text{SO}_4)_3\text{F}$ were prepared and doped with Dy and Tm for different concentration. Halosulphate, $\text{Na}_{21}(\text{SO}_4)_7\text{F}_6\text{Cl}$ was prepared by wet chemical method and Halosulphate, $2\text{K}_3\text{Ca}_2(\text{SO}_4)_3\text{F}$ was prepared by solid state diffusion method. The characterization was done by X-ray diffraction (XRD), Thermo luminescence (TL) was also studied. For Dy doped $\text{Na}_{21}(\text{SO}_4)_7\text{F}_6\text{Cl}$, The peak was observed at 120°C and shoulder at 175°C for 0.2 % molar concentration of Dy. and for $2\text{K}_3\text{Ca}_2(\text{SO}_4)_3\text{F}$ doped with Tm the shoulder peak was observed at 240°C and at 150°C for 0.7 % molar concentration of Tm.

Key words- $\text{Na}_{21}(\text{SO}_4)_7\text{F}_6\text{Cl}$, $2\text{K}_3\text{Ca}_2(\text{SO}_4)_3\text{F}$, XRD, Thermoluminescence, TL

INTRODUCTION Sulphates, as a type of radiation dosimetric materials have been of interest for more than twenty years. Rare earth activated alkaline earth sulphates, such as $\text{CaSO}_4:\text{Dy}$ and $\text{CaSO}_4:\text{Tm}$ phosphors, used in thermoluminescence (TL) dosimetry have very highly sensitive TL responses which are about 30 times greater than LiF:TLD 100 . That their effective atomic number are not close to tissue equivalence, as is LiF TLD limits their application. The complexity of the defect structure in these materials means that the physical mechanism of TL phenomena remains unclear, although it has been of interest to researchers [1-4]. Morton et al [5] proposed that anhydrous magnesium sulphate might be an excellent candidate for electron spin resonance (ESR) dosimetry, because it was found that the MgSO_4 dosimeter was somewhat more sensitive than the traditional alkaline dosimeters of the same mass. Luo et al [6,7] recently carried out an investigation of the ESR and TL of anhydrous MgSO_4 irradiated by gamma rays. The experimental results show that not only the ESR dose response but also the TL dose response of individual peaks can be obtained from anhydrous MgSO_4 irradiated with γ - rays in dose range 1 Gy to 20 kGy. Laxmanan [8] proposed $\text{CaSO}_4:\text{Ag, Tm}$ a new radiation dosimetry phosphor. The x-ray induced luminescence intensity of $\text{CaSO}_4:\text{Tm}$ and $\text{CaSO}_4:\text{Ag, Tm}$ over a wide irradiation temperature range is a new result which could have applications in radiation detection by scintillation technique.

Dixton and Ekstrand [9,10] studied TL in $\text{SrSO}_4:\text{RE}$ phosphors. Intense TL was observed, however the glow peaks were at low temperatures, which resulted in fast fading upon storage. In most of these works Yamashita's method was followed for the phosphors synthesis. Recently Moharil and co-workers reported [11,12] various preparation routes and effect of codopings. $\text{CaSO}_4:\text{P, Dy}$ and $\text{CaSO}_4:\text{Mo, Dy}$ phosphors were found to be more sensitive than $\text{CaSO}_4:\text{Dy}$. $\text{BaSO}_4:\text{Eu}$, $\text{SrSO}_4:\text{Mo, Tb}$ phosphors are much more sensitive than widely used $\text{CaSO}_4:\text{Dy}$ phosphors [13,14].

$\text{Ce}^{3+} - \text{Ce}^{2+}$ redox mechanism for TL in $\text{CaSO}_4:\text{Ce}$ phosphor was reported by Laxmanan [15]. The enhancement in the TL efficiency of Dy and Mn ions by Ce^{3+} ion was reported in $\text{CaSO}_4:\text{Ce, Dy}$ and $\text{CaSO}_4:\text{Ce, Mn}$ phosphor [16]. However the application of similar energy transfer mechanism leading to enhanced sensitivity in the case of TL has to be made continuously. Atone et al [11] reported that the PL intensity of Dy^{3+} when excited via Ce^{3+} ions at 295 nm is 2.5 times higher than that obtained by directly exciting Dy^{3+} ions at 350 nm. The Ce^{3+} emission around 306 nm and 325 nm overlaps well with the Dy^{3+} excitation. Ce^{3+} thus sensitizes the Dy^{3+} PL emission in CaSO_4 .

In recent years, Moharil and co-workers was developed sensitive TL phosphors namely

$K_2Ca_2(SO_4)_3$: Eu [17-19], $K_3Na(SO_4)_2$: Eu [20,21], $CaSO_4$: P, Dy [11], $K_2Mg_2(SO_4)_3$: Dy [22] which could be used in the personal and environmental radiation dosimetry.

Recently, sulphate materials received attention due to the phase transformation and good optical properties [23-26]. These materials have become the subject of numerous studies performed by various techniques.

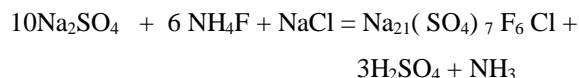
Now, other than sulphates and mixed sulphates, some investigations are going in progress on halosulphate-based materials. Mackie and Young [27] have investigated the Cl-F substitution in the system $Ca_{10}(PO_4)_6(F_xCl_{1-x})_2$. Since then, the group of sulphate apatites has not been studied in details. Piotrowski et al [28] shows the solid solution series of the sulphate apatite system $Na_{6.45}Ca_{3.55}(PO_4)_6(F_xCl_{1-x})_{1.55}$. Recently, Gedam et al [29-32] shows the strong emission of Ce^{3+} , Dy^{3+} , Mn^{2+} ions in $KZnSO_4Cl$, $KMgSO_4Cl$, Na_3SO_4F and $NaMgSO_4F$ halosulphate phosphors first time. Some halosulphates are known such as $LiMgSO_4F$, $CeSO_4Cl$, $Ca_4Al(SO_4)F_{12}$, $K_2MnSO_4F_3$, $K_3Ca_2(SO_4)_3F$, $MgAl(SO_4)_2F$, $Na_{15}(SO_4)_5F_4Cl$, $Na_{21}(SO_4)_7F_6Cl$, $Na_3Pb_2(SO_4)_3Cl$, $Na_6(SO_4)_2FCl$ etc.

The above halosulphate-based materials may be useful for lamp, solid-state lamp and radiation dosimetry. Therefore, it is proposed to undertake work on synthesis and luminescence characterization of mixed anion halosulphate-based phosphors.

EXPERIMENTAL :

Compound: $Na_{21}(SO_4)_7F_6Cl$

Chemical Reaction :



Method of Preparation :

$Na_{21}(SO_4)_7F_6Cl$ was prepared by wet chemical method. Samples were taken in appropriate proportion and dissolved in distilled water. The impurities were added in their proportion and sample was dried. Then using pestle mortar the compound was crushed to powder form and melted in the furnace at

400°C for two hours. The impurity Dy (Dysprosium) was added as per following details.

SAMPLE	COD E	IMPU RITY	IMPURIT Y PERCENT AGE
$Na_{21}(SO_4)_7F_6Cl$	HS 7	Dy	0.05
	HS 8	Dy	0.1
	HS 9	Dy	0.2
	HS10	Dy	0.5
	HS11	Dy	0.7
	HS12	Dy	1

The XRD was recorded at 1 % molar concentration. The TL The Thermoluminescence (TL) measurements were done on Riso TL DA-15 measurement system available in Department Of Physics Rashtrasant Tukdoji Maharaj Nagpur University.

RESULTS AND DISCUSSIONS :

X- RAY Diffraction (XRD) study :

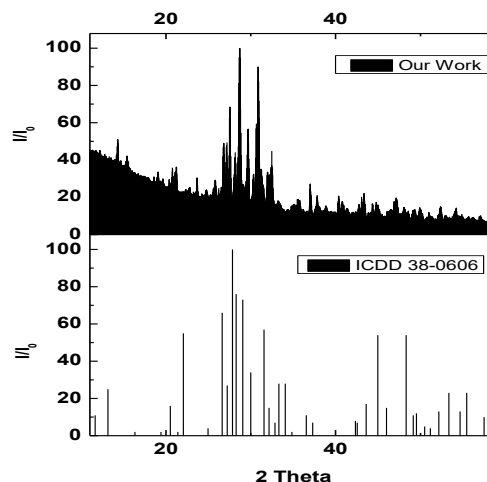


Fig.1

The XRD pattern matches with that of reported in ICDD database file. No.38 0606

Above figure 1 shows XRD pattern of $Na_{21}(SO_4)_7F_6Cl$ And pattern of Database file.

Thermoluminescence : (TL)

Following figure 2 shows comparative graph of TL for different molar concentrations for added impurity Dy doped with $\text{Na}_{21}(\text{SO}_4)_7\text{F}_6\text{Cl}$.

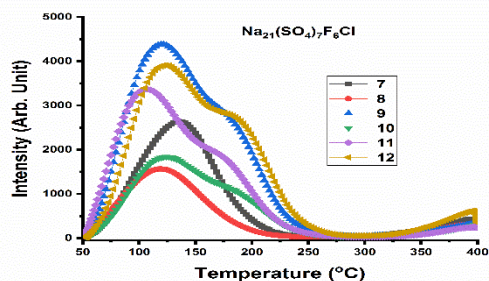
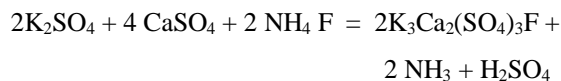


Fig.2

Curve 7 : 0.05 %Dy Curve 8 : 0.1 % Dy
 Curve 9 : 0.2 % Dy Curve 10 : 0.5 % Dy
 Curve 11 : 0.7 % Dy Curve 12 : 1% Dy
 TL curve for $\text{Na}_{21}(\text{SO}_4)_7\text{F}_6\text{Cl}$ doped with Dy for different molar concentration was studied .The peak was observed at 120°C and shoulder at 175°C for 0.2 % molar concentration . Since glow peak was observed at low temperature one can conclude that TL traps are originating From the shallow traps.

Compound: $2\text{K}_3\text{Ca}_2(\text{SO}_4)_3\text{F}$

Chemical Reaction:



The compound was prepared using solid state diffusion method . Samples were taken in appropriate proportion and mixed with Each other in powder form . The impurities were sprinkled in their proportion on the formed compound .Then using pestle mortar the compound was crushed to powder form and melted in the furnace at 800°C for Six hours

The impurities added were as per following details . The impurity Tm (Thulium) was added as per following details

SAMPLE	CODE	IMPURITY	IMPURITY PERCENT AGE
$2\text{K}_3\text{Ca}_2(\text{SO}_4)_3\text{F}$	HS 31	Tm	0.05
	HS 32	Tm	0.1
	HS 33	Tm	0.2
	HS 34	Tm	0.5
	HS 35	Tm	0.7
	HS 36	Tm	1

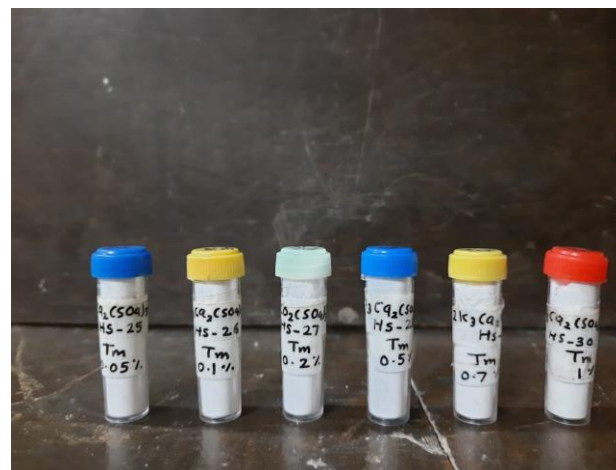


Fig. 3 Prepared compounds of $2\text{K}_3\text{Ca}_2(\text{SO}_4)_3\text{F}$ with different concentrations of Tm The XRD was recorded at 0.05 % molar concentration .The TL The Thermoluminescence (TL) measurements were done on Riso TL DA-15 measurement system available in Department Of Physics Rashtrasant Tukdoji Maharaj Nagpur University.

RESULTS AND DISCUSSIONS :

X- RAY Diffraction (XRD) study :

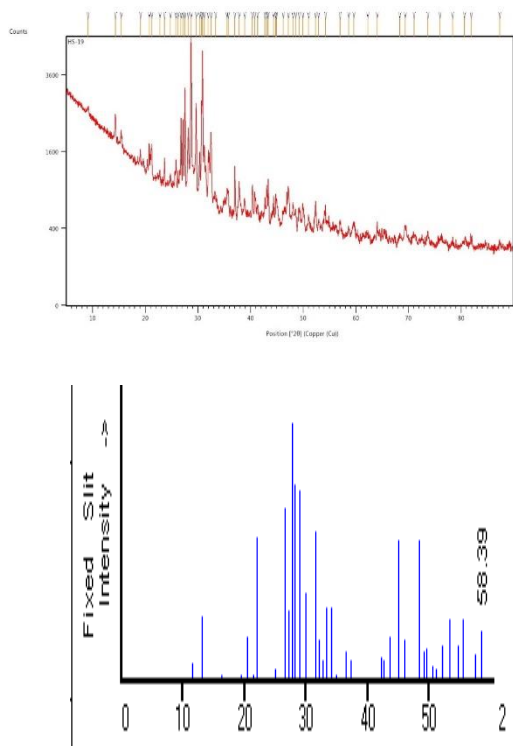


Fig . 4

Above figure 4 shows XRD pattern of $2K_3Ca_2(SO_4)_3F$.

The XRD pattern matched with that of reported in ICDD database file.

Thermoluminescence : (TL)

Following figure 5 shows comparative graph of TL for different molar concentrations for added impurity Tm doped with $2K_3Ca_2(SO_4)_3F$

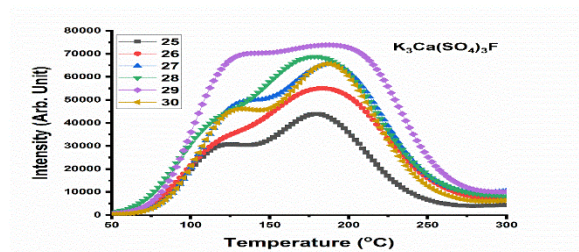


Fig. 5

Curve 25 : 0.05 % Tm Curve 26 : 0.1 % Tm
 Curve 27 : 0.2 % Tm Curve 28 : 0.5 % Tm
 Curve 29 : 0.7 % Tm Curve 30 : 1% Tm

TL curve for $2K_3Ca_2(SO_4)_3F$ dope with Tm for different molar concentration was studied .The shoulder peak was observed at $240^{\circ}C$ and at $150^{\circ}C$ for 0.7 % molar concentration . Since glow peak was observed at low temperature one can conclude that TL traps are originating From the shallow traps.

CONCLUSION :

Thermoluminescence of Dy doped $Na_{21}(SO_4)_7F_6Cl$ and Tm doped $2K_3Ca_2(SO_4)_3F$ for various concentrations was studied . The intensity response in both the cases was observed to be non linear . For Dy doped $Na_{21}(SO_4)_7F_6Cl$, The peak was observed at $120^{\circ}C$ and shoulder at $175^{\circ}C$ for 0.2 % molar concentration of Dy . For $2K_3Ca_2(SO_4)_3F$ dope with various concentrations of Tm the shoulder peak was observed at $240^{\circ}C$ and at $150^{\circ}C$ for 0.7 % molar concentration . Since glow peak was observed at low temperature for both phosphors one can conclude that TL traps are originating From the shallow traps . The conclusion is $Na_{21}(SO_4)_7F_6Cl$ and $2K_3Ca_2(SO_4)_3F$ can be used as good luminescent Materials.

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