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Optically Stimulated Luminescence In Fluorides; A Review

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Abstract. Ionising radiation are detected via optically stimulated luminescence (OSL). In optically stimulated luminescence (OSL), a preirradiated sample is excited by light in the visible/infrared region, which results in the detachment of either the hole or the electron. Recombination then causes the emission of radiation with a shorter wavelength than the exciting radiation. The best options for OSL phosphors are those materials that emit light with a wavelength between 350 and 425 nm and have strong photo-ionization cross sections in the blue-green (450–550 nm) or infrared (650–800 nm) regions. Since most fluorides satisfy these requirements when doped with ions like Cu, Ag, or Eu, they have been researched for use in OSL dosimeter development. Various fluorides include Fluoride perovskites, ABF₃ (A: Na, K; B: Mg, Ca) fluorides with Colquirite structure (LiCaAlF₆), alkali silico fluorides, alkali fluorides, alkaline earth fluorides, and fluoride perovskites were explored. The OSL in various fluorides is reviewed in this work along with how it can be used in OSL dosimetry.

INTRODUCTION

The high band gap (10 eV) and stiffness of fluoride minerals make them interesting. The majority of them have high densities and are not hygroscopic. From these materials large crystals can be produced, making them excellent for prospective applications. Fluorides exhibit greater transparency due to their large band gap, making them interesting materials for optical applications. Alkali and alkaline earth fluorides are particularly interesting. These fluorides can be used in a variety of applications, including tunable lasers, scintillators, radiation dosimeters, etc., when doped with rare earth elements including Ce, Eu, Tm, Dy, and elements of the 3D group. Thermoluminescent Dosimetry Phosphors like Lithium fluoride doped with Mg, Cu, P and lithium fluoride doped with Mg, Ti are widely recognized[1-2]. NaI:Tl is a well-known scintillator[3].

The commercial radiation dosimetry phosphors are CaF₂:Dy and CaF₂:Mn. [4-5] As a viable candidate for the RPL dosimetry, CaF₂:Eu has been put forth[6].

Ionizing radiations are detected via optically stimulated luminescence (OSL) [7-8]. In OSL, a pre-irradiated sample is excited by light in the visible or infrared area, which causes either an electron or a hole to be freed. Recombination then results in the emission of radiation with a shorter wavelength than the exciting radiation. Those materials are thought to be an excellent fit for OSL phosphors that emit light in the 350–425 nm range and have defects that have a high photo-ionization cross-section in the 450–550 nm range or in the infrared (650–800 nm) region. Due to the availability of inadequate filters for separating the exciting wavelength from the emission wavelength, stimulation sources, and the sensitivity of PM tubes in this wavelength range that provides a better Signal/Noise ratio, the wavelength range has been restricted. Since most fluorides satisfy these requirements when doped with ions, they have been investigated for use in OSL dosimeter development. The OSL in various fluorides is reviewed in this work along with how it can be used in OSL dosimetry.

OPTICALLY STIMULATED LUMINESCENCE IN VARIOUS FLUORIDES

Alkali fluorosilicates: (A_2SiF_6 (A= Li, Na,K))

Fluorides with the general formulas M_2SiF_6 (M= Li, Na, K..) and $NSiF_6$ (N=Mg, Ca, Sr, Ba) are known as fluoro-silicates. These materials' phase structures have been extensively researched. Li_2SiF_6 and Na_2SiF_6 are alkali fluorosilicates that have hexagonal structures with group P321 [9] and a148.859, c145.038. K_2SiF_6 has a cubic structure, but when it is heated to 700 °C in dry air without any moisture, it transforms into K_3SiF_7 , a tetragonal phase material with the space group P4/mbm-D54h [10]. These substances break down during annealing, hence their potential for TL dosimetry was not investigated. Using the OSL approach, Barve et al[11–12] investigated these materials for dosimetry as measurements are made at room temperature.

The doped alkali fluorosilicates show remarkable OSL sensitivity and are capable of detecting very low dosages. Around 358 nm, Cu^+ -doped Na_2SiF_6 exhibits strong photoluminescence in the UV zone. When compared to commercial $Al_2O_3:C$, this material exhibits intense OSL with blue light (450 nm) and is over 14% more intense. Compared to commercial $Al_2O_3:C$, the GSL (Green Stimulated Luminescence) sensitivity is 28%. The impact of pentavalent P and trivalent Al dopants on the different OSL characteristics is also investigated. These contaminants have a considerable impact on the photo-ionization cross-section. In comparison to Cu-doped samples, the inclusion of Al impurity reduces the photo-ionization cross-section. The greater decay constants in the Al co-doped sample than in the Cu-doped sample are also observed.

The TL glow curve has two peaks, one at a low temperature of 100° C and the other at 350° C. The peak at roughly 100 °C and the deep traps above 350 °C account for the majority of the OSL. The sample exhibits fading as a result of the low-temperature TL peak fading. The OSL signal is stable if this peak is thermally eliminated. The phosphors $Na_2SiF_6:Cu$ and $Na_2SiF_6:Cu,Al$ are said to be suitable candidates for online dosimetry with the CW-OSL technique. In Cu-doped Na_2SiF_6 , the Mdd (minimum detectable dose) is also determined. The estimated MDD is found to 16.6 mR. The sample with phosphorus doping greatly lessens low-temperature peak fading, resulting in the creation of the new stable OSL phosphor $Na_2SiF_6:Cu, P$ [13]. The estimated minimum detectable dosage (equal to 3 sigma of the OSL reading of the annealed and unirradiated d sample) for this phosphor, which exhibits strong OSL sensitivity, is 10 mR. Due to the low contribution of the low-temperature peak at 100 °C to OSL, the observed post-irradiation fading is 28%, mostly within 3 days. Fading can be prevented in personnel monitoring when the doses are assessed after a month or a quarter by postponing the OSLD readout by three days.

The authors suggest that $Na_2SiF_6:Cu,P$ is an excellent candidate for dosimetric applications due to its straightforward synthesis process and low cost. When compared to alumina, the OSL sensitivity of Cu-doped K_2SiF_6 is only around 10%. Hence in the fluorosilicates family doped Na_2SiF_6 is a promising OSL material.

Alkali Fluorides

$LiF:Mg,Cu,P$, an alkali fluoride, is well known as a superior TL phosphor with extremely high sensitivity, linear dose-response, low fading, and environmental stability [2,14]. Since it is close to tissue equivalent and has a low effective atomic number (Z_{eff}) of 8.2, it is appropriate for use in medical applications and in personnel monitoring[15–17]. This phosphor's great sensitivity is attributed to its high trapping effectiveness, which results from the development of F centres with UV-absorbent bands. Because M centre generation is so minimal, $LiF:Mg,Cu,P$ exhibits weak photo-ionization in the visible region and poor light sensitivity. Thus, this phosphor may exhibit light sensitivity if the creation of M centres with some alteration is promoted. $LiF:Mg,Cu,P$, a

thermoluminescent (TL) phosphor, was modified by Patil et al to create an OSL phosphor with extremely high sensitivity[18]. The observed decay is very fast and the BSL sensitivity is reported to be 27% compared to commercial $\text{Al}_2\text{O}_3\text{:C}$ (Landauer, Inc.) When the whole curve is integrated, The green stimulated luminescence (GSL) sensitivity is stated to be 2.5 times greater than the $\text{Al}_2\text{O}_3\text{:C}$ (Landauer, Inc.) with full curve integration. The minimum detectable dosage is found to be 26 mGy on the set-up in which all measurements were carried out. The green-stimulated luminescence (GSL) is relatively slower than the blue-stimulated luminescence (BSL). The first seven days show no substantial fading but long-term fading is yet to be ascertained. This phosphor differs from LiF:Mg,Cu,P TL material in terms of its properties. In contrast to OSL phosphor, which exhibits broad Cu luminescence spanning the wavelength range of 360 nm-420 nm with a peak at 420 nm, the Cu luminescence in TL phosphor is detected around 360 nm [14]. When compared to TL phosphor, this material exhibits extremely low TL. The major peak of the TL glow curve appears at about 210 °C[18], shifting it towards the lower side of the temperature scale compared to the TL phosphor curve. This phosphor has also been reported to exhibit Photo Transfer Thermoluminescence (PTTL) with blue-green light. After shining with blue-green light, the major dosimetric peak's TL intensity increases by a factor of two[19].

The optical sensitivity of alkali halides is caused by the absorption band of M, which centres in the visible range. The absorption bands for F and M centres are observed in sodium fluoride (NaF) at 341 and 505 nm, respectively[20]. Therefore, blue/green area light can easily bleach the M band at 505 nm. NaF is a suitable contender for OSL material because of this. OSL in NaF:Mg,Cu,P was investigated by Gaikwad et al. [21]. The sample with the highest OSL sensitivity has dopant concentrations of Mg (0.01%), Cu (0.2%), and P (1%). The observed OSL is 37% lower than that of Landauer, Inc.'s commercial $\text{Al}_2\text{O}_3\text{:C}$. It has been noted that the Cu content affects the TL glow structure.

Higher concentrations of Cu(0.2-0.3m%) produce a pronounced peak at 350° C that dramatically diminishes following OSL, showing a partial link between the two parameters. Less fading is so anticipated in this sample. Apart from 2% fading within the first 24 hours, no fading is seen in this sample throughout the first 10 days. As a result, the authors suggest $\text{NaF:Mg(0.01mol\%),Cu(0.2mol\%),P(1mol\%)}$ as a promising choice for OSL dosimetry.

Pervoskite Fluorides Family : Formula ABF_3 (A=Li,Na,K; B=Mg,Zn)

The OSL in the ABF_3 fluorides NaMgF_3 and KMgF_3 has received the most attention. OSL was reported in Ce-doped NaMgF_3 and KMgF_3 by Messon et al [22]. These materials exhibit strong OSL. KMgF_3 : Ce's OSL is 27 times greater than $\text{Al}_2\text{O}_3\text{:C}$ (Landauer Inc.). The authors reported little fading, however, long-term fading is not investigated. Due to its high Z and background signal building from self-irradiation caused by the presence of K40, KMgF_3 is not suited for dosimetry. Although NaMgF_3 : Ce³⁺ appears to be a superior option to KMgF_3 , this material exhibits significant fading. $\text{NaMgF}_3\text{:Eu}^{2+}$ OSL was described by Dotzer et al [23]. This phosphor seems to be appropriate for both environmental and personal radiation dosimetry. With a reported MDD of 130nGy, the activator with Eu (0.2%), greatly reduced fading. The authors assert that its fading could be reduced by maximizing heat treatments. Therefore, if the fading properties of this material are further enhanced, $\text{NaMgF}_3\text{:Eu}^{2+}$ with its low Z_{eff} compared to that of $\text{Al}_2\text{O}_3\text{:C}$ and extremely high OSL sensitivity may make this phosphor a good option as OSL phosphor.

In a recent study, Jog et al. [24] investigated the OSL, TL, and PL in a variety of zinc-based fluoropervoskites (ZnNaF_3 , ZnLi_2F_4) doped with impurities of Cu and Ag. With the exception of ZnKF_3 , all these fluoropervoskites exhibit OSL sensitivity. Cu doped ZnNaF_3 exhibits highest sensitivity, 25% to that of $\text{Al}_2\text{O}_3\text{:C}$. With peaks at 150 °C and 200 °C, the Ag Cu doped sample's measured TL is modest. These two peaks can be correlated with the observed OSL. These samples exhibit a linear dose-response between 10 mGy and 1.2 Gy and have good reusable properties.

Fluorides of Colquiriite Family: Formula ABCF_6 (A= Li ; B= Mg,Ca, Ba, Sr; C= Al, Ga)

LiCaAlF_6 , LiSrAlF_6 , and other collquirites have undergone considerable research for a variety of applications, including window material for UV, VUV, scintillators, and photon cascade emission[25–26],[28] Additionally, the thermoluminescence of this material doped with Ce³⁺ and Eu²⁺ was investigated. These studies found inconsistent TL glow curve structures, which may be explained by the use of various preparation techniques[31–34]. Studying OSL in these materials was prompted by the favourable thermoluminescence response. OSL TL investigations were conducted by Rahangdale et al [35-36] in Eu doped LiCaAlF_6 . It was discovered that different co-doping

modifications alter the glow curve of LiCaAlF₆: Eu. La co-doping produces a single peak at 240 °C, whereas Ce co-doping produces a single peak around 270 °C. With a minimum detectable dose of 17 Gy, LiCaAlF₆:Eu,La exhibits intense OSL that is 4 to 6 times greater than that of Al₂O₃:C (Landauer). The phosphor exhibits a linear dose response with great reusability in the radiation range of 3 mGy to 1 kGy. However, during the course of 90 days, 20% fading was seen[36]. Fading characteristics are enhanced and minimal fading is seen when Y is doped in place of La[35]. This phosphor is a possible candidate for radiation dosimetry utilising OSL due to all of these good characteristics.

CONCLUSION

Most fluorides have the potential to be used as OSL phosphors since they display OSL when doped with ions like Cu, Ag, or Eu. Fluorides with Colquiriite structure (LiCaAlF₆), alkali silico fluorides, alkali fluorides, alkaline earth fluorides, fluoride perovskitesABF₃, and others were explored. Although each class has distinct advantages and disadvantages, these materials can be used in dosimetry when employing OSL. The following table 1 provides a summary of various fluorides' OSL characteristics.

TABLE 1. Summary of various fluorides' OSL characteristics of fluorides

S/N	Material	BSL sensitivity compare to Al ₂ O ₃ :C	GSL sensitivity	Minimum Detectable dose	fading response	Linearity	Reusability	Reference
1	Na ₂ SiF ₆ : Cu	14%	28%	16 mR	N A	10mGy to 1Gy	N A	11,12
2	Na ₂ SiF ₆ : Cu Al	12%	18%	N A	N A	N A	N A	11,12
3	Na ₂ SiF ₆ : Cu P	76%	380%	10.9mR	28% within three	10mGy to 1Gy		13
4	K ₂ SiF ₆ : Cu	10%	07%	NA	NA		N A	11,12
5	K ₂ SiF ₆ Cu,	11%	08%	N A	NA		N A	11,12
6	LiF: Mg,Cu,P	27%	400%	26μGy	practically no fading	10mGy to 1Gy	Reusable	18
7	NaF: Mg,Cu P	37%	N A	N A	2% within 24	10mGy to 1Gy	N A	21
8	KMgF ₃ :Ce	2800	N A	N A	N A	N A	N A	22
9	NaMgF ₃ : Eu	N A	N A	130 nGy	N A	3μGy 10 100Gy	N A	22,23
10	ZnNa F ₃ : Ag	24%	N A	N A	N A	10mGy to 1.2Gy	Reusable	24
11	ZnLi ₂ F ₄ : Ag	9%	N A	N A	N A	10mGy to 1.2Gy	Not Reusable	24
12	LiCaAlF ₆ : Eu La	600%	N A	17μGy	20% in 90 days	1mGy to 3KGy	Reusable	36
13	LiCaAlF ₆ : Eu Y	700%	N A	4.7μGy	Negligible	1mGy to 1KGy	Reusable	35

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