Journal of Engineering Science and Technology
Vol. 5, No. 4 (2010) 373 - 378


# THERMOGRAPHIC APPLICATIONS OF TEMPERATURE SENSITIVE FLUORESCENCE OF SrS:Cu PHOSPHORS

R. PUROHIT*, R. P. KHARE

Instrumentation Unit, Birla Institute of Technology & Science Pilani, Rajasthan, India
*Corresponding Author: rajeshpuro@gmail.com

**Abstract**

The present work aims at investigating the temperature sensitive fluoro-optic behaviour of Cu-activated strontium sulphide (SrS) phosphors and its possible application in thermography. Accordingly, SrS (Cu) phosphors have been synthesized and painted with the help of adhesive on silica substrate. The excitation and emission spectra of such phosphor coatings have been recorded at room temperature (25°C). The temperature dependence of fluorescence intensity and the lifetime of phosphorescence have also been studied. From the systematic variation of these two parameters with temperature, it appears that these phosphors are good candidates for thermographic application, at least, in the temperature range of investigation (25-150°C).

Keywords: Thermographic phosphors, Temperature sensitive fluorescence.

## 1. Introduction

The temperature sensitive fluoro-optic behaviour of a phosphor can provide a viable means of monitoring the temperature profiles of surfaces and also measuring the temperature in a variety of situations. The state-of-art of such thermographic phosphors and related techniques of measurement have been reviewed by Grattan and Zhang [1], Allison and Gillies [2] and Khare [3]. The numbers of such phosphors which satisfy the requirements of linearity of response, stability, ease of synthesis, phosphors/binder (adhesive) compatibility, etc. are indeed very few. Therefore there is a need to investigate more materials for this kind of application. In this context, copper-activated alkaline earth sulphides seem to be promising candidates as they can be easily synthesized, they are quite stable over long period of time, if protected from moisture and their fluorescence is sensitive to temperature. Although these phosphors have been known for a very long time and

**Nomenclatures**

| | |
|---|---|
| $I$ | Fluorescence intensity |
| $I_o$ | Fluorescence intensity at RT |
| $P_{nr}$ | Probability of non-radiative recombination |
| $P_{rr}$ | Probability of radiative recombination |

*Greek Symbols*

| | |
|---|---|
| $\eta$ | Efficiency of fluorescence |
| $\lambda_{max}$ | Peak emission wavelength, nm |
| $\tau$ | Lifetime of phosphorescence, ms |
| $\tau_o$ | Lifetime of phosphorescence at RT, ms |

**Abbreviations**

| | |
|---|---|
| PL | Photoluminescence |
| RT | Room temperature |
| XRD | X-Ray diffraction spectra |

been reported by many investigators in single sulphides as well as mixed sulphides [4-11], almost no effort has been made to study the temperature sensitive behaviour of these phosphors for this kind of application. Therefore, the present work aims at investigating the thermographic properties of SrS (Cu) phosphors.

## 2. Experimental Procedure

### 2.1. Synthesis of phosphors

SrS (Cu) phosphors were prepared by solid-state fusion reaction through firing an intimate mixture of the starting materials ($SrSO_4$, a reducing agent i.e. carbon and activator compound, $CuSO_4$, in desired concentration and an appropriate amount of flux, $Na_2SO_4$) at 900°C in fused silica crucibles for one hour.

In order to see the effect of flux, two series of samples were prepared: one without flux and the other with flux. The conversion of $SrSO_4$ to SrS was verified by X-ray diffraction spectrum which was recorded employing automatic X-ray powder diffractometer (Philips Model PW1390). $K\alpha_1$ line of copper target was used for excitation. XRD is shown in Fig. 1. The latter confirmed that the synthesized phosphors are crystallized in the cubic lattice form with NaCl type structure. The lattice constant of SrS has been found to be 6.02 Å, which is very close to the standard value [12] and that reported by Kaneko et al. [13].

### 2.2. Study of spectral properties

In order to study the excitation and emission spectra of a phosphor, its paint was formed with the help of an adhesive (Quickfix – Indian trade name) and coated on silica glass substrate and then dried at room temperature (RT). The adhesive does not react with or change the spectral properties of phosphors. The excitation spectra and photoluminescence (PL) emission spectra at RT were recorded using a Spectro-fluoro-photometer (Shimadzu Model RF-5301 PC).

The variation of fluorescence intensity (at peak emission wavelength, $\lambda_{max}$) with temperature was recorded employing a separate experimental setup, which comprised of a xenon arc lamp followed by an excitation monochromator, a sample holder attached to the heating element (with a temperature programmer, which can vary the temperature at a linear rate or keep it constant at specific temperature), emission monochromator, photomultiplier and a digital readout. In order to measure lifetime of phosphorescence, pulses of excitation wavelength were obtained using a chopper (driven by a stepper motor) placed at the exit slit of excitation monochromator and the phosphorescence decay (at $\lambda_{max}$) was recorded on a digital storage oscilloscope.

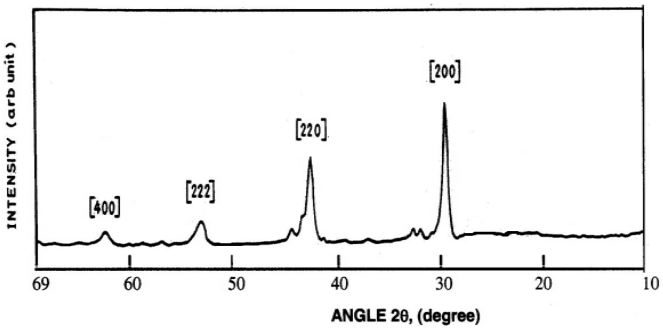


**Fig. 1. XRD of SrS:Cu (0.003 M).**

## 3. Results and Discussion

The excitation and PL emission spectra of SrS (Cu) phosphors at RT are shown in Fig. 2.

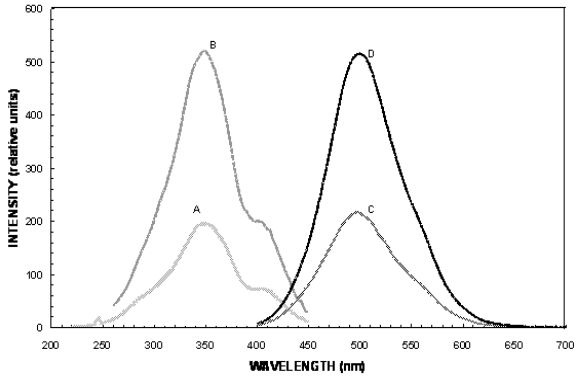


**Fig. 2. Excitation Spectra of (A) –SrS:Cu (0.003 M); (B) – SrS:Cu (0.003 M): Flux (0.01 M), Emission Spectra of (C) –SrS:Cu (0.003 M); (D) –SrS:Cu (0.003 M): Flux (0.01 M).**

For SrS:Cu (without flux), maximum in the excitation and emission spectra have been found to be at 350 nm, and 500 nm respectively. The addition of flux, $Na_2SO_4$,

does not change the spectra; however it increases the intensity in both excitation and emission spectra. No change in the peak wavelength has been found with change in concentration of activator or that of the flux. The optimum concentrations of activator and flux have been found to be 0.003 M and 0.01 M respectively.

In the literature, emission bands of SrS:Cu at different wavelengths have been reported. This disagreement in the results reported by different authors may be attributed to the method of synthesis, the quality of host material and the type of flux or co-activator used. Another probable reason is that the Cu ion in SrS tends to aggregate and form different types of centers [9].

The emission bands in Cu-activated sulphides have been attributed to $Cu^+$ ions in the lattice and they have been thought to be due to a recombination process as is the case in the well known ZnS:Cu phosphors [8]. Such a model can easily explain two emission bands of SrS:Cu by two different acceptor levels within the SrS band gap due to the coexistence of $Cu^+$ and some co-activator such as halogenide ions or vacancies. However, in the work done by Yamashita [9], the lightly doped SrS:Cu powder was found to have a broad band emission located at 0.513 nm at 80 K and it was attributed to the emission from isolated $Cu^+$ center.

In fact, there is a well-established model for $Cu^+$ doped alkali halides [10] where the luminescence mechanism is based on $3d^{10}$ - $3d^9$ 4s transition of $Cu^+$ ion. Most of the alkali halides also have same crystal structure as SrS. With such model, however, it is difficult to explain the thermal quenching of fluorescence. As shown in Fig. 3, the phosphors in the present investigation exhibited strong thermal quenching. In this figure, the fluorescence intensity, $I$, normalized to that at RT, $I_o$, has been plotted as a function of temperature. Curie [14] defines the efficiency of fluorescence, $\eta$, in such cases by the relation:

$$\eta = \frac{P_{rr}}{P_{rr} + P_{nr}}$$

where $P_{rr}$ and $P_{nr}$ are the probabilities of radiative and non-radiative recombination respectively. It is assumed that $P_{rr}$ is almost independent of temperature while $P_{nr}$ rises rapidly with temperature and hence causes $\eta$ to decrease with the increase of temperature.

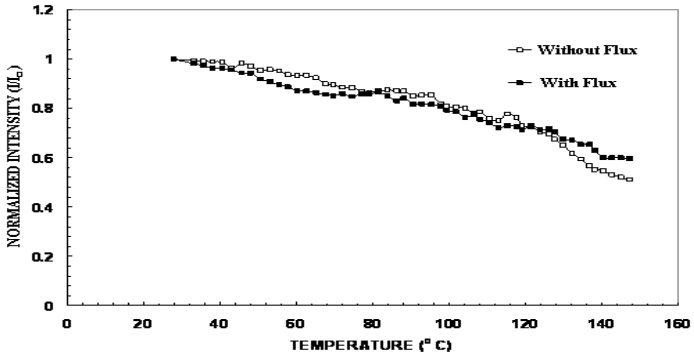


**Fig. 3. Normalized Fluorescence Intensity ($I/I_o$) vs. Temperature for SrS:Cu (0.003 M) and SrS:Cu (0.003 M) with Flux (0.01 M).**

A simple and interesting explanation of thermal quenching in these phosphors can also be given by the generally accepted Schon-Klasens Scheme [15]. An electron in the valence band can enter a luminescence center by a thermal activation. The electron previously removed from the center by optical excitation cannot now return and after diffusing in the conduction band for a while will finally recombine via some defect or other non-radiative transition. Now, there are two ways in which this variation of fluorescence intensity with temperature may be utilized. Employing an appropriate reference, it is possible to use it:

(i) to measure temperature at any point (thermometry), or
(ii) to obtain the image of the temperature profile of any surface (Thermography).

It is in the second context that the temperature sensitive fluorescence of SrS:Cu phosphors may prove to be useful as the intensity varies almost linearly with temperature at least, in the range of investigation.

The lifetime, $\tau$, of phosphorescence as a function of temperature is shown in Fig. 4. This has been normalized to a value of $\tau = \tau_o$ at RT. There has been no significant change in the pattern of $\tau$ vs. temperature with the addition of flux, meaning that the flux does not play any role in the intermediate traps in the host lattice. The decrease in lifetime can be explained in the same way as that for fluorescence intensity. This kind of behaviour of phosphorescence decay may prove to be beneficial in making temperature measurement of remote objects and it will also not to involve fast electronics (as is the case with fluorescence lifetime measurements).

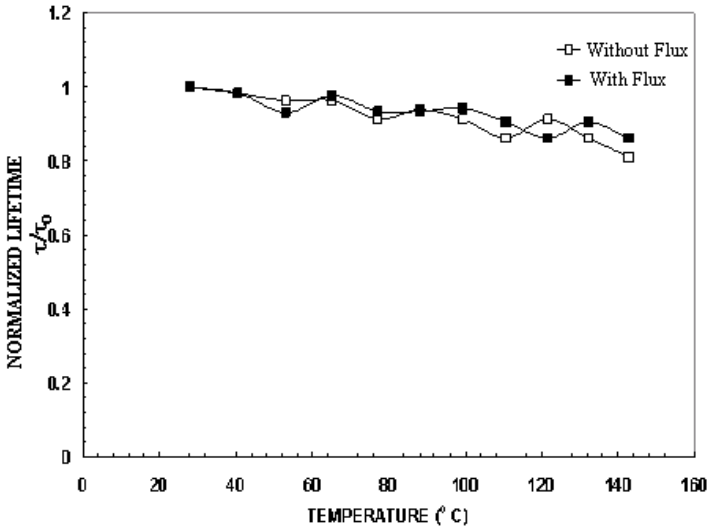


**Fig. 4. $\tau/\tau_o$ vs. temperature for SrS:Cu (0.003 M) and SrS:Cu (0.003 M) with Flux (0.01 M).**

In conclusion, both the PL as well as decay of phosphorescence may be utilized in thermography and thermometric applications.

## Acknowledgements

The authors are thankful to Prof. L.K. Maheshwari, Vice Chancellor, BITS Pilani, Prof. Surekha Bhanot, Chief, Instrumentation Unit, and Prof. V.K. Chaubey, Group Leader EEE & Instrumentation groups, BITS Pilani for providing all the facilities for carrying out the work.

## References

1. Grattan, K.T.V.; and Zhang, Z.Y. (1995). *Fiber optic fluorescence thermometry* (2nd Ed.). Chapman and Hall.
2. Allison, S.W.; and Gillies, G.T. (1997). Remote thermometry with thermographic phosphors: Instrumentation and Applications. *Review of Scientific Instruments*, 68(7), 2615-2650.
3. Khare, R.P. (2004). *Fiber optics and optoelectronics*. Oxford University Press, New Delhi.
4. Sharma, D.; and Singh, A. (1969). Luminescence and trapping in copper activated CaS and SrS phosphors. *Indian Journal of Pure and Applied Physics*, **7**, 310-312.
5. Laud, B.B.; and Kulkarni, V.W. (1979). Photo- and electro-luminescence of polycrystalline BaS:Cu phosphors. *Physica Status Solidi (a)*, 51(1), 269-274.
6. Rastogi, A.M.; and Mor, S.L. (1981). Electroluminescent behaviour of (Ca,Ba) S:Cu, Nd phosphor. *Indian Journal of Pure and Applied Physics*, 19(10), 1019-1021.
7. Rao, R.P. (1986). Role of alkaline earth sulphide phosphors in solid state dosimetry. *Journal of Radiation Protection Dosimetry*, 17(1-4), 403-405.
8. Pandey, R.; and Sivaraman, S., (1991). Spectroscopic properties of defects in alkaline-earth sulfides. *Journal of Physics and Chemistry of Solids*, 52(1), 211-225.
9. Yamashita, N. (1991). Photoluminescence properties of Cu+ centers in MgS, CaS, SrS, and BaS. *Japanese Journal of Applied Physics*, 30, 3335-3340.
10. Li, Wei-Min; Ritala, M.; and Leskelä, M.; Niinistö, L., Soininen, E.; Sun, S.S.; Tong, W.; and Summers, C.J. (1999). Photo- and electroluminescence of SrS:Cu and SrS: (Ag, Cu, Ga) thin films. *Journal of Applied Physics*, 86(9), 5017-5025. ,
11. Anila, E.I.; Aravind, A.; and Jayaraj, M.K., (2008). The photoluminescence of SrS:Cu nanophosphor. *Nanotechnology*, 19(14), 145604.
12. National Bureau of Standards (USA) (1957). *Circular No.* 539, **7**, 15, 52.
13. Kaneko, Y.; Morimoto, K.; and Koda, T. (1982). Optical properties of alkaline-earth chalcogenides. I. single crystal growth and infrared reflection spectra due to optical phonons. *Journal of Physics Society Japan*, 51(7), 2247-2254.
14. Curie, D. (1963). *Luminescence in crystals*. Translated in English by G.F.J. Garlick, Methuen, London, 203-208.
15. Klasens, H.A. (1959).The temperature dependence of the fluorescence of photoconductors. *Journal of Physics and Chemistry of Solids*, 9(3-4), 185-197.