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# Synthesis, thermoluminescence, defect center and dosimetric characteristics of LiF:Mg,Cu,P,Si phosphor

Prince David Preto[a], Vidyavathy Balraj[a,*], Bhushan S. Dhabekar[b], S. Watanabe[c], T.K. Gundu Rao[c], Nilo F. Cano[d]

[a] Solid State Chemistry Research Laboratory, Department of Chemistry, Velammal Engineering College, Surapet, Chennai 600066, India
[b] Radiological Physics and Advisory Division, Bhabha Atomic Research Center, Trombay, Mumbai 400085, India
[c] Institute of Physics, University of Sao Paulo, 05508-090 Sao Paulo, SP, Brazil
[d] Departamento de Ciências do Mar, Universidade Federal de São Paulo, Rua. Doutor Carvalho de Mendonça, 144, CEP 11070-100 Santos, SP, Brazil

## HIGHLIGHTS

- Dosimetric peak for MCPS appears at 220 °C with maximum annealing temperature of 260 °C for 10 min in air.
- Sensitivity of MCPS phosphor is about 1.3 times higher than that of MCP.
- Exhibits very low residual signal of about 0.37%.
- Defect centers induced by gamma irradiation studied by Electron Spin Resonance.
- The $Cu^{2+}$ ion in the phosphor exhibits inverted *g* anisotropy.

## ARTICLE INFO

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## ABSTRACT

LiF:Mg,Cu,P,Si (MCPS), a new tissue equivalent phosphor, was synthesized by solid state method. Powder x-ray diffraction and scanning electron microscope were employed to determine the structural features. The dosimetric characteristics, electron spin resonance (ESR) and defect centers of this newly prepared phosphor were investigated. The MCPS phosphor is highly sensitive when compared with LiF:Mg,Ti and LiF:Mg,Cu,P (MCP), with the TL sensitivity being 35 times and 1.3 times higher respectively. The dosimetric peak occurs at 220 °C with a well defined glow curve structure similar to MCP. MCPS phosphor shows a linear dose response till 10 Gy. The minimum detectable dose has been found to be 8 µGy. The thermal stability of the phosphor could be enhanced by 20 °C from 240 °C to 260 °C when compared to MCP. Defect centers formed in the phosphor by gamma irradiation have been studied by ESR to identify the centers associated with the TL process in this phosphor. Thermal annealing experiments reveal the presence of several defect centers. Center I which shows an isotropic *g* factor of 2.0233 has been found to relate with the TL peaks at 160 °C, 220 °C and 265 °C. Centers II and III are characterized by isotropic *g* values of 2.0096 and 2.0019 respectively and are attributed to *F* centers.

## 1. Introduction

The highly sensitive and tissue equivalent LiF based phosphors with various dopants have been widely investigated (Srivastava et al., 1996; Delgado, 1996; Shinde et al., 2001; Tang et al., 2016) for their use in environmental and personnel monitoring. One of the important LiF based phosphors is LiF:Mg,Cu,P (MCP), first reported by Nakajima et al. (1978). Over the next few decades this phosphor was studied quite extensively with varying dopant concentrations and preparatory procedures (Wu et al., 1984; Wang et al., 1986; Azorin et al., 1984; Horowitz and Horowitz, 1990; Zha et al., 1993). Extending the range of linearity (Preto et al., 2016), improving the thermal stability and reducing the residual signal will greatly improve the use of this phosphor (Horowitz and Horowitz, 1990).

Even though MCP is a highly sensitive tissue equivalent phosphor, it shows a significant loss in TL sensitivity when annealed at temperatures above 240 °C (Lee et al., 2006). The relatively lower annealing temperatures result in a slightly higher residual signal. Nakajima et al. (1978) have reported the LiF:Mg,Cu,Si (MCS) phosphor which was only 7 times more sensitive when compared to LiF:Mg,Ti and much less sensitive compared to MCP (Tang et al., 2002). Later Doh et al. (1989) reported a powder type LiF material with four dopants, Mg, Cu, Na and

* Corresponding author.
*E-mail address:* vidya3000@gmail.com (V. Balraj).

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Si which was subsequently developed at Korea Atomic Energy Research Institute (Nam et al., 1998). However, the sensitivity of this phosphor did not exceed 50% of GR-200A and has poor reusability, i.e., 10% decrease of the readout values after a reuse of 8 times (Junga et al., 2003; Lee et al., 2004), but shows a better thermal stability and could be annealed from 250 to 280 °C.

Hence we have undertaken a systematic study of LiF phosphor with four dopants, Mg, Cu, P and Si to improve the sensitivity, thermal stability, to minimize the high temperature peak at 260 °C and to reduce the residual signal, without compromising on the sensitivity of this phosphor. Herein we report the preparation, TL sensitivity, and various dosimetric characteristics including TL sensitivity, dose response, residual signal, fading, and detection threshold of MCPS phosphor. ESR investigations were also undertaken to study the defect centers and to correlate it with the TL process that could help in fine tuning the desired characteristics of this phosphor.

## 2. Experimental

### 2.1. Materials and synthesis

Polycrystalline MCPS powder was prepared by a conventional solid state method. LiF powder, $MgCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$, $SiO_2$ from Sigma Aldrich and $(NH_4)H_2PO_4$ from Merck were employed for the synthesis. In MCPS phosphor, the dopant concentrations were optimized for obtaining maximum TL sensitivity. In the reactions, 0.2 mol% of Mg, 0.0125 mol% of Cu, 1.92 mol% of P and (0 – 0.8) mol% of Si were used. The stoichiometric mixture of raw materials were taken in a platinum crucible, melted at 985 °C in air and quenched. The sample was then ground, rinsed with 1 N dil. HCl to remove impurities between the microcrystals. Finally it was washed well with distilled water and dried. After sieving, the powder samples obtained with particles of 70–210 µm size were used. Several such batches were prepared by varying the concentration of Si. The batch having highest TL sensitivity was used in the present study.

### 2.2. Measurements and characterization

The powder x-ray diffraction (XRD) patterns were recorded using GE's Inspection Technologies X-ray Diffractometer with the CuKα radiation ($\lambda = 1.5406$ Å) in the range of 10 – 70°, in steps of 0.04°. The surface morphology of the prepared dosimetric materials was investigated using Hitachi S-3400 High Resolution Scanning Electron Microscope (HRSEM).

To determine the TL response as a function of absorbed dose, the samples were exposed to $^{60}Co$ gamma radiation source with a dose rate of 0.89 Gy/min at room temperature. The $^{60}Co$ source is calibrated with reference standard (ionization chamber). The accuracy of dose delivery is within ± 1%. TL measurements were carried out using PC controlled thermoluminescence reader of type TL 1009I designed at Nucleonix System with an infrared filter. Approximately, 5 mg of the irradiated sample was used for readout. The TL signal was integrated from room temperature to 300 °C with a linear heating rate of 2 °C/s. Electron Spin Resonance experiments were carried out using a Bruker EMX ESR spectrometer operating at X-band frequency with 100 kHz modulation frequency. The $g$ factor of signals was determined using a reference sample of Diphenyl Picryl Hydrazyl (DPPH). Temperature dependence of the ESR spectra was studied using a Bruker BVT 2000 variable temperature accessory.

## 3. Results

### 3.1. Structural and morphological characterization

The XRD powder pattern of MCPS phosphors prepared with various silicon concentrations is shown in Fig. 1 along with MCP. The patterns are similar with minimal changes in the peak positions indicating that they are all isostructural. For LiF, the diffraction lines were found to occur at $2\theta = 38.76°$, 45.08° and 65.64°, for MCP at 38.60°, 44.92° and 65.44° and for MCPS at $2\theta = 38.64°$, 44.82° and 65.44°. LiF has a cubic lattice parameter of 4.0200 Å (JCPDS 72–1538 diffraction card). The observed lines in MCPS could be indexed similarly, with lines corresponding to diffraction from (111), (200) and (220) planes and a cubic lattice parameter of 4.0415 Å. The incorporation of dopant atoms into the crystal lattice leads to a small expansion of the lattice. This could be attributed to the interstitial inclusion of the dopant atoms or to the replacement of the atoms at the lattice site by the dopant atoms (McKeever, 1985). The HRSEM image shows that the phosphor is highly crystalline with numerous tiny microcrystalline particles on its surface (Fig. 2).

Powder XRD patterns have been recorded for all the phosphors prepared in this LiF system with four dopants with varying concentrations of Si (from 0 to 0.8 mol%) (Fig. 1). The TL sensitivities of these phosphors with lattice parameters are given in Table 1. They are all isostructural and change in lattice parameter with variation in silicon concentrations used is very small. However, the MCPS sample exhibiting maximum TL sensitivity shows the maximum increase in lattice parameter compared to LiF, which shows that at this particular concentration (0.1 mol% of Si), maximum inclusion of the dopant occurs in the lattice. Also the 200 reflection shows the largest intensity which could be due to preferential orientation that occurs in the polycrystalline sample when silicon is added as the dopant.

### 3.2. Thermoluminescence sensitivity

The glow curve structures of MCPS phosphors were well defined with the main dosimetric peak at 220 °C. TL sensitivity was found to increase with an increase in Si concentration from 0.025 to 0.1 mol% and then decrease gradually (Fig. 3). Thus the optimum dopant concentration for obtaining maximum TL intensity was found to be 0.2 mol % of Mg, 0.0125 mol% of Cu, 1.92 mol% of P and 0.1 mol% of Si. The optimized MCPS phosphor was found to be 1.3 times more sensitive than MCP phosphor prepared in our laboratory which is given in Fig. 3 (inset). The reproducibility of the preparation procedure was checked with five different batches and the sensitivity was found to vary within 5%. The optimized MCPS phosphor with the maximum TL intensity was used for further studies.

### 3.3. Annealing treatment

To find out the optimum annealing temperature, MCPS phosphor was annealed at temperatures ranging from 220 to 340 °C for 10 min in nitrogen and air. After annealing, the phosphors were rapidly cooled to room temperature. The effect of annealing in air and nitrogen on the glow curves of MCPS phosphor is shown in Figs. 4(a) and 4(b) respectively. For the phosphor annealed in air, the intensity of the main dosimetric peak increases from 220 to 260 °C and then decreases remarkably above 280 °C. It was observed that the position of the main peak moves towards the high temperature region and also the height of low temperature peak decreases as the annealing temperature increases, which is in agreement with the studies on MCP as shown in Fig. S1. Similar results were also obtained by Cai et al. (1996) and Tang (2000).

In the case of phosphor annealed in nitrogen, the intensity of the main dosimetric peak increases gradually from 240 °C, reaches a maximum at 300 °C, and then decreases (Fig. 4(b)) similar to MCP phosphor (Fig. S2). The decrease in the TL sensitivity of the phosphor with temperature could be attributed to the thermal damage of the recombination centers (Cai et al., 1996), or due to the dissolution of the precipitated phase of Mg (Yang et al., 2008). The rate of decrease in TL sensitivity of the main dosimetric peak is less for the sample annealed in nitrogen when compared to that annealed in air. This could be