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On the role of copper impurity in LiF:Mg, Cu, P phosphor

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Abstract. LiF:Mg, Cu, P is an important phosphor for the dosimetry of ionizing radiations using thermoluminescence. The luminescent processes in this phosphor are not well understood. The purpose of various impurities has not been properly explained. Some results on the LiF:Mg, Cu, P phosphor, prepared using a new synthesis aimed at incorporating copper in a monovalent form, are presented. Experimental evidence is presented here which shows that Cu^+ is the luminescence centre in this phosphor.

1. Introduction

LiF:Mg, Cu, P is a high-sensitivity low- Z phosphor, having good tissue equivalence, which is used in the thermoluminescence (TL) dosimetry of ionizing radiations (DeWerd *et al* 1984, Driscoll *et al* 1986, Bhatt *et al* 1989, Horowitz and Horowitz 1990b, Ziyung *et al* 1986). The commercial forms of the material are marketed by several manufacturers (e.g. as NTL 50p (Nemoto and Co., Ltd., Japan), GR-200 (Beijing Radiation Detector Works, People's Republic of China), MCP-N (Henryk Niewodniczanski Institute of Nuclear Physics, Poland) etc). However, it is commonly acknowledged that the efforts to prepare the phosphor in the laboratory do not yield the phosphor in a consistent way. Obviously, some minute but vital details of the preparation procedure adopted in commercial manufacture have not been disclosed. Despite several studies related to the dosimetric applications and the properties of the phosphor, not much is known about the mechanism of luminescence and the roles of the various impurities.

Nakajima *et al* (1978, 1979) prepared the phosphor with 'special'-grade LiF as a starting material. LiF powder together with the impurities was melted in a platinum crucible under a flow of nitrogen at 1050 °C. It is not known what is 'special' about the 'special'-grade LiF. It is still more mysterious as to why the material was melted at 1050 °C while it is known that the melting point of LiF is 845 °C and it becomes volatile at higher temperatures. Shoushan *et al* (1986) and Kolotilin *et al* (1993) followed a similar procedure. Horowitz and Horowitz (1990a) started with high-purity optical-grade LiF and other necessary salts. The phosphor was prepared by melting in a nitrogen–oxygen atmosphere at 1000 °C. Incorporation of oxygen in the molten stage was stated to be absolutely necessary for obtaining high-sensitivity phosphor in a reproducible manner.

Shoushan (1988) found that all the peaks except that at 250 °C which appears on the high-temperature side of the dosimetry peak increased with increasing Cu concentration. Mg^{2+} increased the intensities of the dosimetry peak and 250 °C peak. With increasing phosphorus concentration, the 250 °C peak increases. Horowitz and Horowitz (1990a), on the other hand, found no systematic dependence of the 250 °C peak on the dopant concentrations.

The reason for choosing these specific impurities and the form in which they enter LiF is far from clear. MgF_2 is sparingly 'soluble' in LiF; the solubility is of the order of several parts per million, and yet it is necessary to use as much as 0.2 mol% MgF_2 . The state and the role of the excess MgF_2 have not been investigated beyond the speculation that it will remain as a precipitate (McKeever 1991) or Suzuki phase $6\text{LiF}:\text{MgF}_2$ (Bhatt *et al* 1989). Recently, Sun and Jiao (1991) and Sun *et al* (1994) reported that phosphorus is incorporated as $\text{Li}_4\text{P}_2\text{O}_7$ and an unidentified phase which is responsible for the high trapping efficiency. Wang (1993) tried several phosphorus compounds for incorporating P and found that $\text{NH}_4\text{H}_2\text{PO}_4$ and H_3PO_4 were most suitable. P was found to be incorporated in the form of PO_3^- . The loss of TL sensitivity after heating beyond 250°C was attributed to $(\text{LiPO}_3)_n$ —polymerized metaphosphate—formation. Sun and Jiao on the other hand attributed the loss of sensitivity to the formation of $\text{Li}_4\text{P}_2\text{O}_7$. Similar studies were carried out by Horowitz and Horowitz (1993). The role of Cu is still obscure. Cu can exist as Cu^+ , Cu^{++} or Cu^0 . Most reports state this impurity to be Cu^{2+} . McKeever (1991) and McKeever *et al* (1993b) studied several samples in which the starting copper salt was used in monovalent form in some while in divalent form in the others. They did not find any change in emission. From this observation and the fact that the emission of LiF:Mg, Cu, P is different from that of LiF:Mg or LiF:Cu, they concluded that Mg and Cu impurities do not play any role in the emission processes and thus, by 'elimination', P was assigned the role of activator. McKeever *et al* (1993a) found that the optical absorption bands corresponding to various radiation-induced defects in LiF: Mg, Cu, P show the same concentration dependence as the TL intensity, which may suggest that all three impurities contribute to the increase in trapping efficiency. Kelmen (1993) also found that the intensities of the 310 and 380 nm bands of LiF: Mg, Cu, P are greater than those observed for LiF: Mg, Ti and thus the higher sensitivity of the former is due to more efficient trapping. However, none of the workers has ascertained the valency of Cu in their phosphors. Cu^{2+} can be easily detected by the characteristics ESR, while Cu^+ gives characteristic luminescence in alkali halides, although it is not reported for LiF (Bohun and Dolejsi 1972, Bertolaccini *et al* 1976, McClure and Weaver 1991).

In this paper we report some results on LiF: Mg, Cu, P phosphor which establish the role of Cu^+ in the emission process.

2. Experimental details

LiF: Mg, Cu, P was prepared from freshly synthesized LiF (from lithium carbonate and HF) and MgF_2 . Cu was added in the form of CuCl_2 . All chemicals were of analytical-reagent-grade purity. LiF powder mixed with CuCl_2 was heated with a fluxing agent, which was necessary to remove adsorbed moisture. It was then transferred to a graphite crucible containing MgF_2 and $\text{NH}_4\text{H}_2\text{PO}_4$ maintained at 100°C . The crucible was subsequently inserted inside a furnace. The material was rapidly (within 15 min) melted in air and quenched by pouring the melt onto an ice-cooled graphite plate. The typical procedure used for obtaining the phosphor with a high sensitivity, which is similar to the well known (Pastor and Arita 1975) 'reactive atmosphere processing' (RAP), is being patented and more details cannot be given here. Cu^+ -doped phosphors have often been prepared using the RAP technique (DeShazer 1981, Tanimura *et al* 1985, Choudhari and Debnath 1994). LiF:Mg, LiF:Cu and LiF:Mg, P samples were also prepared in a similar way. Study of these samples was useful in deciding the role of Cu impurities. The results obtained for our samples were compared with the corresponding results for the commercially available sample (LiF: Mg, Cu, P powder from Beijing Radiation Detector Works). LiF:Mg, Cu, P

prepared by us will be called sample S, while the commercial sample will be referred to as sample C. TL glow curves were recorded with the usual set-up consisting of a small metal plate heated directly using a temperature programmer, photomultiplier (931 B), DC amplifier and millivolt recorder. 5 mg of phosphor in the form of fine (72–210 μm) powder was heated every time at the rate of 150 $^{\circ}\text{C min}^{-1}$. Prior to irradiation all samples were annealed at 240 $^{\circ}\text{C}$ for 10 min.

TL emission spectra were recorded by inserting the monochromator between the heater plate and the PMT. The monochromator (central electronics) used a 25 cm grating having 1200 grooves mm^{-1} , providing a resolution of 3 nm. 50 mg of the sample was heated at the rate of 300 $^{\circ}\text{C min}^{-1}$ until the desired temperature and then it was held constant. A Hamamatsu R-955 PMT with a flat response over a wide spectral range was used.

A ^{60}Co source was used to expose the samples to γ -rays. Photoluminescence (PL) from various samples was studied on a Hitachi F-4000 fluorescence spectrophotometer. The same amount of sample was used every time. Emissions and excitation spectra were recorded using a spectral split width of 1.5 nm.

ESR measurements were carried out on a Varian E-112, E-line Century Series, X-band ESR spectrometer which utilizes 100 kHz field modulation. TCNE ($g = 2.00277$) was used as a standard for g -factor measurements.

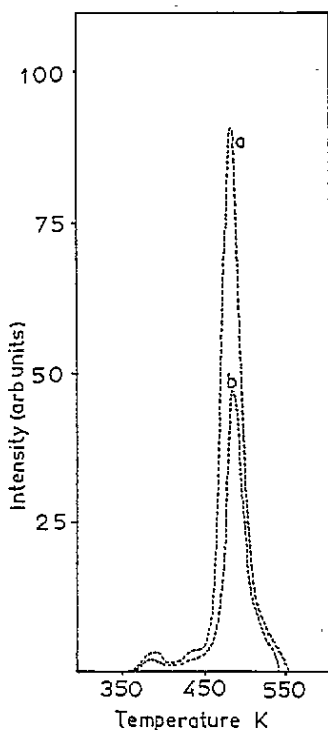


Figure 1. TL glow curves of LiF:Mg, Cu, P phosphors exposed to γ -rays (0.26 C Kg^{-1}): curve a, sample C; curve b, sample S.

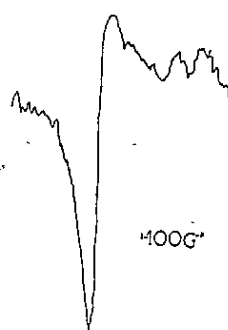


Figure 2. ESR of LiF:Mg, Cu, P (sample C). Sample S exhibited a similar but very weak signal.

3. Results and discussions

Figure 1 shows the glow curve of the LiF: Mg, Cu, P sample prepared in the present work. The glow curve for the commercial phosphor (obtained from Beijing Radiation Detector Works) is also given for comparison. The structures of the glow curves are identical. The intensity of the dosimetry peak around 210 °C in our sample is about 50% of that corresponding to the commercial sample. Other dosimetric properties of our samples were similar to that for commercial phosphor, and they will be reported separately, notable properties being the negligible fading, the linear response up to 10 Gy and little batch-to-batch variation. Some disadvantages of sample C were noticed for our samples also, e.g. heating beyond 250 °C caused irreversible loss of sensitivity to the dosimetry peak.

It was further found that the dopant concentrations affect both the glow curve shape and the intensity. The glow curve shown corresponds to the concentration 20 ppm Cu, 2000 ppm Mg and 0.5 mol% P. The same results were obtained when CuCl₂ or Cu₂Cl₂ was used as the source of Cu. Increasing the Cu concentration above 20 ppm resulted in an increase in the glow peaks at lower temperatures and a decrease in the dosimetry peak. An increase in the P concentration above 0.5 mol% resulted in an increase in the 250 °C peak and a decrease in the dosimetry peak. On the other hand, for a P concentration of 0.2 mol%, both the 250 °C peak and the dosimetry peak decreased. The presence of MgF₂ in rather a high concentration of the order of 0.2 mol% was found to be necessary to obtain the desired TL sensitivity (table 1). A sample prepared with a Mg concentration of the order of 170 ppm (as used in LiF: Mg, Ti (Daniels *et al* 1961)) exhibited poor sensitivity. The observation that the dopant concentrations affect the glow curve structure is in broad agreement with the results of Shoushan (1988). However, the optimum concentration of P is found to be much less. This is not surprising; it is known that, depending upon the preparation procedure, the optimum dopant concentrations change (Zha *et al* 1993). Table 2 lists the optimum dopant concentrations found in various studies.

Table 1. TL intensities with various dopant concentrations.

Mg concentration (mol%)	Cu concentration (mol%)	P concentration (mol%)	TL intensity ^a
0.2	0.002	0.2	3.5
0.2	0.002	0.5	100
0.02	0.002	0.5	0.8
0.2	0.00	0.5	8
0.2	0.002	0.7	41.66
0.2	0.002	1.00	32.65
0.2	0.002	1.92	21.3

^a TL intensity of the dosimetric peak.

Figure 2 shows the ESR for LiF: Mg, Cu, P samples. Sample C shows a strong ESR signal with $g(\text{parallel}) = 2.073$ and $g(\text{perpendicular}) = 2.191$ corresponding to Cu²⁺. However, the signal is rather unusual. It may be inferred that the Cu²⁺ ion is at a site experiencing severe distortion. A similar but very weak signal was found in sample S (not shown in the figure). Thus, even though the fraction of Cu entering in divalent form is quite small for our phosphor, the TL intensity is quite comparable.

Figure 3 shows PL emission and excitation spectra. For sample C, emission is observed in the form of a band at around 385 nm. The emission could be excited by 250 nm light. A similar emission was observed for LiF:Cu. However, its excitation is at 269 nm. When

Table 2. Optimum dopant concentrations for LiF:Mg, Cu, P.

Mg concentration (mol%)	Cu concentration (mol%)	P concentration (mol%)	Reference
0.2	0.005	2	Horowitz and Horowitz (1990)
0.1	0.0005	0.0065	Sun <i>et al</i> (1992)
0.2	0.002	3-5	Walker and McKeever (1992)
0.2	0.05	2.3	Nakajima <i>et al</i> (1978)
0.2	0.00196	1.92	Shoushan (1988)
0.2	0.05	0.05-0.25	Doh <i>et al</i> (1989)
0.103	0.0005	?	Wu <i>et al</i> (1984)
0.2	0.05	0.25	Niwa <i>et al</i> (1984)
0.2	0.002	5.0	McKeever <i>et al</i> (1993)
0.2	0.008	3.0	Horowitz and Horowitz (1993)
0.2	0.002	0.5-0.7	This work

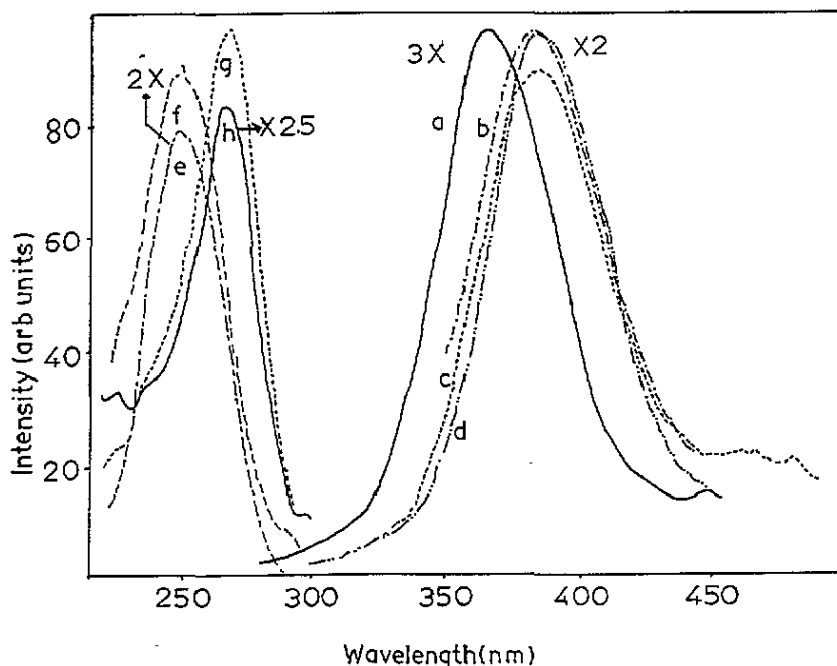


Figure 3. PL spectra of various LiF phosphors: curve a, emission spectrum, sample S, $\lambda_{ex} = 250$ nm; curve b, emission spectrum, sample C, $\lambda_{ex} = 269$ nm; curve c, emission spectrum, LiF:Cu (with optimum flux), $\lambda_{ex} = 269$ nm; curve d, emission spectrum, LiF:Cu (with excess flux), $\lambda_{ex} = 273$ nm; curve e, excitation spectrum, sample S, $\lambda_{em} = 365$ nm; curve f, excitation spectrum, sample C, $\lambda_{em} = 385$ nm; curve g, excitation spectrum, LiF:Cu (with excess flux), $\lambda_{em} = 385$ nm; curve h, excitation spectrum, LiF:Cu (with optimum flux), $\lambda_{em} = 387$ nm.

LiF:Cu was prepared with a fluxing agent in excess of the optimum amount, the emission was observed at 385 nm and the excitation for this sample had a maximum at 273 nm. In LiF:Mg, Cu, P sample S, the PL is weaker. The emission maxima is observed at 365 nm and the excitation maxima at 250 nm. No PL was observed for LiF:Mg and LiF:Mg, P samples.

Since the emission of LiF:Mg, Cu, P (sample C) is similar to that observed for LiF:Cu, and further no emission is observed for pure LiF, LiF:Mg or LiF:Mg, P, the PL of LiF:Mg, Cu, P has to be assigned to the Cu impurity. The most common emission exhibited by the copper impurity corresponds to the transition $3d^{10} \rightarrow 3d^9 4s$ of Cu^+ , and in alkali halides the reported PL emission is exclusively from this process (Bohun and Dolejsi 1972, Bertolaccini *et al* 1976, Patil and Moharil 1995a). On the other hand, McClure and Weaver (1991) report that no Cu^+ could be doped in LiF. They have also discussed the difficulties in doping Cu^+ in fluorides. It appears that the specific preparation procedures enable incorporation of Cu^+ in LiF. Recently, Cu^+ has been doped in CaF_2 (Pedrini *et al* 1992, Voronina *et al* 1993b). More detailed arguments for assigning the observed PL of LiF to Cu^+ can be found elsewhere (Patil and Moharil 1995a, b). It will be shown later that the success of the various procedures for preparation of LiF:Mg, Cu, P phosphor depends on the incorporation of Cu^+ . The small changes in the emission and excitation maxima in various LiF:Cu samples can be attributed to the use of various co-dopants and fluxing agents. The Cu^+ ions in the various samples may find themselves in different local environments which modify the PL. Such a change in emission has been observed (Voronina *et al* 1993a, Choudhari and Debnath 1994), e.g. Kurobori *et al* (1993) reported that Cu^+ ions in the vicinity of OH^- ions emitted at longer wavelengths. The results presented here also show that the Cu^+ emission of LiF can be at different wavelengths, depending on the local environment in which the Cu^+ ion exists. This is significant in the context of the mechanism of luminescence in LiF:Mg, Cu, P. This will become clear while discussing the TL emission spectra which are described next.

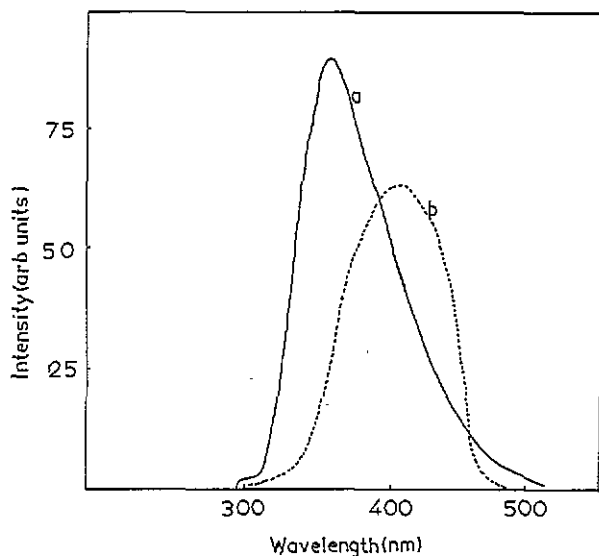


Figure 4. TL emission spectra: curve a, LiF:Mg, Cu, P (sample S); curve b, LiF:Mg, P.

Figure 4 shows TL emission spectra for LiF:Mg, P and LiF:Mg, Cu, P phosphors corresponding to the dosimetry peak, recorded at 190°C . The TL emission of sample S peaks at 365 nm while the reported (DeWerd *et al* 1984) emission of sample C has a maximum at 380 nm. These wavelengths are close to those observed in the corresponding PL emission spectra. It has been reported (Matsuzawa 1978) that the TL emission of LiF:Mg, Cu, P (Nemeto) peaks at 340 nm with another shoulder at around 410 nm. Bhuwanchandra

et al (1983) reported TL emission peaking at 362 nm for these samples. Kolotinin *et al* (1993) reported TL emission at around 345 nm for their samples. It is quite likely that the PL of the Nemeto sample would be different from that shown in figure 3. However, this sample was not available. McKeever (1991) has carried out most extensive TL emission measurements on various LiF:Mg, Cu, P samples. He found that the emission was the same irrespective of the monovalent or divalent Cu salt as a starting dopant. He also noticed small changes in the emission spectra of the various peaks. These observations prompted him to suggest that Cu does not play any role in emission. This interpretation is not tenable in the light of the results presented here. The similarity between the TL emission spectra and the PL emission spectra is unmistakable. Of the impurities doped, only Cu^+ can lead to PL. The TL emission also has to be identified with the Cu^+ emission. The differences in the emission spectra of various peaks can arise because the Cu^+ ions in differing local environments act as luminescence centres for the various peaks. Kurobori *et al* (1994) observed variation in the PL emission maxima of Cu^+ ions in the vicinity of OH^- in NaCl with relatively small changes in temperature. They attributed these changes to the temperature dependence of Cu-OH arrangements. To verify the suggestion of McKeever (1991) that P is the activator in LiF:Mg, Cu, P, the TL emission spectrum of LiF:Mg, P was also recorded (figure 4, curve b). The emission of LiF:Mg, P is totally different from that observed for LiF:Mg, Cu, P, exhibiting a maximum at around 405 nm. Thus, there is a strong case for the hypothesis that the TL emission of the dosimetry peak arises in the transitions of Cu^+ . It is thus proposed that Cu^+ acts as a luminescence centre. This role of Cu^+ is known for alkali halides (Heeros and Jaque 1974, Takeuchi *et al* 1979, Tomito and Takeuchi 1985) and other phosphors (Choudhari and Debnath 1994). It would prove conclusive to study the TL emission in LiF:Cu and to find similarity between TL and PL. However, the TL of LiF:Cu was very weak and emission spectra could not be obtained.

The role of Cu^+ in the TL processes could be verified indirectly also. In the absence of the fluxing agent, LiF:Mg, Cu, P could not be prepared consistently. It was observed that the samples showing poor TL sensitivities also failed to exhibit Cu^+ PL. Cu^+ incorporation thus seems to be a necessary condition for obtaining a phosphor with good sensitivity. This may explain the various conditions for obtaining good sensitivity in the samples prepared by different routes, e.g. Shoushan (1988) and Nakajima *et al* (1978) reported heating in a nitrogen atmosphere, and Horowitz and Horowitz (1990a) used oxygen bubbling through melt. It is apparent that these peculiar procedures are necessary for the incorporation of Cu in luminescent form. In our method this is achieved by use of the RAP technique; the use of a platinum crucible or the inert atmosphere was then found unnecessary. It can be further conjectured that the use of different processes for incorporating Cu in luminescent form leads to minor differences in the phosphor properties, e.g. differences in the emission spectra of the Nemeto and Chinese phosphors, differences in the dependence of the glow curve structure on the dopant concentrations (Horowitz and Horowitz 1990a), and different optimum concentrations obtained by various workers (table 2). It is also plausible that the various procedures used facilitate incorporation of Cu^+ by neutralizing the effects of hydroxyl ion which is known to be a strong quenchant of luminescence. The RAP technique which has been adopted in this work is quite commonly used to remove OH^- (Tanimura *et al* 1985).

Once the role of Cu^+ as luminescence centre is accepted, one may speculate about the mechanism of TL in LiF:Mg, Cu, P. The radiation creates excess electron colour centres and the defects associated with trapped interstitial halogen atoms. During the heating, the halogen atoms are released from interstitial positions and they recombine with electrons. The energy of recombination is efficiently transferred to nearby Cu^+ ions which act as

luminescent centres. The role of Mg (in rather a high concentration) and P impurities is not yet clear. Mg, obviously, like other alkaline-earth ions, accelerates the first stage of colouration. However, the amount of Mg that can be 'dissolved' in LiF is of the order of hundreds of parts per million. It is not yet clear why Mg^{2+} in concentrations as high as 2000 ppm is required to obtain the phosphor with high sensitivity. MgF_2 has been used as a fluxing agent for producing OH^- -free fluoride crystals (van Uitert *et al* 1969). It is quite likely that, in LiF:Mg, Cu, P, at least part of MgF_2 is utilized in eliminating the effects of OH^- ions. We found that the addition of P impurity to NaCl:Ca, Cu, P phosphor decreased the PL emission that was associated with Cu^+ ions in the vicinity of hydroxyl ions. A similar role for P may be envisaged for LiF:Mg, Cu, P phosphor. It is worth mentioning that, for the phosphors prepared by Nemoto, Kitahara ([5] of Nakajima *et al* (1978)) mentioned TL emission at 340 and 410 nm bands. The addition of P increased the 340 nm emission at the cost of the 410 nm band. It is quite likely that the 340 nm emission in Nemoto phosphors is due to Cu^+ while that at 410 nm is due to Cu^+ ions near OH^- .

4. Conclusions

The main conclusions of the present work can be summarized as follows.

(1) LiF:Mg, Cu, P phosphor can be prepared by a simple procedure which does not involve a nitrogen atmosphere, the use of a platinum crucible or very-high-purity starting material. The sensitivity of the phosphor so prepared is about 50% of that prepared by the more elaborate procedures.

(2) LiF:Cu samples exhibit PL which can be assigned to Cu^+ . The emission is in the range 340–400 nm and excitation in the range 250–270 nm; the exact position of the maximum is influenced to some extent by the presence of other impurities. LiF:Mg, Cu, P also exhibits weak luminescence quite similar to that observed for LiF:Cu.

(3) There is good correlation between the PL of Cu^+ in LiF and the TL emission spectra of the dosimetry peak. The TL emission is thus characteristic of Cu^+ .

(4) Some of the Cu added enters in the monovalent state even when the starting dopant material is a divalent copper salt. Similarly, even when the dopant is chosen as a monovalent copper salt, the incorporation of Cu^+ still depends on the preparation conditions.

(5) The peculiarities of the preparation procedures and to some extent the co-dopant concentrations are most probably decided by the conditions necessary for incorporation of monovalent copper impurity.

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