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LETTER TO THE EDITOR

An electron energy loss spectroscopy (EELS) study of thermal effects in LiF:Mg,Cu,P phosphors

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Abstract. LiF:Mg,Cu,P is a promising new high sensitivity material for use as a solid state radiation dosimeter. However, it suffers from a considerable loss in sensitivity upon heat treatment above 265 °C, for reasons not yet understood. This electron energy loss spectroscopy study of this phosphor indicates the presence of previously undetected inclusion particles in this material. As-received pellets contain small concentrations of inclusions analysed to contain Li, F and O. After heat treatment at 320 °C, the inclusions are found to contain principally Li, P and O. Evidence is also found that the Li–F–O particles may be the precursor to the formation of the Li–P–O particles. Since this heat treatment also causes a 95% loss in thermoluminescent sensitivity in this material, this observation may be important in understanding the cause of this loss in sensitivity, and may also indicate an important role for oxygen in the process. Along with other reactions that occur in this temperature range, these results indicate the importance of defect interactions, which appear to be complex in this system, in determining the mechanisms of luminescence in halide systems.

The unique combination of high sensitivity, good tissue equivalence and very good stability at ambient temperature makes LiF:Mg,Cu,P a very attractive material for thermoluminescent dosimetry (TLD). It has 20–45 times higher TL sensitivity to gamma radiation and better response to other radiation than the extensively used TLD-100 (LiF:Mg,Ti) [1, 2, 3]. However, LiF:Mg,Cu,P phosphors cannot be heat treated to temperatures higher than 270 °C without a degradation in performance [4]. This problem restricts the applications of LiF:Mg,Cu,P phosphors since they cannot be ‘annealed’ to remove radiation damage and thus be ‘reset’, as can other solid state dosimeter materials.

Recent studies have shown that at least a partial cause of this loss in sensitivity after high temperature annealing relates to a valence change in the copper impurity: Cu⁺ was shown to change state to Cu⁺⁺ upon annealing using extended x-ray analysis fine structure (EXAFS) studies [5]. Additionally, the magnesium impurity is generally considered to act as the principal component of the TL trapping centre, as in LiF (Mg,Ti), a result in agreement with TL glow curve analysis results [6]. However, the role and state of the phosphorous impurity is not well understood at present.

The present work focuses on the understanding of defects, inclusions, and cluster formation in this material before and after heat treatment, as related to the phosphorous impurity. Transmission electron microscopy (TEM) accompanied by electron energy loss spectroscopy (EELS) analysis provides information on the physical state of precipitates and their chemical analysis.

Ion milling was used initially for the preparation of TEM samples of MCP-N dosimeter grade pellets, supplied by TLD Niewiadomski and Co. (ul. Robotnicza 7, PL-30-545, Kraków, Poland). The thin section of the MCP-N sample turned black after two hours ion milling even though cold stage ion milling was used. No diffraction pattern was obtained from this sample. This could be caused by radiation damage during ion milling.

To avoid the above phenomena, an ultramicrotome was used to prepare the TEM sample of MCP-N pellets. The thickness of each slice was 400 Å. However, the material was so fragile that the cut slices broke into small pieces. Since these pieces were too small to be held by normal copper grids, a special grid coated with a lacy carbon thin film was used. Two different types of samples were prepared in this manner: one type was from as-received MCP-N pellets, the other from MCP-N pellets which had been heat treated at 320 °C for 12 minutes followed by a rapid cool to room temperature.

An analysis of the MCP-N samples was performed using glow discharge mass spectroscopy. This analysis indicated the presence in the bulk of the pellet of 500 ppm Mg, 200 ppm Cu and 2600 ppm P, all on the basis of mole ppm with an accuracy of $\pm 25\%$.

EELS spectroscopy was performed using a Philips 430T TEM equipped with a Gatan PEELS 666 system. The experimental conditions were: high voltage, 100 kV; 2mm spectrometer entrance aperture; dispersion setting of 0.5 eV/ch; zero loss energy resolution, 2 eV. A liquid nitrogen temperature double tilt sample holder was used, and Gatan EL/P 2.11 acquisition software with Acqloug Custom functions [7] was used for data acquisition. All spectra were taken in the diffraction mode with a camera length of 250 mm.

The major elements observed in as-received MCP-N pellets are Li and F, as may be seen

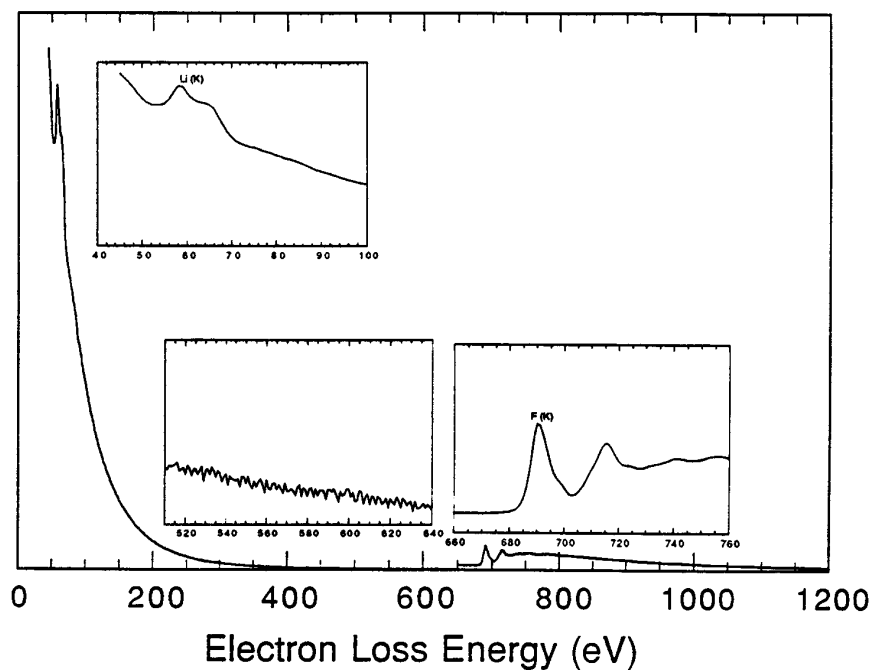


Figure 1. The EELS spectrum of LiF compound in as-received MCP-N samples.

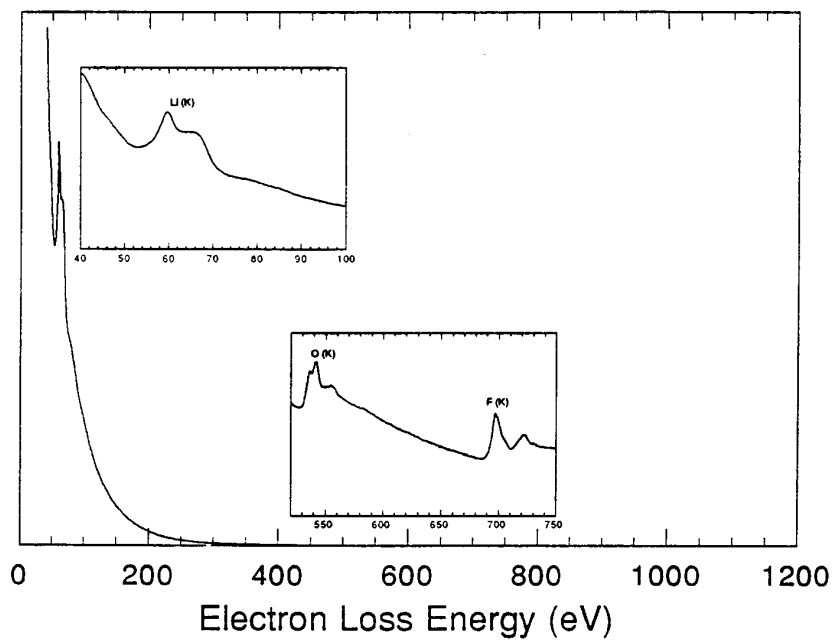


Figure 2. The EELS spectrum of the Li-F-O compound in as-received MCP-N samples.

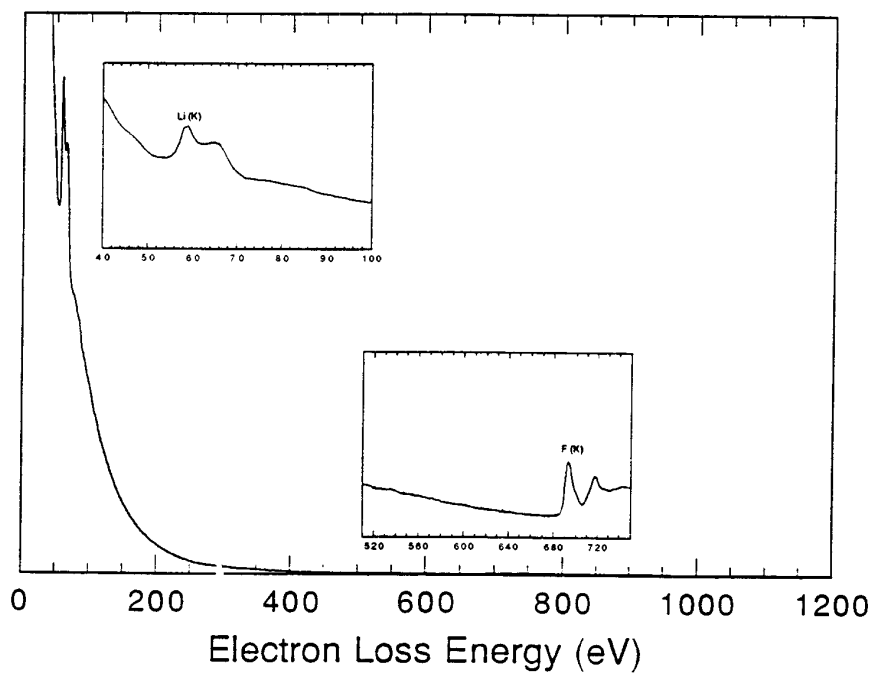
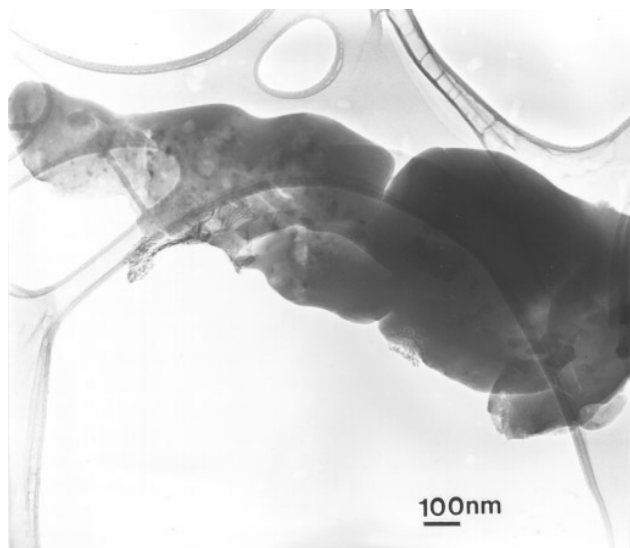
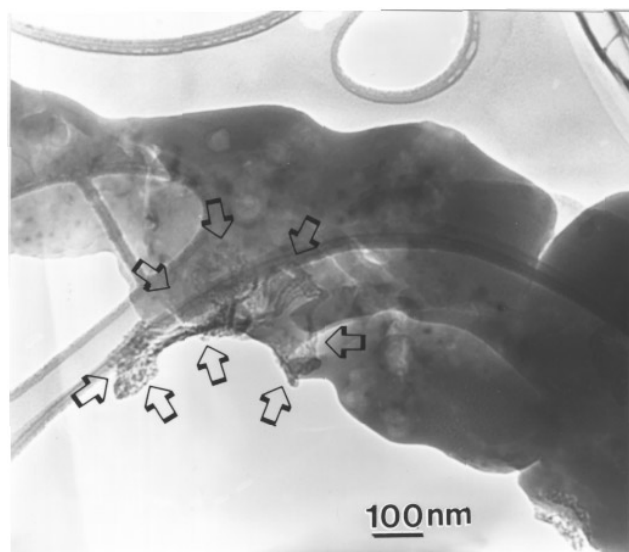


Figure 3. The EELS spectrum of LiF compound in MCP-N samples after 320° C annealing.



(a)



(b)

Figure 4. TEM image of the one of the particles seen in MCP-N samples after 320° C annealing. (a) 46000X showing a Li-P-O particle. (b) 69000X showing a small particle of different composition in the sample (indicated by arrows).

in the EELS spectra shown in figure 1. The ratio of Li to F is calculated by the quantitative analysis to be 0.99, with an accuracy of $\pm 15\%$. A standard diffraction pattern is observed, with lattice constant calculated as 4.105 Å. The only phase different from the LiF matrix found in the as-received MCP-N samples is a Li-F-O compound. These particles were analysed using

the EELS method with a resulting spectrum that is shown in figure 2. The analysis shows a Li:F:O ratio in these particles of 4:3:6.

The major elements found in MCP-N pellets after the 320 °C heat treatment are Li and F as verified by the EELS spectrum in figure 3. In these samples, additional particles were also observed: the TEM image of one of these particles on top of a porous carbon finish is shown in figure 4. Compared to the LiF matrix, there are approximately 1% of these particles in the sample. Most of these particles are a Li-P-O compound, as seen in the EELS spectrum shown in figure 5. However, the area indicated by arrows in figure 4(b), which has a size of ~300 nm (0.3 μm), has a different structure from the rest of the particle. We could obtain no diffraction pattern from the Li-P-O particle; however, a weak and blurred selected area diffraction pattern is seen from the arrow indicated area. A small probe EELS analysis of the circled area, shown in figure 6, indicates that the circled area is a Li-F-O compound. The ratio of the elements in the Li:P:O particles is 3:2:11; in the circled region, Li:F:O is 5:9:6. The carbon seen in the EELS spectra originates from the grids used.

The phases which have been found by TEM in the as-received LiF:Mg,Cu,P samples are LiF and a Li-F-O compound. Since these samples were broken into small pieces during microtoming, it is not possible to determine the location of these Li-F-O particles within the LiF matrix. However, it may be logical to consider that these Li-F-O particles are precipitates that may be formed as inclusions at the grain boundaries in the polycrystalline LiF:Mg,Cu,P MCP-N material.

The phosphorus inclusions, which are in the form of the Li-P-O compound, are seen only in the LiF:Mg,Cu,P samples after the 320 °C heat treatment. This implies that the phosphorus

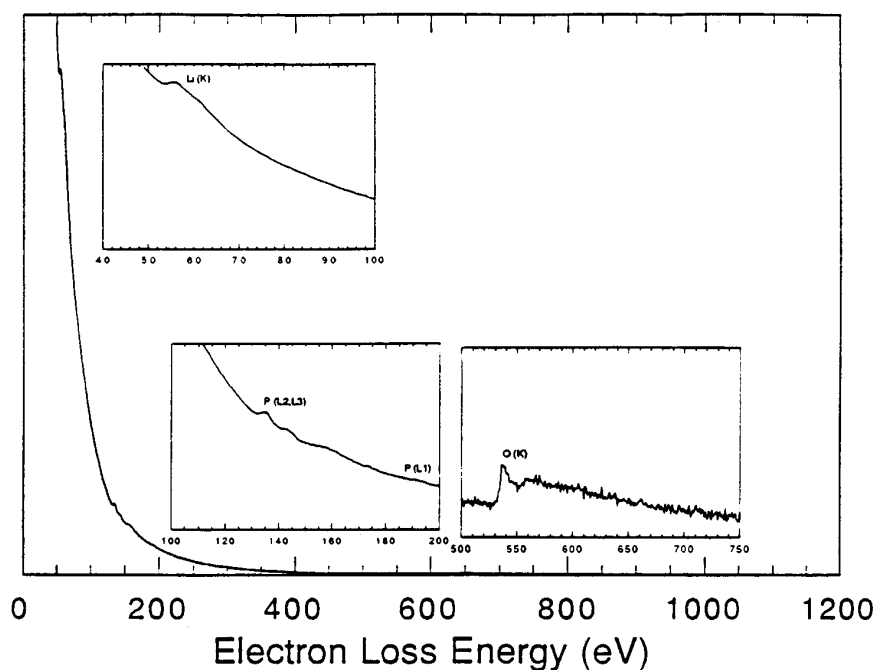


Figure 5. The EELS spectrum of the Li-P-O compound in an MCP-N sample after 320° C annealing.

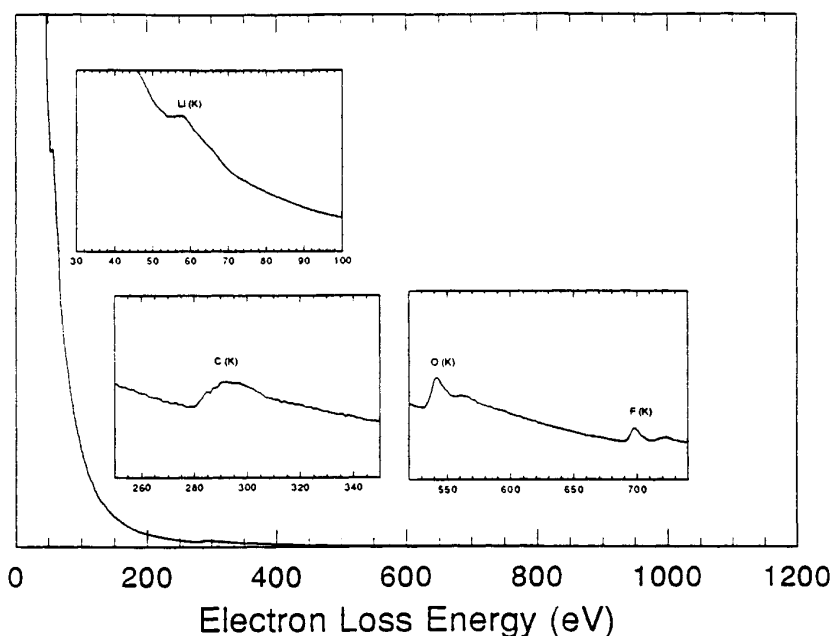


Figure 6. The EELS spectrum of the Li-F-O compound in MCP-N samples after 320° C annealing.

inclusions are formed during the heat treatment process. The small amount of Li-F-O seen in figure 4 indicates that the Li-F-O could be an oxygen source and hence a precursor for the formation of this Li-P-O compound. The processing of the LiF:Mg,Cu,P phosphors includes a fast cool from high temperature [8], which would hold the phosphorus ions in metastable substitutional sites in the material. On heating, these phosphorus ions could diffuse to grain boundaries or other low energy sites and react there with oxygen in the Li-F-O particles, and/or other oxygen present in the sample, to form the Li-P-O particles.

The diffraction patterns observed in this study show that both the as-received and heat treated LiF:Mg,Cu,P show the NaCl structure with lattice constants very close to the expected 4.027 Å. The diffraction pattern of the Li-F-O compound in the as-received LiF:Mg,Cu,P sample, as well as that from the Li-F-O seen in the heat treated sample, is not as clear as that of the LiF compound. This may be caused by a lack of specific structure for this compound; indeed the ratios of Li:F:O ions are not the same between the two observations of Li-F-O, indicating either that there are several structures possible or that the structures are highly defective, thus yielding the poor diffraction patterns. There was no diffraction pattern observable for the LiPO compound, probably caused by a similar reason.

T Niwa *et al* [9, 10] have shown that there was no degradation in TL sensitivity of LiF:Mg,Cu,P single crystals under N₂, even with a heat treatment of 350 °C for one hour. If the same samples are annealed in air, there is a significant degradation of TL sensitivity. However, MCP-N pellets suffer a serious degradation in TL sensitivity after annealing even when they are annealed under N₂ [11]. This indicates that the presence of oxygen in the polycrystalline LiF:Mg,Cu,P is important in the observed degradation of the TL sensitivity after heat treatment.

It is not clear whether the loss in TL sensitivity in LiF:Mg,Cu,P seen in these experiments is caused by the observed phosphorous precipitation. Indeed, the concentration of precipitates observed is small in these samples. The change in Cu valence also occurs in parallel with the precipitation process [5]. In all probability, the loss in TL sensitivity is a result of a complex set of reactions involving the LiF matrix and the Mg, Cu and P dopants, along with the oxygen impurities in these materials. A more detailed understanding of these interactions will require modelling of the defect structure of the materials and an analysis of the interactions of the defects and impurities involved.

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