LUMINESCENCE IN THE LiF-MgF_2 SYSTEM ACTIVATED BY RARE EARTHS

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In recent years, several reports have appeared on luminescence in $LiMgF_3$. Important applications have also been claimed. There is no record of $LiMgF_3$ in the ICDD database. In light of the crystallographic studies on ABF_3 compounds and especially the finding that $LiMgF_3$ is not formed, the reports on the $LiMgF_3$ based phosphors appear interesting. Our reinvestigation confirmed that $LiMgF_3$ does not exist. It is quite likely that the interesting properties described in the literature for $LiMgF_3$, in fact, belong to the frozen eutectic or two-phase system. All the same, the existence of eutectic was exploited to melt MgF_2 at much lower temperature (735°C) than the melting point of MgF_2 (1263°C). We prepared LiF-MgF_2:Eu^{2+} and LiF-MgF_2:Ce^{3+} by melting at 735°C. These materials exhibited properties similar to those of MgF_2:Eu^{2+} and MgF_2:Ce^{3+} phosphors, respectively. Thus, using the lower melting point of eutectic, it might be possible to prepare various MgF_2 based phosphors at temperatures as low as 735°C, against the high melting point of 1263°C for MgF_2.

Keywords: *luminescence, eutectic, fluoride, phosphor, Eu^{2+}, Ce^{3+}.*

ЛЮМИНЕСЦЕНЦИЯ СИСТЕМ LiF-MgF_2, АКТИВИРОВАННЫХ РЕДКОЗЕМЕЛЬНЫМИ ЭЛЕМЕНТАМИ

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Подтверждено, что $LiMgF_3$ не существует. Описанные в литературе свойства $LiMgF_3$ относятся к замороженной эвтектике или двухфазной системе. Тем не менее существование эвтектики использовалось для плавления MgF_2 при гораздо более низкой температуре (735°C), чем точка плавления (1263°C). Системы LiF-MgF_2:Eu^{2+} и LiF-MgF_2:Ce^{3+} получены с помощью плавления при 735°C. Эти материалы проявляли свойства, аналогичные свойствам люминофоров MgF_2:Eu^{2+} и MgF_2:Ce^{3+}. Таким образом, используя более низкую температуру плавления эвтектики, можно получить различные люминофоры на основе MgF_2 при температурах до 735°C по сравнению с высокой температурой плавления 1263°C для MgF_2.

Ключевые слова: *люминесценция, эвтектика, фторид, люминофор, Eu^{2+}, Ce^{3+}.*

Introduction. Though the $LiMgF_3$ molecule has been studied [1, 2], there is no record of $LiMgF_3$ in the ICDD database. In recent years, several reports have appeared on the luminescence in $LiMgF_3$. Also, significant applications have been claimed. $LiMgF_3$ doped with Ce, Er [3–5] or Dy was found applicable for beta dosimetry measurements [6]. Mn doped $LiMgF_3$ was found useful for optically stimulated luminescence (OSL) dosimetry and X-ray imaging [7]. There are no reports on $LiMgF_3$:Eu^{2+}. On the other hand, several Eu^{2+} fluoroperovskites like $NaMgF_3$ [8, 9], $KMgF_3$ [10, 11], and $LiBaF_3$ [12, 13] are important phosphors for various applications. Thus, we have attempted the synthesis of LiF-MgF_2:Eu^{2+} phosphor.

MgF_2 is an important material. MgF_2:Eu phosphors as an efficient luminescence material have been investigated with a variety of applications in radiation detection, solid state lighting, and also for increasing solar cell efficiency [14–18]. Optical properties like absorption and luminescence crystals have been reported in MgF_2 [19, 20]. Also, studies on color centers produced due to X-ray were conducted [21]. A detailed study of 3D impurity-ion spin-forbidden absorption enhanced by defects in MgF_2 crystals has been made by Sibley and co-workers [22–24]. Eu^{2+} activated MgF_2 as a good luminescent material for blue emission has been investigated by Lizzo et al [17]. MgF_2:Mn^{2+} has also proved to be an efficient phosphor. Even energy transfer between Mn^{2+} and Eu^{2+} in MgF_2:Mn^{2+} and Eu^{2+} co-doped phosphors has been observed, due to the overlapping of Eu^{2+} emission band with that of absorption of Mn^{2+} [25].

In light of the crystallographic studies on ABF_3 compounds and especially the finding that $LiMgF_3$ is not formed, the reports on the $LiMgF_3$ based phosphors appear interesting. None of these reports discuss the crystal structure of $LiMgF_3$. If $LiMgF_3$ is not formed, then what compounds are formed which show interesting luminescence properties as depicted in these reports? Are these two-phase compounds similar to the eutectics reported for LiF/CaF_2 [26, 27] and LiF/SrF_2 [28]? We have therefore decided to investigate the formation of $LiMgF_3$ and its luminescence properties.

Experimental. 64 LiF-36 MgF_2 samples were prepared by melting the constituent fluorides in a graphite crucible. Fluorides are highly prone to hydrolysis [29]. They are also very reactive and attack the crucible material during high temperature processes. Hence, freshly prepared constituting materials were used to minimize the hydrolysis. Thus, LiF and MgF_2 powders were freshly synthesized by neutralization of HF with Li/Mg carbonate. LiF and Eu^{2+}/Ce^{3+} doped MgF_2 were taken in the proportion of 64 and 36 mol.%, respectively, mixed together, and transferred to a graphite crucible. The sample was heated up to 735°C. When reaching the melting point for quenching purpose, the melt was poured immediately on a graphite plate, which is at room temperature. It was found that the sample melted and quenched in this way directly showed luminescence.

X-ray diffraction patterns were recorded on a Philips PANalytical X'pert Pro diffractometer. Photoluminescence spectra were recorded on a Hitachi F-4000 spectrofluorimeter with a spectral slit width of 1.5 nm in the spectral range of 220–700 nm. Thermoluminescence glow curves were recorded on a Nucleonix, Hyderabad (India) TL reader (Model no. TL 1009I) with a heating rate of 5°C per second using a Hamamatsu R.6095 PMT (S11 response), which is sensitive over the region of 300–650 nm with maximum sensitivity of about 420 nm. Irradiations were performed using ^{60}Co source. The samples were exposed to 1 Gy.

Results and discussion. *Phase identification using XRD.* The phase diagram of LiF-MgF_2 is discussed by Jackson [30]. Previously in 1924, Tacchini investigated the LiF-MgF_2 system [31] and concluded that there exists an eutectic nearly at 50 mol% of MgF_2. In the same year Bruni and Levill [32], and later on Ferrari [33], analyzed different parts of the system using X-ray techniques. Zintl and Udgird [34] extended this work and discovered that a small amount of MgF_2 actually gets into the lattice of LiF at room temperature and the structure of LiF does not change even on melting it with MgF_2. Later, Bergman and Dergunov [35] also investigated the system and found that there exists a series of solid solutions with up to 33 mol.% MgF_2. Further, Ferrari [33] suggested that the reason behind the existence of this extensive range of solid solutions lies in the fact that the unit-cell volumes of these two compounds are almost same. However, even this explanation was not sufficient regarding the occurrence of a complete solid solution between such end members having different crystal structures (cubic and tetragonal) at higher temperatures. In 1953 Counts et al. [36] studied at least eight mixtures by phase identification using petrographic microscopy, the visual thermal method, and X-ray techniques at room temperatures in this system. The most relevant points made after this study were that no compound formation was observed and the eutectic exists at 735°C for 36 mol.% MgF_2.

Mixtures examined at room temperature containing these two phases LiF and MgF_2 by using the X-ray diffraction as well as by the optical properties, identification techniques, were found similar to that of their respective pure end members. Hence, it was concluded that the solid solution between LiF and MgF_2 becomes complete at temperatures above 670°C, whereas an exsolution occurs on cooling the system below this temperature. Therefore, there exists no appreciable solid solution between MgF_2 and LiF at room temperature.

These findings are confirmed from XRD of Fig. 1. The compound formed by melting 64 LiF-36 MgF_2 together at about 750°C is a mixture of LiF and MgF_2. XRD patterns show lines of both LiF (ICDD 88-2298) and MgF_2 (ICDD 72-2231).

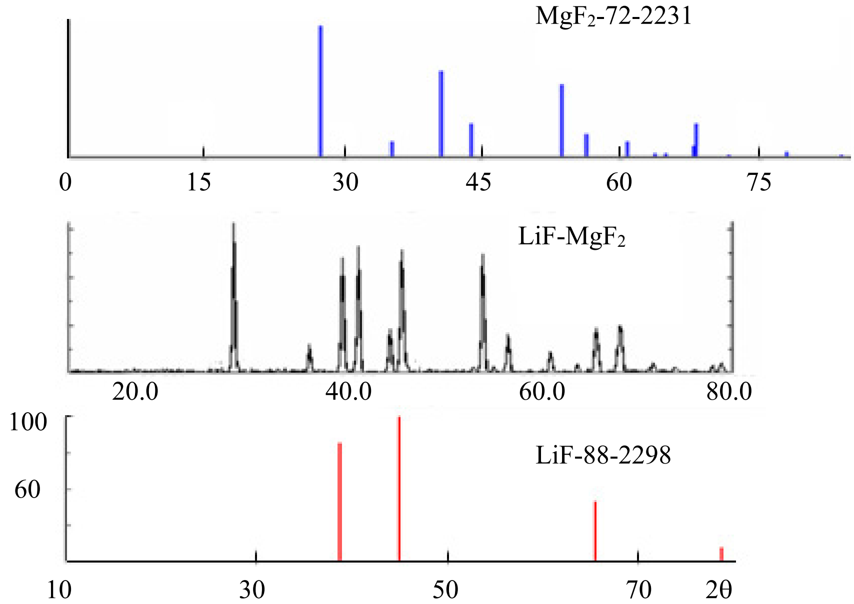

Fig. 1. XRD pattern of $LiF\text{-}MgF_2$ at room temperature.

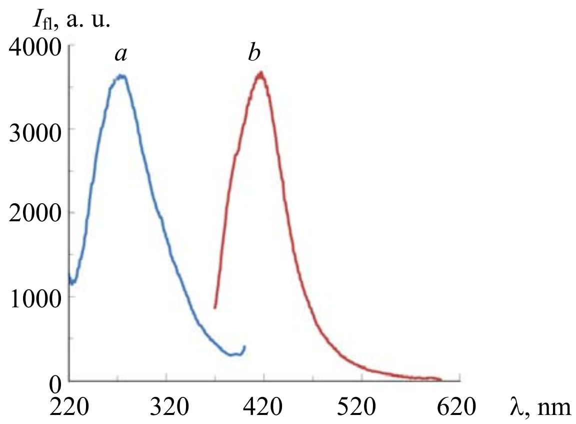

Fig. 2. PL spectra of $LiF\text{-}MgF_2$:Eu (1%) eutectic: a) excitation for 420 nm emission; b) emission for 270 nm excitation.

Photoluminescence. Figure 2 shows the PL spectra obtained from $LiF\text{-}MgF_2:Eu^{2+}$ eutectic. It can be seen that at an emission wavelength of 420 nm, the excitation band starts from 230 nm and extends up to 380 nm with a broad peak of about 275 nm. Emission taken at 270 nm consists of a band emission with maxima at 420 nm. For $MgF_2:Eu^{2+}$, Lizzo et al. [17] reported excitation consisting of a broad band between 270–430 nm and emission band at 438 nm. Hence, it may be concluded from the results that both emission and excitation maxima were shifted towards shorter wavelengths. This may be attributed to the presence of LiF phase in $LiF\text{-}MgF_2:Eu^{2+}$.

Synthesis of MgF_2:Ce phosphor was also attempted by melting MgF_2:Ce and LiF powders together at 735°C. Figure 3 shows PL for this sample. Emission of about 336 nm is obtained for 254 nm excitation. This is in good agreement with the earlier reports [37].

Thermoluminescence. The $LiF\text{-}MgF_2:Eu^{2+}$ described above also exhibits thermoluminescence. Figure 4 shows TL glow curves for $LiF\text{-}MgF_2:Eu^{2+}$. It contains a prominent peak of about 175°C with a shoulder at 120°C.

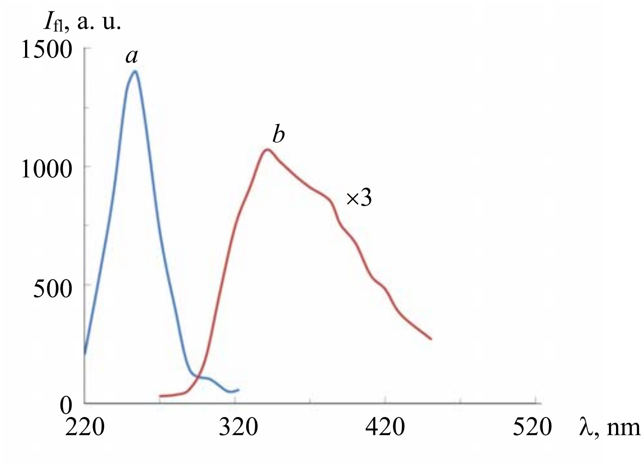

Fig. 3. PL spectra of LiF-MgF_2:Ce (1%) eutectic: a) excitation for 330 nm emission; b) emission for 254 nm excitation.

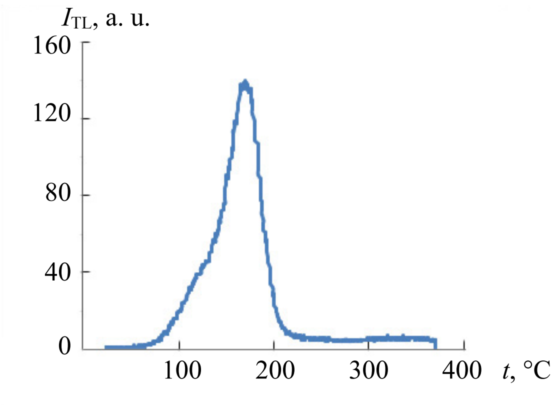

Fig. 4. TL glow curve of LiF-MgF_2:Eu^{2+} eutectic.

Conclusions. The results show that MgF_2 based phosphors can be made at temperatures as low as 735°C, against the melting point of 1263°C for MgF_2. Though $LiMgF_3$ based phosphors are described quite often in the literature, it does not exist. The properties correspond to the mixture of LiF and MgF_2 phases. However, the mixture melts at a considerably lower temperature. Eu or Ce doped mixtures show PL characteristics of MgF_2:Eu and MgF_2:Ce phases, respectively. There is some blue shift in PL spectra which may be due to the presence of LiF in the mixture. It may be possible to prepare other MgF_2 based phosphors such as MgF_2:Mn^{2+}, Eu^{2+} at lower temperatures exploiting the melting properties of eutectic phases. Hence by taking the advantage of lower melting point of eutectics, it is possible to prepare all these phosphors at temperatures as low as 735°C against the melting point of 1263°C for MgF_2.

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