VUV and UV Study of Mn^{2+}-Doped $LiZnPO_4$: A Yellow-Green Phosphor for UV-LED

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White light emitting devices (LEDs) are considered as next generation solid-state lighting systems because of their excellent properties such as high energy efficiency, long lifetime, low power consumption and environmental protection. It is well known that white light can be produced by many approaches; one of the most common and an earlier strategy is a combination of blue LED with yellow luminescence from $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce) phosphor materials. Although this kind of white-light blending method has been used for many years, some serious problems such as poor colour rendition, thermal quenching and narrow visible range still exist. To overcome these problems, more and more attention has been paid to the development of new phosphors that can be excited in the range of near-UV (370-420 nm), since UV LED can offer highly efficient solid state light.

On the other hand, phosphors based on phosphate host matrix having the general formula $ABPO_4$, where A is a monovalent cation (Li^+, Na^+, K^+) and B is a divalent cation (Ca^{2+}, Sr^{2+}, Ba^{2+}) are of interest for their optical or ferroelectric properties and are considered to be efficient luminescent hosts. Recently, Eu^{2+}-activated $KSrPO_4$ phosphors that emit strong blue lights under UV-light (360-400 nm) irradiation and exhibit excellent thermal stabilities have been reported. However, there is hardly any report on the photoluminescent properties of $LiZnPO_4:Mn^{2+}$ for potential application in UV-LEDs. Hence, in this work, we have explored a yellow-green Mn^{2+}-doped $LiZnPO_4$ phosphor, which can be efficiently excited by VUV and UV light.

The polycrystalline samples of $LiZn_{1-x}PO_4:Mn_x$ ($0 < x \leq 0.22$) phosphors were synthesized by solid-state reaction using Li_3PO_4, $NH_4H_2PO_4$, ZnO and $MnCO_3$ as raw materials. The molar ratio of Li:Zn:PO_4:Mn was kept at 1:1-x:1:x, respectively. Stoichiometric homogeneous mixtures of highly pure raw materials were obtained by thorough grinding and then sintering in argon gas at 900 °C for 4 h followed by additional sintering at 850°C for 2 h in a 25% H_2/75% N_2 gas mixture to reduce manganese. The VUV PL and PLE spectra were measured at the National Synchrotron Radiation Research Center (NSRRC) in Taiwan by using a BL03A beam line. The PLE were recorded on scanning a 6 m cylindrical grating monochromator with a grating 450 *l*/min, which spans the wavelength range of 100-350 nm. A CaF_2 plate served as a filter to remove the high-order light from synchrotron. The emission from the phosphor was analyzed with a 0.32 m monochromatic and detected with a photomultiplier tube in a photon-counting mode.

Fig. 1 shows the VUV-UV PL and PLE spectra of $LiZn_{0.9}PO_4:Mn_{0.1}$. (a) VUV PLE spectrum under the λ_{em} = 560 nm; (b) UV PLE spectrum under the λ_{em} = 560 nm; (c) UV PL spectrum under the λ_{exc} = 414 nm; (d) VUV PL spectrum under the λ_{exc} = 185 nm. The excitation spectra between 130 and 300 nm shows three excitation peaks which are similar to previous reports on the Mn^{2+}-activated $ZnSiO_4$ system. The first peak at 260 nm can be ascribed to a localized charge transfer (CT) state in which Mn^{2+} is involved as well as to an auto-ionization state of Mn^{2+}. The second excitation peak at about 185 nm is related to the host lattice or band-to-band excitation in the $LiZnPO_4$ matrix. Finally, the peak at 156 nm is due to the energy transfer process from host to Mn^{2+} via exchange interaction. Between 300 and 500 nm, five excitation peaks at 350, 375, 414, 431 and 464 nm were observed, which can be ascribed to the similar transitions of Mn^{2+} in the $ZnSiO_4$ host from $^6A_1(S)$-$^4E(^4D)$, $^6A1(S)$-$^4T_2(^4D)$, [$^6A_1(S)$-$^4A_1$, $^4E(^4G)$], $^6A_1(S)$-$^4T_2(^4G)$ and $^6A_1(S)$-$^4T_1(^4G)$ excited levels, respectively. Moreover, both the VUV-UV PL spectra (460-650 nm) show a single intense broadband at 550-560 nm under λ_{exc} = 185 and 414 nm, respectively. This emission band is attributed to the spin-forbidden *d-d* transition $^4T_1(^4G) \rightarrow {}^6A_1(^6S)$ of Mn^{2+}. As shown in Fig. 1, the broad yellow-green emission band centering at 560 nm does not depend on excitation wavelength ,indicating only one emission center in the Mn^{2+}-doped $LiZnPO_4$ phosphor.

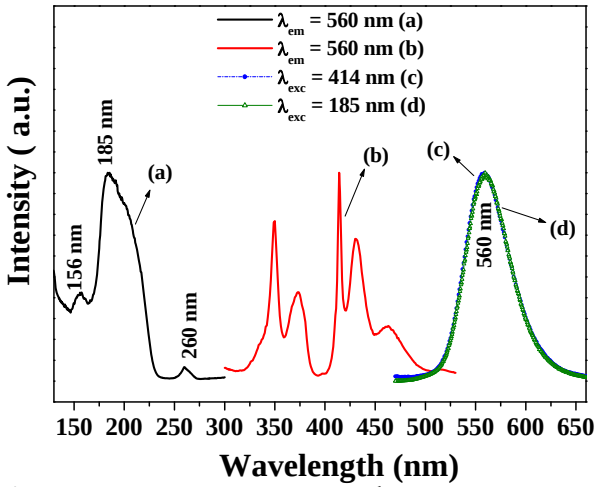

Figure 1. VUV-UV PL and PLE spectra of $LiZn_{0.9}PO_4:Mn_{0.1}$