B *K*-Edge and P *L*-Edge XANES Spectra of Mn^{2+}-Doped BPO_4 Prepared by Sol-Gel Method

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It has recently been reported that Ba^{2+}-doped BPO_4 prepared by the sol-gel process is a stable, efficient, and environmentally friendly luminescent material emitting bluish-white light [1].

We prepared Mn^{2+}-doped BPO_4 by a sol-gel method and investigated its properties by B *K*-Edge and P *L*-Edge XANES Spectra as well as XRD, IR, ^{11}B MAS-NMR, ^{31}P MAS-NMR, and fluorescence measurements.

$(NH_4)_2HPO_4$ and $(CH_3COO)_2Mn$ were dissolved in a 0.01 M aqueous solution of HNO_3. H_3BO_3, citric acid and poly(ethylene glycol) were dissolved in an aqueous solution of ethanol. The two solutions were mixed with stirring and then dried at 100 ℃ to obtain dried gels. By heat treatment of the dried gels at 450-1000 ℃ were obtained powdered samples of Mn^{2+}-doped BPO_4.

B *K*-edge and P *L*-edge XANES spectra for Mn^{2+}-doped BPO_4 and some reference samples were measured using a beamline BL-2 of the SR Center at Ritsumeikan University. All samples were powdered to collect their XANES spectra in the total electron yield mode. The vacuum level in the sample chamber was higher than 1.0×10^{-5} Pa during measurements.

Figure 1 shows B *K*-edge XANES spectra of Mn^{2+}-doped BPO_4 along with reference samples of B_2O_3 and BPO_4. For B_2O_3, an intense peak at 194.0 eV and a structured absorption band around 202.5 eV are assigned to the transitions from B1s to the unoccupied B2p π^* and σ^* states, respectively, of the trigonal $[BO_3]$ unit. For BPO_4, a significant peak located at 198.4 eV and a broad absorption band around 202.8 eV are assigned to the transitions from B1s to the unoccupied B2pσ^* and unoccupied high energy B2pσ^* states, respectively, of the tetrahedral $[BO_4]$ unit.

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From the spectra of the Mn^{2+}-doped BPO_4 samples, it is found that in the samples heat treated at 450 and 600 ℃, B_2O_3 exists, the form of which was revealed as both amorphous and crystalline states by XRD measurements. On the other hand, BPO_4 crystals probably containing Mn^{2+} ions is formed even in the sample heat treated at 450 ℃, and the amount increases with increasing the heat-treatment temperatures. In the samples heat treated at 750 and 1000 ℃, we can obtain only the Mn^{2+}-doped BPO_4 because no 194.0-eV peak due to B_2O_3 is observed in these samples.

Figure 2 shows P *L*-edge XANES spectra of Mn^{2+}-doped BPO_4 along with a reference sample of BPO_4. The spectra of the samples heat treated at 600, 750, and 1000 ℃ are similar to the spectrum of BPO_4, while the spectrum of the sample heat treated at 450 ℃ differs from the others, with a relatively strong peak at 143 eV. Further work will clarify this difference, although the detection of the local structure difference around a phosphorus atom may be difficult because the atom usually locates in a [PO_4] unit in most of the phosphates.

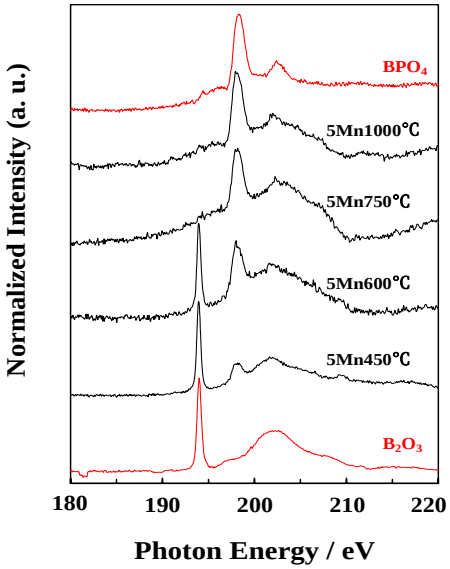

Figure 1. B *K*-edge XANES spectra of Mn^{2+}-doped BPO_4 and reference samples. Sample of 5MnO-95BPO_4 heat treated at 450 ℃ is, for example, indicated as 5Mn450℃.

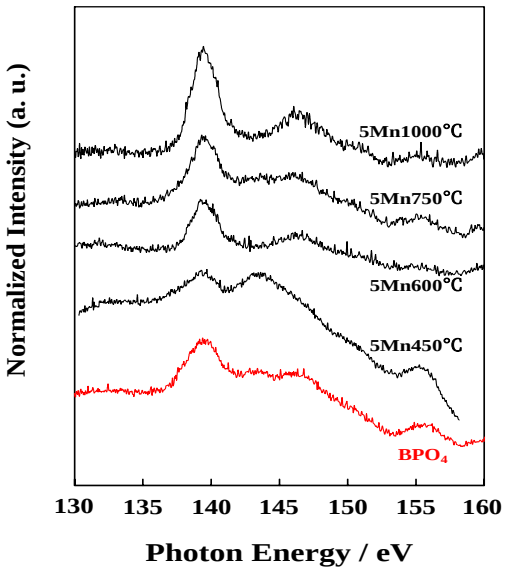

Figure 2. P *L*-edge XANES spectra of Mn^{2+}-doped BPO_4 and a reference sample of BPO_4. Sample of 5MnO-95BPO_4 heat treated at 450 ℃ is, for example, indicated as 5Mn450℃.

References

[1] C. K. Lin, Y. Luo, H. You, Z. Quan, J. Zhang, J. Fang and J. Lin, *Chem. Mater.*, **18**, 458 (2006).