

# First-Principles Electronic-Structure Calculations of Mn<sup>4+</sup>-Doped Red Phosphors for White LED Application

関西学院大学大学院理工学研究科  
化学専攻 小笠原研究室 Mega Novita

The development of white light emitting diodes (LEDs) is quite promising for both saving the global energy and reducing the atmospheric carbon dioxide concentration. However, the general white LED really is pseudo white which lacks red hue. Therefore, the research of new red phosphors with good luminescent properties is an indispensable work for realization of next generation lighting source using white LED. Many researchers have been experimentally investigating candidate materials for the red phosphors. Among them, Mn<sup>4+</sup>-doped compounds are one of the promising materials as red phosphors for white LEDs. In this work, I investigated some red phosphors and related materials with respect to the following three themes.

1. Mn<sup>4+</sup> in fluorides such as K<sub>2</sub>SiF<sub>6</sub>, K<sub>2</sub>GeF<sub>6</sub>, and K<sub>2</sub>TiF<sub>6</sub>
2. Isoelectronic 3d<sup>3</sup> ions such as V<sup>2+</sup>, Cr<sup>3+</sup>, and Mn<sup>4+</sup> in α-Al<sub>2</sub>O<sub>3</sub>
3. Isoelectronic 3d<sup>3</sup> ions in Mg<sub>2</sub>TiO<sub>4</sub>

First, I constructed cluster models including the doped transition metal (TM) ion such as V<sup>2+</sup>, Cr<sup>3+</sup>, and Mn<sup>4+</sup> at the center. Several thousand point charges were located at the external atomic sites so as to produce the effective Madelung potential. First-principles calculations of multiplet energy levels were performed based on the DVME method [1]. In order to improve the accuracy of the theoretical transition energies, I took into account several effects i.e., the orbital relaxation, the lattice relaxation, the configuration-interaction correction (CDC), and correlation correction (CC).

The theoretical and experimental  ${}^4A_2 \rightarrow {}^4T_2$  (U-band) and  ${}^4A_2 \rightarrow {}^4T_{1a}$  (Y-band) transition energies of Mn<sup>4+</sup> in fluorides and oxides are compared in Fig.1. In the theoretical results, both of the U-band and Y-band energies decrease as the increase of Mn-F bond length in fluorides, while they increase as the increase of Mn-O bond length in oxides. On the other hand, in the experimental results, the U-band energy of all cases and Y-band energy of fluorides decrease as the increase in Mn-ligand bond length, indicating that the theoretical prediction of the tendency between the completely different crystal structures is still a difficult issue.

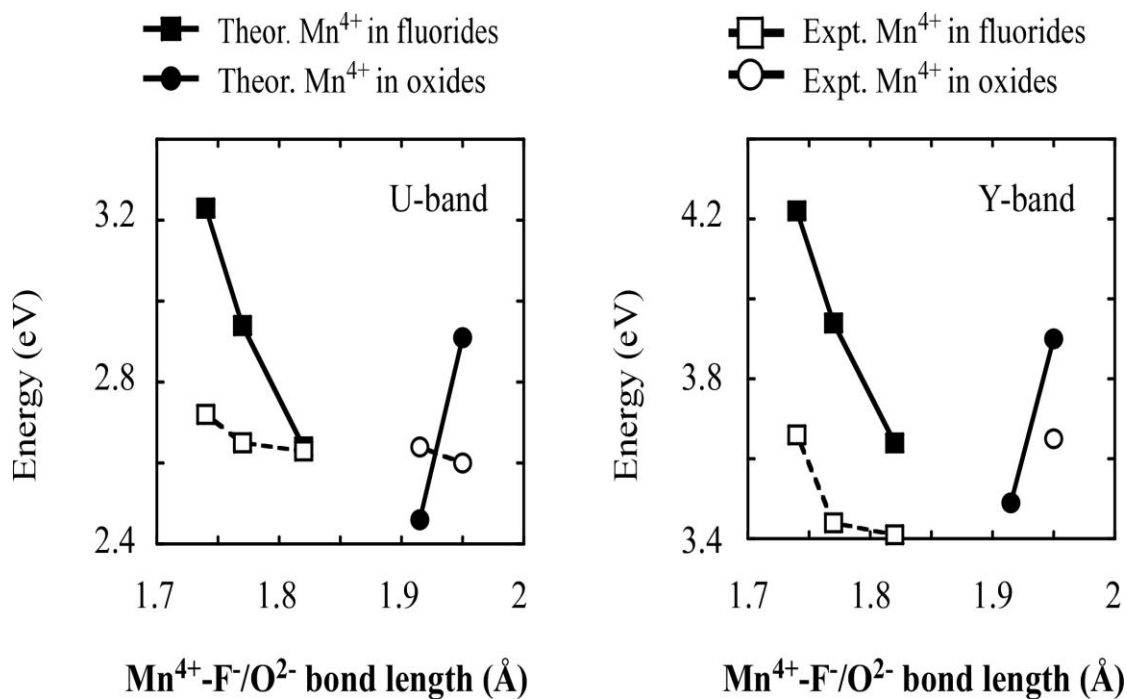


Fig. 1. Comparison of U-band and Y-band energies of Mn<sup>4+</sup> in fluorides and oxides.

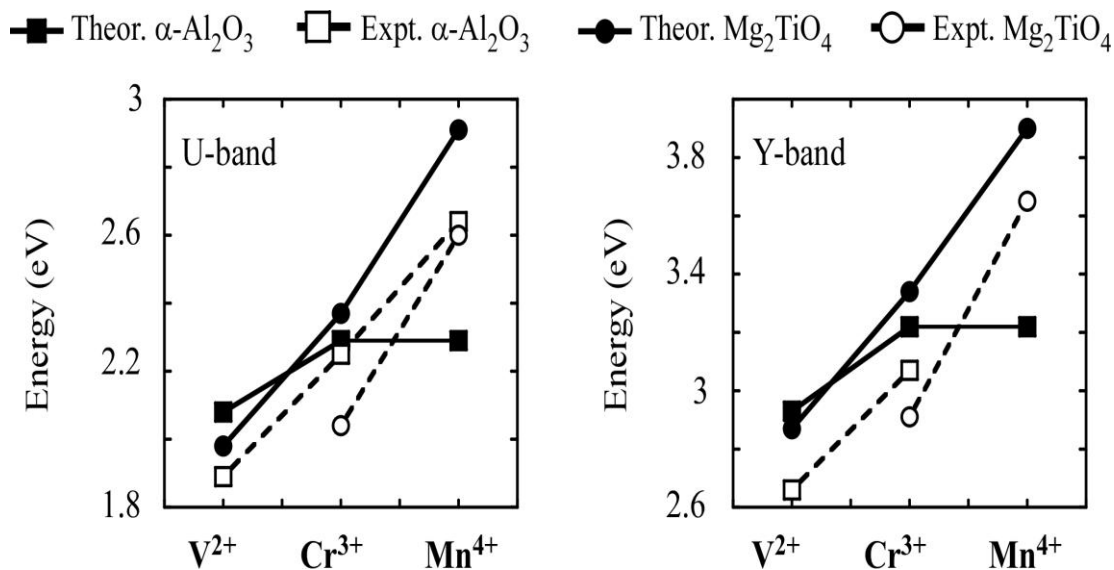


Fig. 2. Comparison of U-band and Y-band energies of 3d<sup>3</sup> ions in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and Mg<sub>2</sub>TiO<sub>4</sub>.

In the case of isoelectronic 3d<sup>3</sup> ions doped in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and Mg<sub>2</sub>TiO<sub>4</sub>, the tendency of the variation of the U-band and Y-band energies depending on the charge of the cation was clearly reproduced by the first-principles calculations. The results in Fig. 2 show that both theoretical and experimental U-band and Y-band energies increase as the increase in charge of the TM ion.

## Reference

[1]. K. Ogasawara, T. Ishii, I. Tanaka, and H. Adachi: Phys. Rev. B 61 (2000) 143.