

2014年度 博士論文要旨

Theoretical Investigation on the Electronic Structures of Novel Red Phosphor Materials Based on Mn^{4+} Ion and Its Isoelectronic Ions

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In recent years, many researchers have much attention in Mn^{4+} due to its potential applications as red phosphors for the current white light emitting diode (LED) devices. Specifically, Mn^{4+} doped in K_2SiF_6 or in K_2TiF_6 has recently been used as a red phosphor in LED lamps which exhibits white light source with correlated color temperature (CCT) ~ 3000 K and color rendering index (CRI) ~ 90 . It is therefore known to be suitable to improve the white LED quality. However, due to instability problem, it is quite difficult to use these compounds for industrial scale. A more stable red phosphor material is desired.

Since there are infinite numbers of possible red phosphor materials, trial and error experiments are rather inefficient. In this dissertation, the guidelines to develop novel red phosphor materials based on the non-empirical first-principles discrete-variational multi-electron (DVME) method have been explored. The structure and electronic properties of Mn^{4+} doped in variety of host crystals with fluorine or oxygen anions have been studied thoroughly. Considering that the spectroscopic properties of the red phosphor materials are characterized primarily by the absorption and emission spectra, the transition energies such as ${}^4A_2 \rightarrow {}^4T_2$ (U-band), ${}^4A_2 \rightarrow {}^4T_{1a}$ (Y-band) and ${}^2E \rightarrow {}^4A_2$ (R-line) were investigated in detail. The effect of lattice relaxation on the multiplet energies was also examined. Some energy corrections such as configuration dependent correction (CDC) and correlation correction (CC) were considered to improve the accuracy of the calculations.

In this work, the investigation of novel red phosphor materials was started with the study of Mn^{4+} activated in fluoride host crystals. The optical properties of Mn^{4+} doped in A_2BF_6 host crystals with (1) cubic structure such as Cs_2MnF_6 , Cs_2GeF_6 , Rb_2GeF_6 , Rb_2SiF_6 , Cs_2SiF_6 , K_2SiF_6 , and Rb_2MnF_6 and (2) rhombohedral structure such as Na_2GeF_6 , Na_2SiF_6 , Na_2TiF_6 , Rb_2GeF_6 , K_2GeF_6 , K_2TiF_6 , and Li_2MnF_6 have been studied in detail. The lattice relaxation rate was estimated by performing the Mn K-edge Extended X-ray Absorption Fine Structure (EXAFS) measurement of K_2MF_6 ($M = Si, Ge, \text{ or } Ti$): Mn^{4+} . The observed Mn-F bond lengths were then used to estimate the

lattice relaxation rate of the other compounds. The multiplet energies of the Mn^{4+} doped in A_2BF_6 crystals were qualitatively reproduced by considering lattice relaxation, CDC, and CC. When the Mn-F bond length decreased, the U- and Y-band energies increased whereas the R-line energy decreased. The low symmetry effect was also investigated by comparing the polytypes of fluoride crystals with different symmetry.

In order to get deeper understanding on Mn^{4+} ion, a comparative study on the multiplet energies of MgO : V^{2+} , Cr^{3+} , and Mn^{4+} has been performed. The lattice relaxation effect was estimated by geometry optimization using the Cambridge Serial Total Energy Package (CASTEP) code. The effect of spin polarization was considered and the calculations based on the Local Density Approximation and Hubbard U (LDA+U) approach were also performed for comparison. The results show that the multiplet energies increase as the charge of the transition metal (TM) ion increases. The detailed comparison between the experimental and the theoretical values shows that the multiplet energies are well reproduced by the first-principle calculations with considering CDC-CC correction based on the optimized clusters including the spin-polarization effect. This fact indicates that the consideration of lattice relaxation is very important to reproduce the tendency of the multiplet energies. However, a simple calculation using the geometry optimization without consideration of LDA+U approximation would be effective for the prediction of the multiplet energies.

In addition, we also investigated the effect of pressure on the multiplet energy levels of d^3 ions such as Cr^{3+} or Mn^{4+} in $\alpha\text{-Al}_2\text{O}_3$. Two types of model clusters; non-optimized and optimized clusters were used for the calculations. The non-optimized cluster was constructed based on the experimental crystal structure of $\alpha\text{-Al}_2\text{O}_3$ having the applied pressures from 0 to 113 GPa. On the other hand, the optimized cluster including the lattice relaxation effect was constructed using CASTEP geometry optimization with considering the effect of spin polarization. The pressure from 0 to 120 GPa was applied. The results show that the calculated multiplet energies with considering lattice relaxation, CDC, and CC agree with the experimental data excellently and are consistent with our calculation of Mn^{4+} doped in fluoride crystals. The results also show that when the applied pressure increases, the U- and Y-band energies increase whereas the R-line energy decreases. Furthermore, an interesting result has also been found in this study. The detailed analysis show that the electron-electron repulsion decreased due to the significant increase of the electron correlation effect in spite of the contraction of the molecular orbitals which indicates that the decrease of the Coulomb repulsion is not necessarily due to the expansion of molecular orbitals as explained by the ordinary Nephelauxetic effect.