Effect of Mn Doping on the Electronic Structure of $ZnGa_2O_4$ with Spinel-Type Structure

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The electronic structures of $ZnGa_2O_4$ and $ZnGa_2O_4$:Mn are calculated by the discrete variational Xα method on model clusters. For $ZnGa_2O_4$, it is found that Zn–O and Ga–O bondings are not perfectly ionic but partially covalent. When a central Zn atom of the cluster is replaced with a Mn atom, the new energy states originating from Mn 3d orbitals appear in the energy gap. The energy levels of t_2 up-spin states and e down-spin states seem to relate to the green emission.

X-ray or γ-ray irradiated alkali halides are well known to be mechanoluminescence (ML) materials, i.e. they exhibit a light emission by a mechanical stress.[1] The ML for alkali halides is supposed to arise from the recombination process in the F- and V-centers created by X-ray or γ-ray irradiation. Recently, we have researched new UV-irradiated spinel oxides as $ZnGa_2O_4$: Mn and $MgGa_2O_4$: Mn, in which the strong ML and the long-lasting phosphorescence (LLP) were observed on both spinels.[2] The mechanism is also discussed; doped Mn^{2+} ions locate at the tetrahedral sites of Zn^{2+} and Mg^{2+} ions and can act as a luminescence center. This phenomenon is considered to result from a fundamental change of the electronic structure of the host compound by doping Mn^{2+} ion. Therefore, theoretical information about the effect of Mn^{2+} doping on the electronic structure is indispensable from the standpoint of quantum theory. In this paper, we performed first principles molecular orbital (MO) calculations by the discrete variational (DV) Xα method[3] and elucidated the difference of the electronic structures between the $ZnGa_2O_4$ crystal and its Mn-doped variant.

$ZnGa_2O_4$ crystallizes into the normal spinel-type structure whose space group is $Fd3m$ (O^7_h). The lattice constant a used is 0.833 nm and the parameter u is 0.387.[4] Oxygen ions form a face-centered cubic close packed arrangement in a crystal. Zinc ions occupy one eighth of the tetrahedral sites, gallium occupying one half of the octahedral sites. A cluster model composed of 149 atoms $[Zn_{17}Ga_{28}O_{104}]^{90-}$ was used in the MO calculation by the non-relativistic DV-Xα method.[3] The electronic structure of the model cluster was self-consistently calculated by using numerical atomic basis functions. The atomic orbitals used are 1s–4p for Zn and Ga, and 1s–2p for O. The cluster was embedded in a Madelung potential generated by point charges outside the cluster. A similar calculation was also performed on $[MnZn_{16}Ga_{28}O_{104}]^{90-}$ cluster for the Mn-doped $ZnGa_2O_4$ crystal, which is obtained by substituting a Mn atom for the central Zn atom. A Mn ion has d^5 configuration and is assumed to be down spinning;[5] therefore, spin was taken into account in the calculation.

Figure 1 shows the total (TDOS) and the partial (PDOS) densities of states, and the overlap population diagrams for

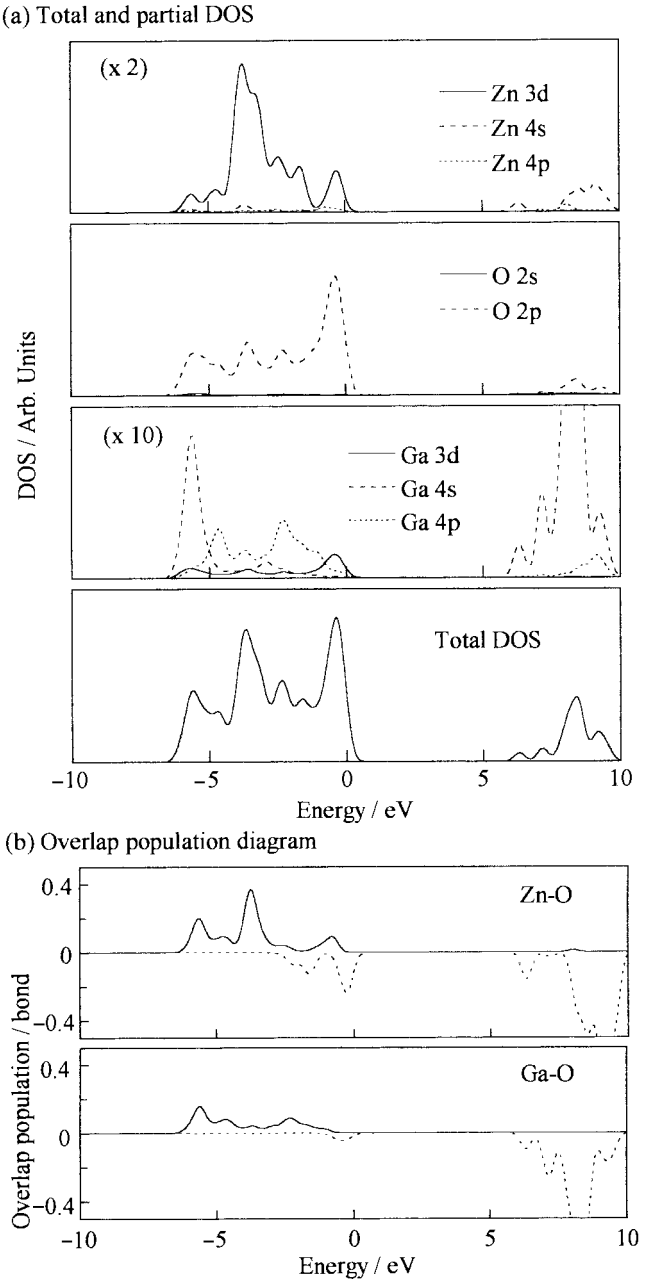

Figure 1. Total and partial DOS, and overlap population diagrams for $[Zn_{17}Ga_{28}O_{104}]^{90-}$ cluster. A solid line shows a bonding contribution and a broken line shows an anti-bonding contribution.

$[Zn_{17}Ga_{28}O_{104}]^{90-}$ cluster. The highest occupied MO (HOMO) is adjusted to zero point on the energy axis. For the DOS, all the curves are made by broadening the discrete energy eigenvalues by Gaussian functions with 0.2 eV full width at half maximum. For the overlap population diagrams, a solid line and a broken line shows a bonding and an anti-bonding contribution, respectively. Each nearest neighbor interaction in the cluster (Zn–O: 0.198 nm, Ga–O: 0.199 nm) was used in the overlap population analysis. The band gap between HOMO and the lowest unoccupied MO (LUMO) is 6.31 eV which seems reasonable as compared with the experimental data (4.4 eV),[6] because the band gap is usually overestimated and gradually approaches the experimental value with increasing cluster size in the cluster calculations.[7] The valence band is mainly constructed from Zn 3d and O 2p orbitals, and slightly from Ga dsp orbitals. In particular, the hybridization of the filled Zn 3d orbitals with O 2p orbitals is noteworthy. Such the DOS curves show a tendency similar to the one obtained by TB-LMTO method.[8] The net charges are +1.27e, –1.18e and +1.74e for Zn, O and Ga, respectively. As the overlap population diagrams indicate, there exist covalent interactions in both the Zn–O and Ga–O diagrams. The bond overlap populations defined as a sum of the overlap population of occupied orbitals are 0.20 for Zn–O and 0.21 for Ga–O.

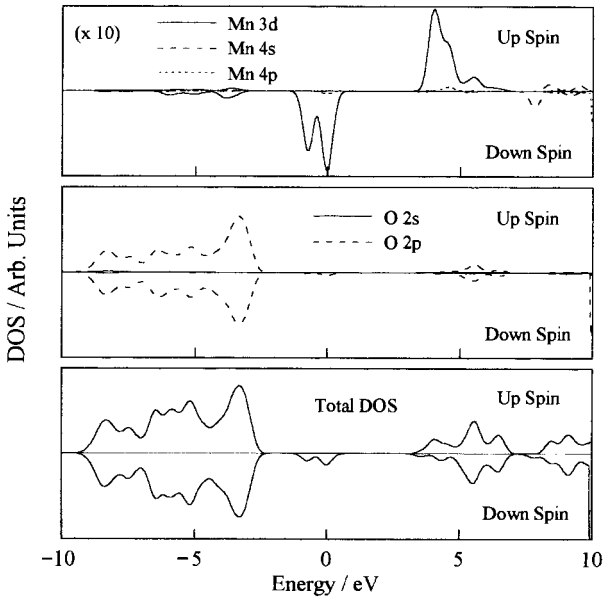

Figure 2. Total and partial DOS for $[MnZn_{16}Ga_{28}O_{104}]^{90-}$ cluster.

Figure 2 shows the DOS curves for $[MnZn_{16}Ga_{28}O_{104}]^{90-}$ cluster. Substituting a Mn atom for the central Zn atom, the band gap between HOMO and LUMO decreased to 3.57 eV because the new energy states originating from Mn 3d orbitals appear in the energy gap. The Mn-related gap states correspond to HOMO. The gap states split into doubly degenerate *e* states and triply degenerate t_2 states, as predicted by the ligand field theory.[9] As we noted in the previous paper, the green emission is ascribed to the optical transition from $^4T_1(^4G)$ to $^6A_1(^6S)$ levels of Mn ions that locate at the tetrahedral sites by using Tanabe–Sugano diagram.[2] Therefore, this transition is considered to correspond to a change of the electron configuration from $t_2^4e^1$ to $t_2^3e^2$. In order to theoretically reproduce the experimental results, we performed Slater's transition state

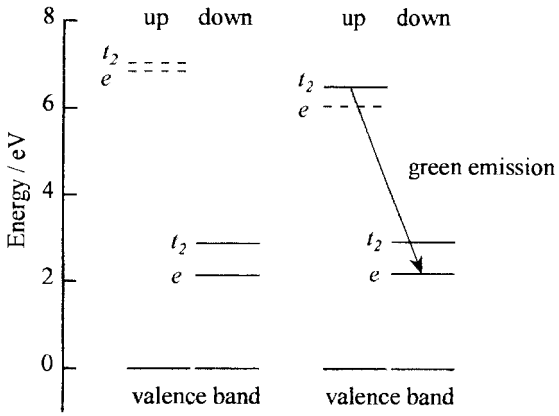

Figure 3. Schematic energy level diagrams for $[MnZn_{16}Ga_{28}O_{104}]^{90-}$cluster (a) at the ground state and (b) at the transition state. A solid line shows an occupied orbital and a broken line shows an unoccupied orbital.

method for $[MnZn_{16}Ga_{28}O_{104}]^{90-}$ cluster, where a half-filled electron of Mn ion is removed from the occupied *e* down-spin states to the unoccupied t_2 up-spin states.[10] Figure 3 shows the schematic energy level diagrams for the transition state, together with the ground state for comparison, where the top of the valence band is adjusted to zero point. A solid line shows an occupied orbital and a broken line shows an unoccupied orbital. The occupied t_2 up-spin states appear near the bottom of the conduction band and the unoccupied *e* up-spin states just below the t_2 up-spin states at the transition state. The energy levels of t_2 up-spin states and *e* down-spin states seem to relate to the green emission, because the sign of the spin becomes reverse accompanied by optical transition. As the result, the calculated energy difference between these levels is 4.29 eV, which is 1.83 eV larger than the experimental value (2.46 eV). The result is satisfactory enough in the framework of DV-Xα method, because the energy gap of $[Zn_{17}Ga_{28}O_{104}]^{90-}$ cluster also tends to be overestimated as mentioned above.

References and Notes

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