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Thermal Stabilities, Electronic Structures and Optical Properties of Intrinsic Defects and Dopant Cerium in $Ca_4F_2Si_2O_7$

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The thermal stabilities, electronic structures and optical properties of intrinsic defects and dopant Ce^{3+} in $Ca_4F_2Si_2O_7$ host are studied by using density functional theory (DFT) calculations (with PBE and hybrid PBE0 functionals) and wave function-based embedded cluster *ab-initio* calculations (at the CASSCF/CASPT2/RASSI−SO level). The calculated formation energies reveal that anion vacancies (V_O and V_F) are always much more energetically favorable than cation vacancies (V_{Ca} and V_{Si}) in $Ca_4F_2Si_2O_7$ host, which is generally prepared under reducing atmospheres. According to the thermodynamic transition energy levels of intrinsic defects readily generated in undoped $Ca_4F_2Si_2O_7$ (e.g. anion vacancies and antisite defects), we may identify the defect-induced host absorption and emission, whose exact origins are unclear previously. Moreover, on the basis of *ab-initio* calculated energies and relative oscillator strengths of the 4f→5d transitions of Ce^{3+} at calcium sites with charge-compensating defect O_F in their local environments, the excitation bands in the experimental spectra of Ce^{3+}-doped $Ca_4F_2Si_2O_7$ phosphors are also assigned. The main purpose of this work is to understand luminescence mechanisms of intrinsic defects and extrinsic dopants in the hosts for phosphors by using first-principles approaches.

Keywords: Thermal stabilities; Intrinsic defects; 4f→5d transitions; Ce^{3+}; First-principles; Phosphors

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