

First-Principles Calculations of 4f-5d transition Spectra for Ce³⁺ in Silicate Garnets

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1. Introduction

In order to clarify the electronic origin of the centroid shift of 4f-5d transition energy of Ce³⁺ in garnets, we have recently performed first-principles electronic-state calculations based on the relativistic DV-X α molecular orbital method. The calculated 4f-5d transition energies were consistent with the experimental values and the results indicated that there is a significant correlation between the centroid shift and the charge transfer from O²⁻ to Ce³⁺ [1].

On the other hand, silicate garnets doped with Ce³⁺ such as Ca₃Sc₂Si₃O₁₂ (CSSO): Ce³⁺ [2] are also important materials due to their applications as phosphors used in white LED devices.

In this work, we have performed first-principles calculations of Ce³⁺ in silicate garnets such as Ca₃Sc₂Si₃O₁₂ (CSSO), Ca₃Al₂Si₃O₁₂ (CASO), Ca₃Cr₂Si₃O₁₂ (CCSO), Ca₃Mn₂Si₃O₁₂ (CMSO), Ca₃Fe₂Si₃O₁₂ (CISO), and Ca₃In₂Si₃O₁₂ (CInSO) and investigated the structure-property relationship of these materials.

2. Computational method

Molecular orbital calculations were performed based on the relativistic discrete variational-X α (DV-X α) method [3]. The relativistic Vosko-Wilk-Nusair (RVWN) potential was used as the exchange-correlation potential. We constructed CeO₈ cluster models based on the crystal structures of the host crystals, assuming that Ce substitutes for Ca. The effective Madelung potential was produced by locating several thousand point charges at the atomic sites outside the cluster. The effect of the lattice relaxation was considered by changing the Ce-O bond lengths based on the difference in the Shannon's crystal radii of Ca²⁺ and Ce³⁺.

3. Results and discussion

Figure 1 shows the calculated absorption spectra. The results show that the peak position shifts toward the longer wavelength in the order of CSSO, CASO, CCSO, CMSO, CISO, CInSO. According to the comparison between the theoretical absorption spectrum and the experimental excitation spectrum reported by Shimomura et al.[2], the theoretical peak

energy is overestimated by ca. 0.5 eV. However, we expect that the systematic variation is qualitatively predicted. The effects of covalency and charge-transfer on the centroid shift of the 4f-5d transitions were also investigated in detail.

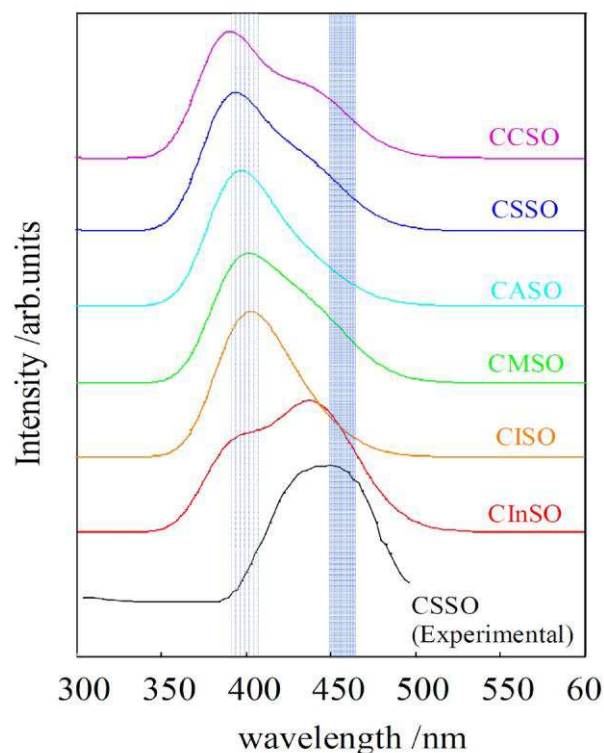


Fig. 1. Theoretical absorption spectra of Ce³⁺ in Ca₃Sc₂Si₃O₁₂ (CSSO), Ca₃Al₂Si₃O₁₂ (CASO), Ca₃Cr₂Si₃O₁₂ (CCSO), Ca₃Mn₂Si₃O₁₂ (CMSO), Ca₃Fe₂Si₃O₁₂ (CISO), and Ca₃In₂Si₃O₁₂ (CInSO) and the experimental excitation spectrum of Ca₃Sc₂Si₃O₁₂ (CSSO) reported by Shimomura [2].

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