

Site occupancy of Ce³⁺ in β-Ca₂SiO₄: A combined experimental and ab initio study



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ABSTRACT

Low-temperature photoluminescence properties of the β-Ca_{2(1-x)Ce_xNa_xSiO₄ (x = 0.0005) phosphor synthesized by a solid-state reaction method are investigated with excitation energies in the vacuum ultraviolet (VUV) to ultraviolet (UV) range. Two distinct types of emission and excitation spectra are observed, which are attributed to 4f–5d transitions of two different sets of Ce³⁺ centers. On the basis of density functional theory (DFT) calculations within the supercell model and wave function-based CASSCF/CASPT2 embedded cluster calculations, the two sets of Ce³⁺ centers are ascribed to the Ce³⁺ located on the seven-coordinated Ca1 and eight-coordinated Ca2 sites, respectively. Furthermore, from the observed relative spectral intensities, DFT total energy calculations, and comparison of experimental and calculated 4f → 5d transition energies, it is concluded that the occupation of Ce³⁺ on the Ca2 site is more energetically favorable than the occupation on the Ca1 site. Finally, the redshift of the lowest 4f → 5d transition of Ce³⁺ on the Ca2 site relative to that on the Ca1 site is discussed in terms of the changes of the 5d centroid energy and crystal-field splitting with the local coordination structure.}

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1. Introduction

Photoluminescence properties of cerium-doped silicate compounds have been widely studied for applications in solid-state lighting and field-emission displays, due to their good thermal and chemical stabilities and suitable wavelengths of light emissions in the visible spectral region [1–6]. The light emission originates from the spin- and parity-allowed 5d → 4f transition of Ce³⁺ with a radiative lifetime of several tens of nanoseconds. The energy positions of excited 5d levels relative to the ground 4f level depend strongly on the chemical composition and geometric structure of the local environment around Ce³⁺ because of the large crystal-field interaction of the 5d electron with its surroundings. Empirical trends have been established for the dependence of the first 4f → 5d transition energy of Ce³⁺ on its local environment from two independent aspects of 5d centroid shift and crystal-field splitting [7].

Recently, great interest has been shown in the Ce-doped alkaline earth orthosilicate, Ca₂SiO₄, for its potential applications as phosphors in white light emitting diodes (LEDs) [8–10]. At room

temperature, the undoped Ca₂SiO₄ stabilizes in the γ-phase, having an orthorhombic olivine structure with the space group Pbnm (No. 62) [11]. When doped with Ce³⁺, the compound exhibits intense yellow emission upon excitation by blue light [8,9]. There is also a metastable β-phase of Ca₂SiO₄ at room temperature, which crystallizes in monoclinic symmetry with the space group P2₁/n (No. 14) [12], and can be stabilized by addition of various dopants [9,13]. The Ce-doped β-Ca₂SiO₄ displays intense blue emission upon near-UV excitations [9,10]. Two crystallographically different Ca sites exist in β-Ca₂SiO₄ with coordinations of seven and eight oxygens, denoted by Ca1 and Ca2 sites, respectively (see Fig. 1a). In view of the similar ionic radii of Ce³⁺ and Ca²⁺, the dopant Ce³⁺ are most likely to be located on Ca sites, and thus two sets of Ce³⁺ centers are expected. However, only one type of Ce³⁺ 5d emission spectrum was observed under excitation with different wavelengths at room temperature [10]. It is thus possible that only one set of Ce³⁺ centers exists in β-Ca₂SiO₄, or both two sets of Ce³⁺ centers were present but the difference between their emission spectra was masked by the temperature-induced band broadening.

In the present work, we extend previous measurements of emission and excitation spectra of Ce-doped β-Ca₂SiO₄ by using VUV–UV excitations with synchrotron radiation at a low temperature of 77 K. DFT calculations within the supercell model are performed to optimize the local structures of Ce³⁺ located on the

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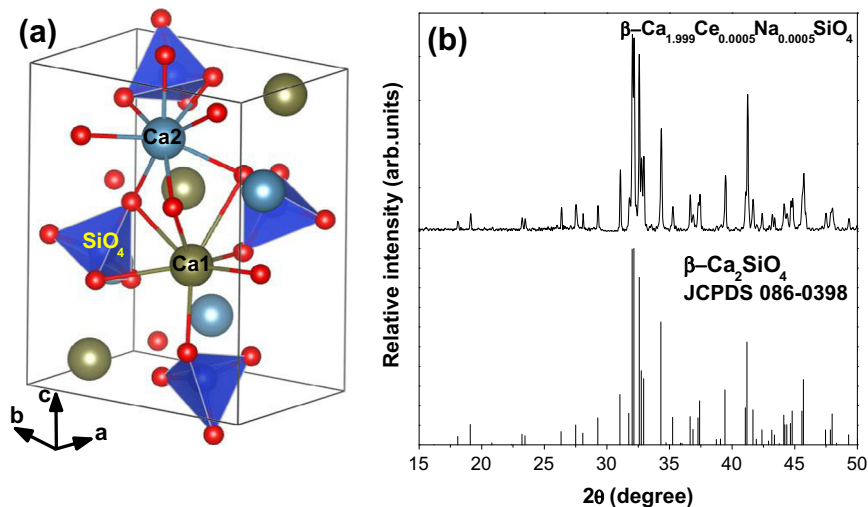


Fig. 1. (a) A schematic representation of the geometric structure of the β - Ca_2SiO_4 unit cell. (b) The XRD pattern of the sample $\beta\text{-Ca}_{2(1-x)}\text{Ce}_x\text{Na}_{0.0005}\text{SiO}_4$ ($x = 0.0005$) at room temperature along with the standard pattern (JCPDS 086-0398) of $\beta\text{-Ca}_2\text{SiO}_4$ for comparison.

Ca1 and Ca2 sites. On the basis of these local structures, wave function-based CASSCF/CASPT2 calculations within the embedded cluster model are then carried out to derive the $4f^1$ and $5d^1$ energy levels of Ce^{3+} on the two Ca sites. By comparing the calculated DFT total energies for the $\text{Ce}_{\text{Ca}1}$ - and $\text{Ce}_{\text{Ca}2}$ -doped supercells and the calculated and experimental $4f \rightarrow 5d$ transition energies, the site occupancy of Ce^{3+} in $\beta\text{-Ca}_2\text{SiO}_4$ is discussed in association with the local coordination structure.

2. Methodology

2.1. Experimental details

Power samples of Ce-doped $\beta\text{-Ca}_2\text{SiO}_4$ were synthesized by the solid-state reaction technique. The reactants included analytical reagents Ca_2CO_3 , SiO_2 , Na_2CO_3 , and 99.99% purity CeO_2 , among which Na_2CO_3 was to introduce Na_{Sr} point defects to compensate for the excess charge of Ce^{3+} on the Ca^{2+} site. Stoichiometric amounts of the starting materials were homogenized in an agate mortar, and then pre-fired in air at 800°C for 2 h. After being slowly cooled down to room temperature, the sample was thoroughly reground and sintered at 1220°C for 10 h in a reducing atmosphere (5% H_2 + 95% N_2). The crystal structures of final products were examined by powder X-ray diffraction (XRD) using $\text{Cu K}\alpha$ radiation on a Rigaku D/max 2200 vpc X-ray diffractometer. The VUV-vis excitation and the corresponding emission spectra were measured at the VUV spectroscopy experimental station on beam-line (U4) at the National Synchrotron Radiation Laboratory (Hefei, China).

2.2. Computational details

The Ce-doped $\beta\text{-Ca}_2\text{SiO}_4$ crystal was modeled by a $2 \times 2 \times 1$ supercell containing 112 atoms, in which one of the 32 Ca^{2+} ions was replaced by a Ce^{3+} , corresponding to the chemical formula $\beta\text{-Ca}_{2-x}\text{Ce}_x\text{SiO}_4$ ($x \approx 0.0625$). The lattice parameters and atomic coordinates of the supercells were first optimized by periodic DFT calculations with the pure PBE functional [14,15]. The excess charge of Ce^{3+} on the Ca^{2+} site was compensated by introducing a uniform background charge density, and the spurious Coulomb interaction in charged supercells is expected to be small due to the large size of supercells [16]. The Ca ($3s^2 3p^6 4s^2$), Si ($3s^2 3p^2$), O ($2s^2 2p^4$), and Ce ($5s^2 5p^6 4f^1 5d^1 6s^2$) were treated as valence electrons, and their interactions with the cores were described by

the projected augmented wave (PAW) method [17]. The convergence criteria for total energies and atomic forces were set to 10^{-6} eV and 0.01 eV \AA^{-1} , respectively, with a cutoff energy of 550 eV for the plane wave basis. One k -point Γ was used to sample the Brillouin zone. All DFT calculations were carried out using the Vienna ab initio simulation package (VASP) [18,19].

Based on the DFT-optimized supercell structures, the Ce-centered embedded clusters, $(\text{Ce}_{\text{Ca}1}\text{O}_7\text{Si}_5)^{9+}$ and $(\text{Ce}_{\text{Ca}2}\text{O}_8\text{Si}_6)^{11+}$, were constructed, which contain the central Ce^{3+} , the coordinating O^{2-} ions, and the Si^{4+} ions in the second coordination spheres. Their immediate surroundings within a sphere of radius 10.0 \AA were simulated by 774 and 782 embedding ab initio model potentials (AIMPs) [20] at lattice sites, to account for the electrostatic, exchange, and Pauli interactions of the clusters with their environments. The remainders of the crystalline surroundings were represented by 80,860 and 80,851 point charges at lattice sites, respectively, as generated with Lepetit's method [21]. For the two embedded clusters, the wave function-based CASSCF/CASPT2 calculations were carried out to obtain the $4f^1$ and $5d^1$ energy levels of Ce^{3+} , by using the program MOLCAS [22]. In the CASSCF calculations, a [4f,5d,6s] complete active space was adopted, and in the CASPT2 calculations the dynamic correlation effects of the Ce^{3+} ($5s$, $5p$, $4f$, $5d$), and O^{2-} ($2s$, $2p$) electrons were taken into account. More details on the calculation can be found in Refs. [23,24]. A relativistic effective core potential ([Kr] core) with a (14s10p10d8f3g)/[6s5p6d4f1g] Gaussian valence basis set from Ref. [25] was used for cerium, and a [He] core effective core potential with a (5s6p1d)/[2s4p1d] valence basis set from Ref. [26] was used for oxygen.

3. Results and discussion

3.1. XRD patterns and photoluminescence spectra

The XRD pattern of the synthesized sample $\beta\text{-Ca}_{2(1-x)}\text{Ce}_x\text{Na}_{0.0005}\text{SiO}_4$ ($x = 0.0005$) is shown in Fig. 1b, together with the standard pattern (JCPDS 086-0398) of $\beta\text{-Ca}_2\text{SiO}_4$ as a reference. Comparison of the two patterns shows that the sample under investigation is of single phase and the Ce^{3+} ions are completely dissolved into the host by partially substitution for Ca^{2+} ions. Fig. 2 shows the emission and excitation spectra of $\beta\text{-Ca}_{1.999}\text{Ce}_{0.0005}\text{Na}_{0.0005}\text{SiO}_4$ recorded at 77 K. The emission spectra in Fig. 2a were measured under excitation at 326 and 355 nm,

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