Higher Conductivity and Enhanced Optoelectronic Properties of Chemically Grown Nd-Doped CaSnO₃ Perovskite Oxide Thin Films

Hamza Shaili,* Elmehdi Salmani, Mustapha Beraich, Mustapha Zidane, M’hamed Taibi, Mustapha Rouchdi, Hamid Ez-Zahraouy, Najem Hassanain, and Ahmed Mzerd

ABSTRACT: Stannous-based perovskite oxide materials are regarded as an important class of transparent conductive oxides for various fields of application. Enhancing the properties of such materials and facilitating the synthesis process are considered major challenging aspects for proper device applications. In the present paper, a comprehensive and detailed study of the properties of spray-coated CaSnO₃ thin films onto the Si(100) substrate is reported. In addition, the substrate effect and the incorporation of rare-earth Nd³⁺ on engineering the characteristics of CaSnO₃ thin films annealed at 800 °C are included. X-ray diffraction (XRD) analysis results revealed the orthorhombic structure of all the samples with an expansion of lattice spacing as the substitution of Nd at the Ca site increased. The Raman and FT-IR analysis further confirmed the structural results collected via the XRD analysis. Surface scanning using field-emission scanning electron microscopy revealed the formation of quasi-orthorhombic CaSnO₃ grains with an increase in size as dopant content increased. Energy-dispersive X-ray analysis allowed quantification of the elements, while atomic mapping permitted visualizing their distribution along the surfaces. UV–visible spectroscopy and first-principles calculations using density functional theory (DFT) were conducted, and a thorough investigation of the optical and electronic properties of the pure material upon Nd³⁺ insertion was provided. Electrical properties collected at room temperature revealed a growing conductivity upon doping ratio increase with a simultaneous enhancement in the carrier concentrations and mobility. The findings of the present work will help facilitate the synthesis procedure of large-area stannous-based perovskite oxide thin films through simple and efficient chemical solution methods for optoelectronic device applications.

1. INTRODUCTION

The extensive advancement in energy technologies devices demands the uncovering of novel types of transparent conductive oxides that possess superior functionalities in comparison with conventional and widely used oxides employed in the various fields of applications, particularly, in solar cell devices, LEDs.¹⁻⁴ Despite their good performance, several limitations were attached with their applications, mainly the ones related to the scarcity of the employed elements (indium and gallium in the case of In₂O₃ and Ga₂O₃) and quality degradation. In order to fulfill such a quest, several criteria have to exist in the candidate, mainly the visible light transparency and the controllable conductivity. For that purpose, numerous candidates were the subject of extensive developments in order to find suitable TCOs capable of enhancing the efficiency of optoelectronic devices.

Perovskite oxides have attracted growing technological attention and have been rapidly developed as an emerging type of transparent conductive oxide with an aim of surpassing the performance of conventional oxides. Stannous-based perovskite oxides ASnO₃ (A = Ca, Sr, and Ba) are regarded as promising TCO candidates that attracted a considerable amount of interest to become a nontoxic alternative for their lead-based counterparts. Furthermore, this attractive type of oxides is considered as an important class of materials integrated into a wide range of applications such as in ceramic technology as components of dielectric materials and gas-sensing applications, and also utilized as substrates for superconductor applications, in photocatalysis, and as an electron transport layer in heterojunction perovskite solar cells.⁶

Received: July 29, 2021
Accepted: November 9, 2021
Published: November 23, 2021
To date, numerous reports have indicated the engineering of the properties of alkaline-earth stannate oxide using rare-earth elements as doping agents. Particularly, widespread attention was directed toward the development of La-doped SrSnO₃ with several device applications, especially in solar cell applications, mainly as electrodes for photostable perovskite solar cells. Nonetheless, several factors are causing a major holdback for the practical device integration of such oxides including the complex synthesis process, the very high crystallization temperature, and the non-cost-effective fabrication procedure. Several works considered other types of rare-earth elements for doping, especially neodymium which is known to be very effective in engineering the properties of several perovskite oxide materials. Liu et al. reported the Nb and Nd doping effect on the SrSnO₃ thin films epitaxially grown on SrTiO₃ (001) substrates by pulsed laser deposition with enhanced optical and electrical properties. The common thing about the previously mentioned works is the complex synthesis route and the sophisticated substrates employed. In this paper, the emphasis will be on the stannous-based CaSnO₃ oxide that is composed of earth-abundant elements with attractive optical and electrical properties. Even that the CaSnO₃ oxide is a quite attractive material yet the papers reporting the exploration and engineering of its properties are very much scarce, particularly in the thin-film form. Generally, the synthesis procedure conducted in the fabrication of CaSnO₃ thin films employed physical methods, including pulsed laser deposition and radio frequency magnetron sputtering. A limited number of reports employed chemical methods using, for example, the polymeric precursor method which is not an industrially preferred deposition method. To the best of our knowledge, no reports indicated the synthesis of high-quality CaSnO₃ thin films using the chemical spray coating method. Therefore, in the present report, a simpler approach is composed of employing a simple chemical synthesis of such material in the thin-film form deposited on a conductive substrate [Si(100) substrate in our case] and evaluating its effect on the quality of the as-synthesis samples. Also, the calcination procedure was performed at a relatively low temperature (800 °C) in comparison with previous reports. In addition, a doping process was applied to engineer the properties of the CaSnO₃ thin films using the rare-earth element (neodymium Nd). Several characterization analyses were carried out to identify the insertion effect of Nd³⁺ ions into CaSnO₃ lattice with a particular interest in the optical and electrical properties. Furthermore, a computational part is included to strengthen the experimental findings by performing first-principles calculations based on the density functional theory. The theoretical part will allow the identification of the doping effect on the electronic properties and its eventual effect on the overall properties.

2. EXPERIMENTAL DETAILS

2.1. Chemicals. Calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O) (molecular weight 236.15 g·mol⁻¹ and purity 99.0%), tin(IV) chloride pentahydrate (SnCl₂·5H₂O) (molecular weight 350.60 g·mol⁻¹ and purity 98%), neodymium(III) nitrate hexahydrate (Nd(NO₃)₃·6H₂O) (molecular weight 330.25 g·mol⁻¹ and purity 99.9%), and hydrochloric acid (HCl) (37%) were used. All chemicals were purchased from Sigma-Aldrich and used as received without further purification.

2.2. Solution Preparation and Thin-Film Synthesis. In a typical synthesis process, a series of homogeneous aqueous solutions were prepared by mixing (0.02 M) calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O) and (0.02 M) tin(IV) chloride pentahydrate (SnCl₂·5H₂O) with the addition of various fractions of neodymium nitrate (Nd(NO₃)₃·6H₂O) (3 and 5 atom %) in 25 mL of distilled water at room temperature. A few drops of hydrochloric acid (HCl) were added, and the mixtures were kept under vigorous magnetic stirring at 60 °C for 1 h, resulting in very clear solutions. The solutions were transferred to the deposition chamber equipped with the ultrasonic spray setup (SONAER-Ultrasonics) set at a frequency of 130 kHz and an applied power of 2.8 W. The selected substrates were the silicon wafer Si(100) with dimensions of 1–1.5 cm. The substrates were ultrasonically cleaned with distilled water, ethanol, and acetone consecutively for 15 min and finally dried in an air stream. The solution flow rate was fixed at 0.9 mL/min and compressed air was used as a carrier gas. The substrates were placed horizontally on the surface of the hot plate with a distance of 12 cm below the spray nozzle. The hot plate is initially heated in a slow rate to reach 250 °C controlled temperature using a thermocouple. Multiple attempts were performed to reach optimal temperature conditions. Finally, the prepared films were placed in a furnace and calcined in air at 700, 750, and 800 °C for 2 h with a step of 15 °C/min to reach the correct phase, and the best results were obtained at 800 °C.

2.3. Characterization. 2.3.1. Structure Analysis. Structural and phase identification were performed by X-ray diffraction (XRD) on the as-synthesized oxide thin films and after the calcination process. The XRD scan was recorded using a Bruker D8 Discover Advanced diffractometer with Cu Kα radiation at a wavelength of λ = 0.154056 nm. The sample stage was rotated at 15 rpm. The spectra were taken for a duration of 2 h. The values of 2θ varied in the range of 15–70° with a step of 0.008° and an integration time of 0.25 s.

2.3.2. Scanning Electron Microscopy. Surface quality and compositional analysis were performed to scan the morphology of the resulted surfaces and to measure the percentage of each element using field emission scanning electron microscopy (FE-SEM, Quattro S FEI), alongside with an energy-dispersive X-ray spectrometer from Hitachi with a 15 kV accelerating voltage. Atomic mapping was also performed to quantify the distribution of each element on the film surfaces.

2.3.3. Raman Measurements. Vibrational modes were recorded at room temperature using a Raman spectrometer microscope (DXR2, Thermo Scientific) with a laser excitation wavelength of 633 nm. The measurements were collected from 100 to 800 cm⁻¹.

2.3.4. FT-IR Measurements. The transparency of the films was collected by Fourier transform-infrared spectroscopy (FT-IR) [FT/IR-4600 (FTIR-ART); JASCO] spectra recorded in a range of 400–2000 cm⁻¹ at room temperature.

2.3.5. UV–Vis Spectroscopy. Optical properties were investigated by absorbance measurement using a UV–vis spectrophotometer (Lambda 900 UV/VIS/NIR spectrophotometer) with a wavelength ranging from 200 to 1200 nm recorded in the absorption mode.

2.3.6. Hall Effect Measurement. Electrical properties of the films were measured using an ECOPIA Hall effect measure-
ment in the van der Pauw configuration collected at room temperature and in the presence of the magnetic field.

3. COMPUTATIONAL METHODS

The ab initio calculations were carried out by density functional theory using the Korringa–Kohn–Rostoker (KKR) with the coherent potential approximation (CPA), which only uses the unit cell for the calculation of physical properties of pure and doped CaSnO₃ materials by different concentrations of Nd. The extremely correlated 4f-related electronic states of Nd were modulated by the self-interaction correction (SIC) approach developed by Toyoda. The SIC approach is utilized to obtain a more realistic description of the disordered local moments of the material under investigation as indicated before. For the parameterization of the exchanged energy, local density approximation (LDA) is employed in which SIC is included in the KKR-CPA–SIC–LDA package as implemented into MACHIKANEYAMAKO2002. A total of 500 K-points in the whole first Brillouin zone were taken into account and the scalar relativistic approximation is incorporated as well. The SIC-LDA approximation allows the calculation to be more precise than the conventional LDA approximation, resulting in an amelioration of the photoemission spectra. For the doping calculations, a fraction of Ca atoms is replaced by Nd atoms randomly, and the same fractions of the experimental part were used. The electronic valence configurations for each element were Ca-3s² 3p⁶ 4s², Sn-4d¹⁰ 5s² 5p², O-2s² 2p⁴, and Nd-4f⁴ 6s². The total energy minimization was performed using the appropriate unit cell of an orthorhombic lattice with the (Pbnm) space group. In current calculations, we fixed the parameters v and b/a which are determined by the geometry. The internal parameters u and c/a ratio were obtained by the energy minimization for the pure CaSnO₃ compound and were fixed for CaₓNdₓSnO₃ alloys. All calculations were performed at T = 0 K from the total energy fitted to the Murnaghan equation. Lattice vibrations, finite temperature effects, and relativistic corrections were not considered in the current work. The electronic and optical properties of the pure and Nd-doped CaSnO₃ were calculated in a stable orthorhombic structure which also conforms to the Pbnm space group, as shown in Figure 1.

4. RESULTS AND DISCUSSION

Structural analysis is a fundamental step to inspect the quality of the resulted phase and to observe whether the synthesis route followed in the present work is effective in producing high-quality CaSnO₃ films. Consequently, considerable attention was given to the structural analysis of our films alongside observing if the substrate type affects the phase quality, as well as the doping ratios. Figure 2 presents the XRD patterns of the pure and Nd-doped CaSnO₃ films deposited on the Si(100) substrate and annealed at 800 °C. The spectrum shows that all the films have a polycrystalline nature with the main phase peaks located at 22.35, 32.01, and 45.73° associated to the (hkl) planes of (020), (121), and (040), respectively. The peaks are corresponded to the orthorhombic (Pbnm) structure of CaSnO₃ matching correctly to the standard ICDD data (no: 77-1797). One minor peak related to the SnO₂ impurity was detected, alongside two strong peaks related to the Si(100) substrates. No peaks related to Nd impurities were detected. Nonetheless, the simple procedure followed in the present work allowed the growth of high-quality films. This proves that chemical methods as simple as spray-coating can be utilized as an efficient route to grow CaSnO₃ films. The results emphasize the fact that the type of substrates employed has no significant effect on the quality of the phase. A preferential orientation along the (121) plane for the pristine sample was observed. In terms of doping effect on the structural properties of the undoped film, the same peaks were found attached as always with the peaks attributed to the silicon wafer. Also, the crystal preferential orientation is not altered after Nd incorporation. The quality of the patterns and the intensity of the peaks were also affected by the doping, where a slight decrease in the intensity of the peaks was noticed which may be due to the internal defects and strain induced by the incorporation of the Nd³⁺ ions into the pristine lattice. In addition, several minor peaks corresponded to the phase partially faded, while the main ones got slightly less intense, and the background noise got less intense as the doping ratios increased. A slight shifting
was observed indicating that the crystallographic positions of Ca$^{2+}$ ions have been occupied by Nd$^{3+}$ successfully in the CaSnO$_3$ host lattice and strain developed in the lattice. Determining the lattice parameters will permit observing the crystallographic defects on the pristine structure generated by the influence of the doping fraction insertion, especially on the lattice parameter distortion. This information can only be obtained by calculating the crystallographic parameters of the structure employing the following equation for the orthorhombic crystal lattice

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (1)$$

The calculated lattice parameters as a function of dopant content are illustrated in Figure 3. The values for the pristine sample are matching with previously reported results for the CaSnO$_3$ structure. It can be clearly observed in Figure 3a that the substitution of Ca$^{2+}$ by the Nd$^{3+}$ in the CaSnO$_3$ pristine structure causes an expansion along all the axes. The lattice parameters (a, b, and c) show the same trend where the lattice constants increased upon Nd addition. This intense increase may be attributed to numerous factors such as the concentration of dopant, defects (vacancies, interstitial, and dislocation), external strains developed due to calcination temperature, and the difference between the ionic radii of Nd$^{3+}$ (1.27 Å) compared to Ca$^{2+}$ (1.34 Å). According to these values, the structure must be compressed, but the experimental values show the opposite, this may be due to the substitution of Sn$^{4+}$ by Ca$^{2+}$ (coordination = 6) [$r$(Sn$^{4+}$) = 0.69 Å and $r$(Ca$^{2+}$) = 1.00 Å], this substitution allows a balance of charges. The structure remains orthorhombic and is not tailored by the addition of different amounts of neodymium into the CaSnO$_3$ lattice. The crystalline size was calculated using the Debye–Scherrer’s formula

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (2)$$

where $\beta$ is the observed angular width at half-maximum intensity (fwhm) of the corresponded peak, $\lambda$ is the X-ray wavelength (0.15406 nm for Cu$K\alpha$), and $\theta$ is Bragg’s angle.
Figure 3b illustrates the variation of the fwhm and the grain size as a function of the dopant content. The fwhm of the (020) reflection is becoming narrower as the dopant fraction increases, leading to an augmentation of the crystallite size in the various samples. This variation indicates that the doped thin films comprised crystallites of different sizes and possess higher crystallinity as the doping ratio is increased. Another noteworthy observation is the augmentation in the crystallite size showing a reversed trend from the fwhm. This increase will have a significant impact on the optoelectronic properties of the films mostly on the carrier mobility.

Studying the vibrational behavior of our material is crucial to further emphasize the phase purity of the prepared films and to observe the dopant insertion effect on the vibrational behavior of the pristine structure. The Raman examination will allow determining the local crystal structures and modifications in cation ordering of the pure and Nd-doped CaSnO3. Therefore, employing Raman analysis will provide an accurate analysis of the resulted structure and better detection of the secondary phases present in the resulted compounds and defects generated from doping impurity insertion. The Raman spectra were collected at room temperature from 100 to 800 cm\(^{-1}\), as shown in Figure 4. According to previous extensive experimental and theoretical analysis, the orthorhombic phase of CaSnO3 has 24 active modes reported as follows\(^{25}\)

\[
\Gamma_{\text{Raman}} = 7A_g + 5B_{1g} + 7B_{2g} + 5B_{3g}
\]

with four antisymmetric and two symmetric octahedral stretching modes, four bending modes, and six octahedral rotation or tilt modes. The remaining eight modes are associated with the calcium cations. Three major bands observed from the Raman spectra located at 185, 281, and 358 cm\(^{-1}\) are all assigned to the Ag symmetry. Additionally, multiple weak signals were detected at 445, 634, and 705 cm\(^{-1}\) that could be attributed to A\(_g\) and B\(_{1g}\) symmetries, respectively. The Raman results for the undoped sample match correctly with previous analysis of the materials in the bulk or thin-film form. One can observe that as the dopant fractions were inserted, a slight shifting was observed particularly, for the main modes. The Ag active mode for the doped samples has a slight shift toward a higher wavenumber (289 cm\(^{-1}\)) when compared to the undoped film (281 cm\(^{-1}\)). This reveals that the Nd\(^{3+}\) cations effectively inserted the Ca\(^{2+}\) sites and consequently impacting the Ca–O bonds. No change in modes was observed. Thus, the doping process has no effect on tailoring the structural properties of the pure sample. Moreover, a slight decrease in the mode intensities was observed with a slight fading of the smaller modes. The Raman analysis further confirmed the formation of the orthorhombic CaSnO3 (Pbnm) compound with high crystallinity.

To further investigate the vibrational behavior of the material under investigation, the FTIR analysis was conducted at room temperature. The FT-IR analysis results of the films with different concentrations of neodymium recorded within the region of 400–2000 cm\(^{-1}\) are shown in Figure 5.

Commonly, the orthorhombic phase of CaSnO3 with the Pbnm space group has 25 IR active modes at \(\Gamma\) of the Brillouin zone,\(^{26}\) given by the irreducible representations

\[
\Gamma_{\text{IR}} = 9B_{1u} + 7B_{2u} + 9B_{3u}
\]

The bands between 1412 and 871 cm\(^{-1}\) in the samples are assigned to C–CH\(_3\) and C=C carbonate vibrations, respectively. After the first doping percentage, the bands partially decreased in the 3% sample and kept on fading as the doping content increased. The band located at 675 cm\(^{-1}\) may be attached to Sn–O–Sn antisymmetric vibrations.\(^{27}\) Furthermore, two intense bands located at 507 and 423 cm\(^{-1}\) represent the characteristics of Ca–O and Sn–O stretching vibrations, respectively.\(^{28,29}\) Several minor peaks detected between 400 and 600 cm\(^{-1}\) are assigned to the metal–oxygen (Nd\(^{3+}\)–O) vibrations at the octahedral sites, indicating once again the effective insertion of Nd\(^{3+}\) into the CaSnO3 lattice. The data from FT-IR analysis are in consistent with previous reports showing the correlation of the obtained results with the literature.

Investigating the morphological properties of the pristine and doped films is crucially significant in determining the anticipated device construction and composition of the films for the optoelectronic devices. Thus, a full thorough scanning of the surface quality was examined by means of FE-SEM alongside the energy dispersive spectroscopy (EDX) to evaluate the modifications induced by Nd doping on the quality, grain size, and composition of the films. Figure 6
of the di percentage, an increase in the grain size was noticed as a result of the formation of high-density quasi-orthorhombic-shaped substrate. In addition, the micrographs in Figure 6a show a homogeneous surface with equal distribution along the CaSnO3 lattice which can have an immense effect on the structural and morphological results. For 3% of Nd content, the thicknesses of the films were measured at an average of 200 nm. The distribution and homogeneity of the elements on the deposited films strongly impact the construction and efficiency of optoelectronic devices. Therefore, EDX analysis and atomic mapping were performed to inspect the compositional elements of the prepared samples and the distribution of the elements along the prepared surfaces. Figure 7a shows the EDX spectrum collected for a doped sample. The data confirm the presence of sufficient quantities of the main elements (Ca, Sn, and O), indicating the high purity and near-stoichiometric nature of the samples with rich oxygen content as presented in Table 1. As expected, a strong Si signal is detected from the Si(100) substrate as a result of the difference between the thicknesses of the films and the high EDX interaction volume and penetration depth of the electron beam. This may slightly reduce the accuracy of the EDX quantitative analysis. The Al signal is attributed to the sample holder during the analysis. In addition, the presence of the dopant element Nd was confirmed by the analysis in the doped films with the variant ratios added. Furthermore, the elemental atomic mapping was implemented to observe the distribution and to quantify each component with high precision. The mapping images manifest the presence of the main elements with the near stoichiometric distribution along the surfaces of films. In addition, the images show an orderly repartition of the elements with a higher concentration for the oxygen element and a small portion of Nd element.

The optical properties of the films were probed mainly to inspect the absorption of the pristine film alongside observing the Nd3+ insertion effect on improving its absorption and tuning the band gap to a certain level convenient for optoelectronic applications. For that purpose, the UV–vis absorption spectra of the pure and Nd-doped CaSnO3 thin films are illustrated in Figure 8a. All the films exhibit strong absorption in the UV light region (200–400 nm), with a prominent decrease in the visible region and kept on decreasing exponentially as the wavelength increases in the near-infrared (NIR) region. It is noticeable that the absorption edge of the doped films is shifted toward higher wavelengths especially for the 5% Nd-doped CaSnO3 film. Moreover, the dopant fraction insertion caused the absorption to decrease in the UV light region and increased in the visible region and onward, showing a reverse trend from the undoped film. The results manifest the effect of Nd3+ insertion on tuning the optical properties of metal oxide materials which was reported before.15 It is clearly seen that the doping process enhanced the photon absorption ability of the films in the visible and NIR region, which is quite suitable for optoelectronic applications. In order to observe the doping effect on the engineering band gap of the samples, the band gap of the pristine and Nd-doped CaSnO3 was calculated using the Tauc plot

\[(ah\nu) = A(h\nu - E_g)^n\]  \(5\)

where A is a constant, h is Planck’s constant, and h\nu is the incident photon energy, while n is a number related to the electronic transition nature between the conduction and valence bands of the material. The number n can have various values which are 1/2, 2, 3/2, and 3 for allowed direct, allowed indirect, forbidden direct, and forbidden indirect transitions, respectively. Previous extensive experimental and theoretical works indicated that CaSnO3 is a directed band semiconductor,30 meaning that in our case, n = 1/2. The optical band gap was determined by extrapolating the linear part of the (ah\nu)^n versus h\nu curve to the energy axis, when (ah\nu)^2 = 0 as plotted in Figure 8b. The band gap for the pure sample was estimated at 3.73 eV, in consistent with previous works reporting the preparation of CaSnO3 thin films corresponding to the orthorhombic phase. The band gap values versus Nd doping ratios are plotted in Figure 8c. As mentioned before in the absorption part, the band gap decreased as the first percentage was added and stabilized at 2.91 eV for 5% of Nd content. The collected results emphasize the effect of neodymium on improving the optical absorption of the prepared samples by enhancing their absorption behavior and tuning the band gap which authenticates the results collected from the XRD and FE-SEM analysis regarding the grain size augmentation and quality enhancement of the films.

First-principles calculations are regarded as a sophisticated computational tool that allows the possibility to inspect the properties of the materials under controlled conditions, which provides an initial expectation of their properties and the impurity integration effect and alterations that may occur on the material experimentally, especially in the case of doping. It also allows the inspection of the nature of the bonds formed
between the different elements and to investigate the electronic properties and the effect of neodymium incorporation on the CaSnO₃ pristine lattice. In the present work, the calculations are performed to observe the effect of the strongly correlated 4f state (in our case, neodymium Nd) on the electronic and optical properties of the CaSnO₃ perovskite compound. Hence, the results from first-principles calculations are considered as a powerful way to strengthen the experimental findings. Figure 9 presents the projectile and total density of states of the pure and Nd-doped CaSnO₃ compound calculated using LDA and SIC-LDA approximations. For the dos generated by regular LDA, it is observable that the conduction band minima (CBM) of CaSnO₃ is composed essentially of Ca-3d states and a nearly negligible contribution from O-2p, while the valence band maxima (VBM) is largely dominated by the O-2p states. The calculated band gap was estimated at 2.04 eV. Regular LDA approximation usually tends to underestimate the optical and electronic properties of the material under investigation, leading to the nonconsideration of the exchange and the correlation effects in metal oxide materials causing important self-interaction errors. The underestimation of the band gap by LDA is due to the lack of a discontinuity in this exchange−correlation potential. Therefore, SIC was included to increase the accuracy of the obtained values. Generally, LDA-SIC approximation is viewed as an

---

**Table 1. Atomic Concentrations of the Different Ca₁₋ₓNdₓSnO₃ Samples Obtained by EDX Analysis**

| samples         | atomic percentages |  
|-----------------|--------------------|
|                 | Ca | Sn | O  | Nd |
| CaSnO₃          | 23.55 | 23.79 | 52.66 | 0  |
| CaSnO₃/Nd³⁺ (3%)| 23.34 | 23.71 | 52.08 | 0.87|
| CaSnO₃/Nd³⁺ (5%)| 23.27 | 23.58 | 51.83 | 1.32|

---

**Figure 7.** (a) EDX analysis and (b) atomic mapping (Ca, Sn, O, and Nd) images of Nd-doped CaSnO₃ thin films.
extension of LDA, the Kohn–Sham wave function is projected onto a set of localized basis orbitals and the SIC approximation is governed by the energy difference between the energy gain due to hybridization of the orbital with the valence band and the energy gain upon localization of the orbital.32 After the SIC, the band gap opened up and increased to 2.85 eV as anticipated. Commonly, doping a semiconductor obligates the Fermi level to shift toward higher energy values due to the fact that the doping process enhances the stability of the compound corresponding to the low energies. The application of SIC approximations will allow us to properly deal with the 4f states in the CaSnO3 lattice doped with a rare-earth (RE = Nd) compound due to the existence of f electrons in Nd. As for the SIC-LDA approximation, the same applies to the conduction band, while growing domination from the O-2p states was spotted in the valence band as can be seen from Figure 9. After the first doping percentage was inserted, a major contribution from the Nd-4f states was spotted in the valence band as can be seen from Figure 9. After the first doping percentage was inserted, a major contribution from the Nd-4f states was spotted especially in the valence band with a band gap value of 2.44 eV. For 5% of doping percentage, we can notice that the Nd-4f state contribution grew and dominated both the valence and conduction bands: this leads the band gap to shrink and to further reduce it to 2.04 eV. This decrease in the band gap is mainly attributed to the 3d–4f strong exchange interactions.33 Along those lines, Majid et al. reported that the 3d–4f exchange interactions are fragile than 3d–3d because of the strongly localized nature of 4f orbitals in rare-earth atoms.34 A first proposition that provided an explanation of 3d–4f interactions is suggested by Campbell.35 In a similar approach, Ma et al. have more discussed in detail how 4f localized electrons polarize 5d states which interact with 3d orbitals.36 The first-principles calculations indeed permitted an accurate analysis of the electronic properties of the pristine compound besides inspecting the effect of the rare-earth (neodymium) doping on engineering its properties in a constructive manner. The results emphasize the fact that the Nd3+ incorporation will have an immense positive impact on the optical and electrical properties of the samples.

Revealing the compatibility of thin-film materials for optoelectronic applications is significantly related to their electrical properties. Hence, it is substantial to determine the electrical properties of the prepared samples and the alterations resulting from the doping process and thereby evaluating their potentials for further applications. Since rare-earth elements are well-known for enhancing the electrical properties of alkali element-based thin film oxides.12,13 Therefore, neodymium was employed to tune the electrical properties of CaSnO3 thin films. The electrical properties of pure and Nd-doped CaSnO3 thin films were collected at T = 300 K to reveal the semiconducting nature and to investigate the alterations on the conductivity and carrier mobility generated from the Nd3+.
insertion. Table 2 shows the collected electrical properties using the van der Pauw configuration in the presence of a magnetic field and their variation as a function of doping content. Extracting the electrical properties of the undoped sample was quite challenging due to the near isolating nature of the material (high resistivity). This behavior changed after the first doping percentage was induced, leading to a significant rise in the conductivity of the samples at room temperature recorded at 18 S/cm for 3% of Nd content and further increased to 32 S/cm for 5% of Nd content. It is seen that the electrical conductivity is highly dependent on the Nd doping content. The same applies to the carrier concentrations that show the same trend as the conductivity, where the carrier concentration increased by doping effect passing from $1.2 \times 10^{19}$ cm$^{-3}$ for the first doping percentage to $4.3 \times 10^{19}$ cm$^{-3}$ for 5% of Nd content. The measurements [Hall coefficient (RH)] indicated the n-type nature of the doped samples. As for the carrier mobility, a slight decrease was spotted showing a value of 2.09 cm$^2$ V$^{-1}$ s$^{-1}$ for 5% of Nd content. Thus, the results demonstrate the capability of neodymium as a doping element in enhancing the transport properties of stannous-based perovskite oxides.

5. CONCLUSIONS

In summary, high-quality pristine and Nd-doped CaSnO$_3$ thin films grown on Si(100) substrates were obtained via a simple and fast chemical route. The samples were thoroughly characterized via several methods to ensure the high quality of the films alongside confirming the effective insertion of Nd at Ca sites. Structural analysis confirmed the high quality of the as-deposited films with the alteration generated by the doping process. The lattice parameters expanded as the doping element was introduced applying a strain along all the axes. The type of substrate employed had no effect on the quality of the phase. The morphological scanning showed the effect of doping ratios on the grain size and surface quality. Optical properties were extensively examined experimentally and through ab initio calculations, revealing the neodymium capability of enhancing the film absorption and tuning the band gap of the CaSnO$_3$ compound. In addition, the DFT calculations showed the electronic structure and density of states of the pure and Nd-doped CaSnO$_3$ with and without the LDA-SIC approximations.

Table 2. Conductivity Type, Carrier Concentration, Mobility, and Resistivity Value of the Pure and Nd-Doped CaSnO$_3$ Thin Films Collected at $T = 300$ K

| samples type of conductivity | carrier concentration (cm$^{-3}$) | mobility $\mu$ (cm$^2$V$^{-1}$s$^{-1}$) | conductivity (S/cm) |
|-----------------------------|----------------------------------|-------------------------------------|--------------------|
| CaSnO$_3$/Nd$^{3+}$ (3%)    | N                                | $1.2 \times 10^{19}$                | 3.41               | 23                 |
| CaSnO$_3$/Nd$^{3+}$ (5%)    | N                                | $4.3 \times 10^{19}$                | 2.09               | 52                 |

Figure 9. Calculated partial and total density of states of the pure and Nd-doped CaSnO$_3$: (a) 0% with LDA approximation, (b) 0% with LDA-SIC, and (c) 3 (d) 5% of Nd content.
calculation permitted the identification of the exchange interactions between the 3d−4f states and its impact on the optical and electronic properties. Hall effect results revealed the increment of conductivity and carrier mobility resulting from the doping process. The results in the present paper will contribute to facilitating the growth and processing of stannous-based perovskite thin films and thereby expanding the opportunities for further device integration.

■ AUTHOR INFORMATION

Corresponding Author

Hamza Shaili − Group of Semiconductors and Environmental Sensor Technologies-Energy Research Center, Faculty of Science, Mohammed V University, 10500 Rabat, Morocco; orcid.org/0000-0003-1197-6335; Phone: +212 604710051; Email: hamza.shaili13@gmail.com

Authors

Elmehdi Salmani − Laboratory of Condensed Matter and Interdisciplinary Sciences, Department of Physics, Faculty of Sciences, Mohammed V University, 10500 Rabat, Morocco

Mustapha Beraich − Laboratory of Physics of Condensed Matter, Department of Physics, Ibn Tofail University, 14000 Kenitra, Morocco

Mustapha Zidane − Laboratory of Condensed Matter and Interdisciplinary Sciences, Department of Physics, Faculty of Sciences, Mohammed V University, 10500 Rabat, Morocco

M’hamed Taibi − CSM, LPCMIO, Ecole Normale Supérieure, Mohammed V University, 10500 Rabat, Morocco

Mustapha Rouchdi − Group of Semiconductors and Environmental Sensor Technologies-Energy Research Center, Faculty of Science, Mohammed V University, 10500 Rabat, Morocco

Hamid Ez-Zahraouy − Laboratory of Condensed Matter and Interdisciplinary Sciences, Department of Physics, Faculty of Sciences, Mohammed V University, 10500 Rabat, Morocco

Najem Hassanain − Group of Semiconductors and Environmental Sensor Technologies-Energy Research Center, Faculty of Science, Mohammed V University, 10500 Rabat, Morocco

Ahmed Mzerd − Group of Semiconductors and Environmental Sensor Technologies-Energy Research Center, Faculty of Science, Mohammed V University, 10500 Rabat, Morocco

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c04054

Funding

This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors are thankful to the National Center for Scientific and Technical Research (CNRST) for providing the characterization facilities (FE-SEM/EDX).

■ REFERENCES

(1) Zhu, L.; Zeng, W. Room-temperature gas sensing of ZnO-based gas sensor: A review. Sens. Actuators, A 2017, 267, 242−261.
(2) Chen, Y.; Meng, Q.; Zhang, L.; Han, C.; Gao, H.; Zhang, Y.; Yan, H. SnO2-based electron transporting layer materials for perovskite solar cells: A review of recent progress. J. Energy Chem. 2019, 35, 144−167.
(3) Prathap, P.; Daihya, A. S.; Srivastava, M.; Srivastava, S. K.; Sivaiab, B.; Haranath, D.; Vandana, P.; Srivastava, R.; Rauthan, C. M. S.; Singh, P. K. Anti-reflection InOx nanocones for silicon solar cells. Sol. Energy 2014, 106, 102−108.
(4) Hwang, D.-K.; Oh, M.-S.; Lim, J.-H.; Park, S.-J. ZnO thin films and light-emitting diodes. J. Phys. D: Appl. Phys. 2007, 40, R387−R412.
(5) Udawatte, C.; Kikihana, M.; Yoshimura, M. Preparation of pure perovskite-type BaSnO3 powders by the polymerized complex method at reduced temperature. Solid State Ionics 1998, 108, 23−30.
(6) James, J.; Kumar, O. B. S.; Senthil Kumar, S.; Prabhakar Rao, P.; Nair, K. V. O. Nanoparticles of Ba,MgSnO3 (M=Ca, La and Nd; x=0 or 0.5): a new group of complex perovskite oxides. Mater. Lett. 2003, 57, 3641−3647.
(7) Zhong, F.; Zhuang, H.; Gu, Q.; Long, J. Structural evolution of alkaline earth metal stannates MSnO3 (M = Ca, Sr, and Ba) photocatalysts for hydrogen production. RSC Adv. 2016, 6, 42474−42481.
(8) Guo, H.; Chen, H.; Zhang, H.; Huang, X.; Yang, J.; Wang, B.; Li, Y.; Wang, L.; Niu, X.; Wang, Z. Low-temperature processed yttrium-doped SrSnO3 perovskite electron transport layer for planar heterojunction perovskite solar cells with high efficiency. Nano Energy 2019, 59, 1−9.
(9) Guo, H.; Zhang, H.; Yang, J.; Gong, W.; Chen, H.; Wang, H.; Liu, X.; Hao, F.; Niu, X.; Zhao, Y. Lanthanum-doped strontium stannate for efficient electron-transport layers in planar perovskite solar cells. ACS Appl. Energy Mater. 2020, 3, 6889−6896.
(10) Myung, C. W.; Lee, G.; Kim, K. S. La-doped BaSnO3 electron transport layer for perovskite solar cells. J. Mater. Chem. A 2018, 6, 23071−23077.
(11) Shin, S. S.; Yeom, E. J.; Yang, W. S.; Hur, S.; Kim, M. G.; Im, J.; Seo, J.; Noh, J. H.; Seok, S. I. Colloidalprepared La-doped BaSnO3 electrodes for efficient, photostable perovskite solar cells. Science 2017, 356, 167−171.
(12) Liu, Q.; Dai, J.; Zhang, X.; Zhu, G.; Liu, Z.; Ding, G. Perovskite-type transparent and conductive oxide films: Sb- and Nd-doped SrSnO3. Thin Solid Films 2011, 519, 6059−6063.
(13) Fan, F.-Y.; Zhao, W.-Y.; Chen, T.-W.; Yan, J.-M.; Ma, J.-P.; Guo, L.; Gao, G.-Y.; Wang, F.-Z.; Zheng, R.-K. Excellent structural, optical, and electrical properties of Nd-doped BaSnO3 transparent thin films. Appl. Phys. Lett. 2018, 113, 202102.
(14) Liu, Q.; Jin, F.; Li, B.; Gong, L. Structure and band gap energy of CaSnO3 epitaxial films on LaAlO3 substrate. J. Alloys Compd. 2017, 717, 55−61.
(15) Ueda, K.; Shimizu, Y. Fabrication of Tb-Mg codoped CaSnO3 perovskite thin films and electroluminescence devices. Thin Solid Films 2010, 518, 3063−3066.
(16) Alves, M. C. F.; Marinho, R. M. M.; Casali, G. P.; Siu-Li, M.; Dépoutier, S.; Guilloux-Viry, M.; Souza, A. G.; Longo, E.; Weber, I. T.; Santos, I. M. G.; Bouquet, V. Influence of the network modifier on the characteristics of MSnO3 (M=Sr and Ca) thin films synthesized by chemical solution deposition. J. Solid State Chem. 2013, 199, 34−41.
(17) Shaili, H.; Salmani, E. M.; Beraich, M.; Essajai, R.; Battal, W.; Ouafi, M.; Elhat, A.; Rouchdi, M.; Taibi, M. h.; Ez-Zahraouy, H.; Hassanain, N.; Mzerd, A. Enhanced properties of the chemically prepared Gd-doped SrSnO3 thin films: Experimental and DFT study. Opt. Mater. 2020, 107, 110136.
(18) Beraich, M.; Shaili, H.; Bengshina, E.; Hafidi, Z.; Taibi, M.; Bentiss, F.; Ghenbour, A.; Bellaouchou, A.; Mzerd, A.; Zarrouk, A.; Fahoume, M. Experimental and theoretical study of new kesterite Cu3NiGeS4 thin film synthesized via spray ultrasonic technique. Appl. Surf. Sci. 2020, 527, 146800.
(19) Shaili, H.; Beraich, M.; El hat, A.; Ouafi, M.; Salmani, E. M.; Essajai, R.; Battal, W.; Rouchdi, M.; Taibi, M. h.; Hassanain, N.; Mzerd, A. Synthesis of the Sn-based CaSn3 chalcogenide perovskite thin film as a highly stable photoabsorber for optoelectronic applications. J. Alloys Compd. 2021, 851, 156790.
(20) Shaili, H.; Salmani, E.; Berai, M.; Elhat, A.; Rouchdi, M.; Tabi, M.; Ez-Zahraouy, H.; Hassanain, N.; Mzerd, A. Revealing the impact of strontium doping on the optical, electronic and electrical properties of nanostructured 2H-CuFeO2 delafossite thin films. RSC Adv. 2021, 11, 25686−25694.

(21) Akai, H. KKR-CPA program package. http://kkr.issp.u-tokyo.ac.jp/ (accessed 2003-03-14).

(22) Toyoda, M.; Akai, H.; Sato, K.; Katayama-Yoshida, H. Electronic structures of (Zn,TM)O (TM: V, Cr, Mn, Fe, Co, and Ni) in the self-interaction-corrected calculations. Phys. B 2006, 376−377, 647−650.

(23) Zhao, J.; Ross, N. L.; Angel, R. J. Tilting and distortion of CaSnO3 perovskite to 7 GPa determined from single-crystal X-ray diffraction. Phys. Chem. Miner. 2004, 31, 299−305.

(24) Mountstevens, E. H.; Attfield, J. P.; Redfern, S. A. T. Cation-size control of structural phase transitions in tin perovskites. J. Phys.: Condens. Matter 2003, 15, 8315.

(25) Redfern, S. A. T.; Chen, C.-J.; Kung, J.; Chaix-Pluchery, O.; Kreisel, J.; Salje, E. K. H. Raman spectroscopy of CaSnO3 at high temperature: a highly quasi-harmonic perovskite. J. Phys.: Condens. Matter 2011, 23, 425401.

(26) Maul, J.; Erba, A.; Santos, I. M. G.; Sambrano, J. R.; Dovesi, R. In silico infrared and Raman spectroscopy under pressure: The case of CaSnO3 perovskite. J. Chem. Phys. 2015, 142, 014505.

(27) Mu, J.; Chen, B.; Guo, Z.; Zhang, M.; Zhang, Z.; Shao, C.; Liu, Y. Tin oxide (SnO2) nanoparticles/electrospun carbon nanofibers (CNFs) heterostructures: Controlled fabrication and high capacitive behavior. J. Colloid Interface Sci. 2011, 356, 706−712.

(28) Lin, Y.; Lin, S.; Luo, M.; Liu, J. Enhanced visible light photocatalytic activity of Zn2SnO4 via sulfur anion-doping. Mater. Lett. 2009, 63, 1169−1171.

(29) Xu, R.; Deng, B.; Min, L.; Xu, H.; Zhong, S. CuSn(OH)6 submicromospheres: Room-temperature synthesis and weak antiferromagnetic behavior. Mater. Lett. 2011, 65, 733−735.

(30) Henriques, J. M.; Caetano, E. W. S.; Freire, V. N.; Costa, J. A. P. d.; Albuquerque, E. L. Structural, electronic, and optical absorption properties of orthorhombic CaSnO3 through ab initio calculations. J. Phys.: Condens. Matter 2007, 19, 106214.

(31) Chañi, F. Z.; Salmani, E.; Bahmad, L.; Hassanain, N.; Boubker, F.; Mzerd, A. First principle calculations with SIC correction of Fe-doped CuO compound. Comput. Condens. Matter 2018, 16, No. e00304.

(32) Perdew, J. P.; Zunger, A. Self-interaction correction to density-functional approximations for many-electron systems. Phys. Rev. B: Condens. Matter Mater. Phys. 1981, 23, 5048−5079.

(33) Chantelle, L.; Menezes de Oliveira, A. L.; Kennedy, B. J.; Maul, J.; Da Silva, M. R. S.; Duarte, T. M.; Albuquerque, A. R.; Sambrano, J. R.; Landers, R.; Siu-Li, M.; Longo, E.; Dos Santos, I. M. G. Probing the Site-Selective Doping in SrSnO3: Eu Oxides and Its Impact on the Crystal and Electronic Structures Using Synchrotron Radiation and DFT Simulations. Inorg. Chem. 2020, 59, 7666−7680.

(34) Majid, A.; Dar, A. A density functional theory study of 3d-4f exchange interactions in Cr-Nd doped GaN. J. Magn. Magn. Mater. 2014, 368, 384−392.

(35) Campbell, I. A. Indirect exchange for rare earths in metals. J. Phys. F: Met. Phys. 1972, 2, L47−L50.

(36) Ma, B.-Q.; Gao, S.; Su, G.; Xu, G.-X. Cyanobridged 4f-3d Coordination Polymers with a Unique Two-Dimensional Topological Architecture and Unusual Magnetic Behavior. Angew. Chem., Int. Ed. 2001, 40, 434−437.