Isovalent Doping Effect on Structural, Optical Properties and Dispersion Parameters of Layered Perovskite $\text{La}_{2-x}\text{AxTi}_2\text{O}_7$ (A = Bi, Ce, and Y, With x = 0.0 and 0.1)

V. Tuyikeze

Universite Hassan II Casablanca

L.H. Omari (✉ bophysiq@gmail.com)

University of Hassan II Casablanca, Faculty of Sciences Ain Chock <https://orcid.org/0000-0002-8655-245X>

F. Fraija

Universite Hassan II Casablanca

Research Article

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Isovalent doping effect on structural, optical properties and dispersion parameters of layered perovskite $\text{La}_{2-x}\text{A}_x\text{Ti}_2\text{O}_7$ (A = Bi, Ce, and Y, with x = 0.0 and 0.1)

V. Tuyikeze, L.H. Omari*, F. Fraija

LERDyS and LPMMAT, Faculty of Sciences Ain-Chock, University of Hassan II of Casablanca, B.P 5366 Maarif, Morocco.

Abstract

Lanthanum titanate nanoparticles of $\text{La}_{2-x}\text{A}_x\text{Ti}_2\text{O}_7$ (the undoped is denoted by LTO and the monodoped with Bi, Ce, and Y is denoted by LBTO, LCTO and LYTO, respectively) were prepared by sol-gel route. X-ray diffraction (XRD) reveals that these compounds crystallize as a monoclinic layered perovskite-like structure with a space group P2_1 . UV-visible diffuse reflectance spectroscopy was employed to characterize the optical properties and hence the dispersion parameters. Optical transmittance and reflectance were investigated to obtain more in-depth insight into the optical properties and optoelectronic behavior of studied nanoparticles. The data collected reveal that the samples have a wide band gap (E_g) that varies between 3.50 and 3.88 eV. By introducing the Ce ion into the host matrix LTO, the optical gap energy was decreased from 3.69 to 3.51 eV despite a low doping content of 5%. However, the Urbach energy (E_U) was increased from 0.28 to 0.85 eV. The dispersion of the refractive index has been studied in terms of a single oscillator by the Wemple and Di-Domenico (WDD) model as well as important parameters such as the dispersion energy E_d , the excitation energy E_0 and the third-order nonlinear (NL) optical susceptibility $\chi^{(3)}$. E_d and E_0 parameters have a crucial role in identifying the characteristics of optical materials and allow the calculations of the factors required for the design of spectral dispersion and optical communication devices.

Keywords: *Nanoparticle of lanthanum titanate; Optical band gap; Refractive index; Optical properties; Dispersion parameters; WDD model.*

1. Introduction

In recent years, the family of layered perovskite-type structure (LPS) has attracted more attention of researchers because of its multifunctional properties. This family has the general formula $\text{A}_n\text{B}_n\text{O}_{3n+2}$, where n is the number of octahedral layers [1,2]. When $n = 2$, the compounds have the formula $\text{A}_2\text{B}_2\text{O}_7$. With more than 500 different combinations of cations

from the A and B sites, they exhibit a wide range of physico-chemical properties, making them indispensable for various applications, including solar energy conversion, electronics, and catalysis [3]. The A-site is often occupied by tri- and/or tetravalent actinides and lanthanides cations, whereas B-site is occupied by transition or post-transition metals. Structural stability is characterized by a ratio of radii between the cations at A site and B site [4]. For $r(A)/r(B)$ ratios ranging from 1.46 to 1.78, an ideal pyrochlore structure with a space group $Fd3m$ was found. If the ratio is more significant than 1.78, a monoclinic perovskite layered structure [5]. As one of the $A_2B_2O_7$ structures, lanthanum titanate $La_2Ti_2O_7$ has been the subject of several research due to its attractive properties such as ferroelectric and piezoelectric for high-temperature applications including automotive, aerospace and energy production [6,7]. Ferroelectrics are materials characterized by a Curie point (T_C) at the ferroelectric - paraelectric transition. Therefore, all ferroelectric materials are limited to function as piezoelectric below their Curie point. Ferroelectrics with a layered perovskite-type structure (LPS) are good candidates for high-temperature applications due to their high Curie point ($> 1200\text{ }^\circ\text{C}$), such as $La_2Ti_2O_7$ (LTO, $T_C = 1461\text{ }^\circ\text{C}$) [8,9]. Nowadays, the layered structure of the $La_2Ti_2O_7$ compound has also a considerable interest due to its electrical, optical, and photocatalytic properties [10,11].

In addition to the above applications, cerium-doped pyrochlore compounds (ex., $La_2Zr_2O_7$ in pyrochlore structure) are used as oxidation catalysts [12], ceramic thermal barrier coatings [13,14], and solid electrolytes in high-temperature fuel cells [15]. A study of the solubility, structural relaxation, and stability of $La_{2-x}Ce_xTi_2O_7$ ($x=0, 0.5, 1, 1.5$, and 2) was performed with the Vienna Ab Initio Package (VASP), and each compound was found to be energetically stable [16]. Despite cerium has similar properties to lanthanum, this study shows that the substitution of Ce^{3+} for the La-site decreases their stability. Because doping with very high levels of Ce^{3+} ions in $La_2Ti_2O_7$ leads to cell distortions, which are related to defects [17]. For this reason, a small amount of substitution of La with Ce is required to preserve the stability of the material.

Inorganic materials doped with trivalent rare-earth ions have excellent chemical and physical properties. One of the most significant advantages of trivalent rare-earth ions is the narrow-band emission due to the forbidden transitions between f-orbits. A narrow band allows efficient filtering of unwanted background noise, especially when samples are excited by UV radiation [18]. Compounds containing Bi^{3+} , whether perovskites or bismuth layered materials, generally exhibit high piezoelectric and ferroelectric performance due to the hybridization between the 6p orbits of Bi and 2p of O due to the stereochemical activity of Bi^{3+} single-pair

electrons [19,20]. In the literature, it has been reported that $\text{Y}_2\text{Ti}_2\text{O}_7$ ceramics with a high Y content have a transmission of $\sim 50\%$ at 1100 nm [21]. $\text{Lu}_2\text{Ti}_2\text{O}_7$ ceramics prepared by plasma spark sintering have an excellent transmission in the near-infrared range (72% at 2000 nm), (40% at 550 nm), and a high refractive index (HRI) (2.57 at 632.8 nm) [22]. An alternative layered perovskite has been also attracting the researcher interests, for example $\text{Ca}_3\text{Ti}_2\text{O}_7$ [23], that exhibits interesting properties such as photocatalysis, high refractive index, wide band gap, and NL behavior.

We concentrate specially on the optical properties of lanthanide layered perovskite doped with trivalent ions (as rare earth), which are of prime reputation for modern optoelectronics. According to our knowledge, very few detailed studies on the optical properties of lanthanum titanate $\text{La}_2\text{Ti}_2\text{O}_7$ have been reported in the literature, therefore the aim of our work is to study these properties in order to help optoelectronics manufacturers interested in this material. In this work, we have synthesized and studied the effect of 5% content of isovalent dopants on the structural and optical properties of $\text{La}_{2-x}\text{A}_x\text{Ti}_2\text{O}_7$ nanoparticles ($\text{A} = \text{Bi, Ce, Y}$; $x = 0.0$ and 0.1). The preparation and results obtained by the used characterization techniques will be discussed.

2. Experiment section

$\text{La}_{2-x}\text{A}_x\text{Ti}_2\text{O}_7$ ($\text{A} = \text{Bi, Ce, Y}$; $x = 0.0$ and 0.1) lanthanum titanate nanoparticles were synthesized by the sol-gel process. Titanium isopropoxide [$\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$, 97% Sigma-Aldrich], lanthanum acetate [$(\text{La}(\text{CH}_3\text{CO}_2)_3 - x\text{H}_2\text{O})$, 99.9% Sigma-Aldrich], bismuth acetate [$\text{Bi}(\text{CH}_3\text{CO}_2)_3$, 99.99% Sigma-Aldrich], cerium acetate [$\text{Ce}(\text{CH}_3\text{CO}_2)_3 - x\text{H}_2\text{O}$, 99.9% Sigma-Aldrich] and yttrium acetate [$\text{Y}(\text{CH}_3\text{CO}_2)_3 - x\text{H}_2\text{O}$, 99.9% Sigma-Aldrich] are raw materials that have been used. Ethylene glycol [$\text{HO}(\text{CH}_2)_3\text{OH}$, 99.8%], and distilled water were added to each preparation of LTO, LBTO, LCTO, and LYTO nanocrystals. The mixture of every sample is kept under magnetic stirring for 5h at 50 °C until it becomes a transparent gel. The resulting gels were then dried in an oven at 90 °C for three days. Calcination was followed at 1050 °C for 3 hours with slow cooling. They were then crushed to break up the agglomerates and reduce the particle size. The calcined and crushed powders were characterized using D8 Advance Bruker diffractometer, applying a $\text{Cu-K}\alpha$ monochromatic beam ($\lambda = 1.54059 \text{ \AA}$) operating at 33 kV and 45 mA. The optical properties were gotten by a spectrometer/Data System JASCO Corp., V-570, Rev.1.00.

3. Results and Discussion

3.1. Structural properties

DRX analysis is a basic technique for characterizing crystalline materials. Fig. 1(a) shows the X-ray diffraction pattern of LTO, LBTO, LCTO, and LYTO powders. The majority of the observed peaks are indexed according to the monoclinic structure with a space group $P2_1$, which is corresponding to PDF 96-100-9077 (ICDD,2006) card [24]. In addition, Fig. 1(b) shows the Rietveld refinement of the XRD pattern of the undoped sample. The results of structural study revealed the obtained parameters tabulated in table 1. From this table, it can be seen a slight change of the cell parameters indicating a small effect of doping on the structural properties due to the radii size as reported in table 2. Indeed, the cell parameters increase with increasing the radius size. The obtained results are in excellent agreement with the obtained experimental cell parameters and those reported [8,10,12,24] (see table 1).

The mean particle size (D) of all samples is estimated using the Williamson-Hall (W-H) formula [25]:

$$\beta \cos(\theta) = \frac{K\lambda}{D} + 4\varepsilon \sin(\theta) \quad (1)$$

Where λ is the X-ray wavelength (0.15406 nm), β is the full width at half maximum height (FWHM). To determine the FWHM, the peaks have been adapted to the Gaussian distribution, θ is the Bragg angle, K is the shape factor of the particles ($K = 0.94$), and ε is the micro strain. By plotting $\beta \cos(\theta)$ versus $4 \sin(\theta)$ we obtain a linear fit for the data. From this fit, particle size and strain are extracted from intercept and slope respectively.

The results of the structural parameters, such as mesh parameters, volume, and mean particle size are tabulated in Table 1. A minor incorporation effect of Bi^{3+} , Ce^{3+} , and Y^{3+} on the structure of $\text{La}_2\text{Ti}_2\text{O}_7$ is observed as it was noted by DRX (Fig. 1 (a)).

For such comparison between doping elements in the studied compounds, the electronic configuration, oxidation states, ionic and atomic radii are reported in Table 2. It can be seen that Y/La ions have the same oxidation state and a different ionic radius, Bi/La ions have almost the same ionic radius and oxidation state. In contrast, Ce/La ions have mixed oxidation states (3 and 4) and slightly different ionic radii.

3.2. Optical properties

The optical properties of the synthesized nanoparticles were examined using a UV-Visible spectroscope, and the results are presented and discussed. For instance, the absorbance, transmission, reflectivity, absorption coefficient, and refractive index are important material properties for technological applications in semiconductors such as photoelectric applications because of their relationship with photon energy. The reflectance spectra R (%) are shown in Fig. 2(a), they can be interpreted in terms of two main regions. In the ultraviolet region (for wavelengths from 250 to 300 nm i.e region I), the reflectance is high (against low transmission), conversely in the visible region (for wavelengths $\lambda \geq 350$ nm i.e region II) the reflectance is low. For this reason, these compounds can be used as UV filters and as light-transparent materials. Clearly, as can be seen in Fig. 2 (b), LCTO and LYTO compounds have more absorption in the visible region than other compounds, despite the lower doping rate of 5%. According to Lambert-Beer's law, the measured absorbance, $A = \log(I_0/I)$, is related to the absorption coefficient α by the following relationship [26]:

$$\alpha = 2.3026 \times \frac{A}{d} \quad (2)$$

Where d , T , and A are the thickness of sample, transmittance, and absorbance successively. The optical gap energy E_g^{opt} of all samples was calculated based on the following to the Tauc's equation [27]:

$$\alpha h\nu = B(h\nu - E_g^{opt})^t \quad (3)$$

Where, α is the absorption coefficient, $(h\nu)$ is incident photon energy, B is parameter independent of incident photon energy. As an experimental value, t represents a direct or indirect transition, and the values are 1/2 and 2, respectively. In our case, the nanoparticles have direct gap energy, where t is equal to 1/2. This result is also in agreement with the theoretical study performed by Bruyer et al. [28] for the undoped LTO nanoparticle. The thickness d was measured by developing a pellet about 0.5 mm thick from the calcined powders. The variation of $(\alpha h\nu)^2$ with photon energy $(h\nu)$ is illustrated in Fig. 3. It has been indicated that the plots of $(\alpha h\nu)^2$ vs $(h\nu)$ are linear over a wide range of photon energies indicating the direct type of transitions. The optical gap energy values were obtained by extrapolating the linear part to the energy axis. For photon energies nearby the direct band gap energy, the absorption is generally due to exciton absorption. In indirect band gap

semiconductors, the photon absorption for photon energies near E_g necessitates the emission or absorption of phonons during the absorption process [29]. In this case, if the photon energy $h\nu$ reaches $E_g + E_{ph}$, then the photon-absorption process can also occur by phonon emission for which the absorption coefficient is larger than that for phonon absorption.

Impurity can be donor, acceptor or isovalent. An inter-band transition leaves an electron on the conduction band and a hole on the valence band. Impurity absorption can be registered as the peaks of absorption coefficient lying below the fundamental (band-to-band) and excitonic absorption [29]. The origin of these peaks lies in the electronic transitions either between electronic states of ions and conduction/valence band or intra-ionic transitions. For small impurity concentrations, transitions from the valence band to the impurity levels, or from these levels to the continuum of states, are possible, leading to sharp absorption lines, especially in semiconductors with large gap [30].

The specific feature of the doping elements as trivalent ions is the incompletely filled 4f and/or 5d shell [29]. The electronic configurations of these elements are summarized in Table 2. In its trivalent form, these elements lose three electrons in 6s, 4f and/or 5d electron. Ce and Bi could lose more than 3 electrons, which may be the origin of additional absorption peaks near the fundamental absorption (nearby E_g). Whereas the compounds with La and Y show similar optical absorption behavior leaving to similar optical phenomena.

According to the calculated values shown in Table 3, E_g^{Opt} has been decreased from 3.69 eV to 3.51 eV and to 3.65 eV, respectively, for LCTO and LBTO nanoparticle, this decrease may be due to mixtures of oxidation degrees (+3/+4) for Ce or (+3/+5) for Bi. It is noticed that the value of the energy gap for LTO compound found experimentally is in agreement with a theoretical study of Ab-initio reported in the literature [31] and in our previous study [32].

The index of refraction (n) enables us to explain the interaction between the photon/electron. The refractive index n and the extinction coefficient k were calculated in the photon energy range 1.5 to 4.5 eV using the following relations [33]:

$$n = \frac{1 + R}{1 - R} + \sqrt{\frac{4R}{(1 - R)^2} - k^2} \quad (4)$$

and

$$k = \frac{\alpha\lambda}{4\pi} \quad (5)$$

Where R is the reflectance and λ is the wavelength of the incident light. Fig. 4(a) illustrate the variations of (n) as function of $h\nu$. n is an indicator of how various frequencies and photon energy of light propagate across a transparent media. The variation of n with $h\nu$ is due to the photon/electron interaction. Refractive index values related to the studied compounds are summarized in Table 4. Materials with a HRI are often combined with contrasting refractive materials to produce translucent components. They gradually dominate more and more in optoelectronic applications, for instance antireflection coatings, ophthalmic lenses, prisms, optical waveguides, non-linear optical materials, and adhesives for optical components, etc. [34,35]. They are also useful for optimizing the visual properties of electronic screens, including LCD, OLED and quantum dot (QDLED) televisions [36].

Fig. 4(b) show the change in extinction coefficient k versus $h\nu$. As seen, the extinction coefficient spectra indicate a minimum point corresponding to optical transitions between valence band and conduction band. In addition to that, the values of k increase with increasing $h\nu$. The optical polarization (P_{opt}) and the optical susceptibility (χ_{opt}) are estimated using the relationships [37]:

$$\chi_{opt} = \frac{n^2 - k^2 - \epsilon_0}{4\pi} \quad (6)$$

and

$$P_{opt} = \frac{\epsilon_0 h c \chi_{op}}{\lambda} \quad (7)$$

Where c is the velocity of light, h is plank's constant, and ϵ_0 is the free space permittivity. Figs. 4(c) and 4(d) illustrate the variation in electrical susceptibility and optical polarization with respect to photon energy for all nanoparticles. Optical susceptibility and optical polarization values are higher in the photon energy range (4 – 4.5 eV).

Let us consider the medium in this case as non-magnetic material for that we can take the relative magnetic permeability equal to unit ($\mu = 1$) [30]. Hence, the complex refractive index and the complex relative dielectric constant could be related by: $n = \sqrt{\epsilon}$ instead $n = \sqrt{\mu\epsilon}$ found through the Maxwell equation's by considering the light as an electromagnetic field (E , B). In materials where an electromagnetic wave can lose its energy during its propagation, the refractive index becomes complex.

The intrinsic material property can be expressed as a complex dielectric constant. It is formed by an imaginary part and real part. The imaginary part (ε_2) of the dielectric constant is due to energy absorption while the real part (ε_1) is a function of the amount of deceleration of the velocity of light in the material. The complex dielectric constant is described by the relationship [38]:

$$\varepsilon = \varepsilon_1 + i\varepsilon_2 \quad (8)$$

The real and imaginary parts of the dielectric constant were calculated from a knowledge of n and k :

$$\varepsilon_1 = n^2 - k^2 \quad (9)$$

and

$$\varepsilon_2 = 2nk \quad (10)$$

The non-typical variation, of ε_1 and ε_2 corresponding to only the electronic polarizability, indicate that there are also other contributions to the polarizability arising from orientation of permanent dipoles (microwave), ionic lattice vibrations (infrared), and displacement of electrons (visible and ultraviolet) [39]. For example, in ionic crystals, in the infrared region, there is an absorption spectrum and polarization associated with the direct stimulation of vibrational modes of the ions by means of electromagnetic radiation [39].

Fig. 5(a) shows graphs of the real and imaginary part of the dielectric constant of all nanoparticles as a function of $(h\nu)$. At first sight, the values of ε_1 and ε_2 increase with increasing photon energy. However, the values of the optimal dielectric properties are obtained in the photon energy range (4 – 5.5 eV). The presence of these peaks is due to the photoexcitation process, in which electrons are excited from the valence band to the conduction band. Larger values of dielectric constant indicate the presence of the polarization effects such as charge, orientation, electronic and/or ionic polarization. Lower values of the dielectric constant may be due to significant loss or attenuation by a gradually polarization. The same study on the change in dielectric constant values as a function of wavelength was carried out by Punitha et al. [40]. The dissipation factor ($\tan \delta$) is calculated from the ratio of the imaginary and real parts of the complex dielectric constant [37], as given by the following equation:

$$\tan \delta = \frac{\varepsilon_2}{\varepsilon_1} \quad (11)$$

Fig. 5(b) illustrates the dependence of the dissipation factor $\tan(\delta)$ versus $(h\nu)$. The maximal dissipation factor $\tan(\delta)$ is achieved at 4.13 eV, clearly showing that the activation threshold is located in this energy region.

The loss tangent denotes the phase angle between the displacement field D and electric field strength E [30]. The magnetic field in the electromagnetic waves is also transverse, and in this case, its effect is neglected. While the electric field composed on the longitudinal and transversal components. The longitudinal component of E is related to scalar electrical potential, whereas the vector potential determines the transverse part of the electric field [30]. The electrical potential is responsible for longitudinal conductivity (electrical conductivity σ_{el}) by moving the charge carriers, which can be induced by an external source. Whereas, the transverse component is responsible for the optical conductivity (σ_{opt}) arising from electronic transitions accompanying photon absorption leading to a transverse current density [39]. In the case of interaction light- matter, the electrical conductivity may occur by thermal or field ionization that broken up the excitons into separate free carriers (electrons and holes) [41].

The values of the optical conductivity σ_{opt} are estimated from the absorption coefficient α and the refractive index n according to the following relationship [41]:

$$\sigma_{opt} = \frac{\alpha n c}{4\pi} \quad (12)$$

Where c is the light velocity. Fig. 5(c) show the variation of optical conductivity σ_{opt} as a function of $(h\nu)$. The dependence of conductivity on photon energy shows two different regions and results from different optical processes. Conductivities increase with increasing photon energy. In region 1, the optical conductivity (σ_{opt}) is relatively smaller, which is explained by the fact that the free carriers do not have enough energy to pass to the conduction band, whereas in region 2, the opposite phenomenon of the former is observed. Furthermore, it is interesting to note that the introduction of Bi, Ce, and Y dopants into the LTO matrix has increased the optical conductivity at high photon energies, which may be due to the electrons excited by the photon energy.

Urbach energy E_U specifies interpreted as the width of the localized states in the forbidden gap, indicating the defect levels and disorders in the forbidden band gap region, and thus follows the expression [42]:

$$\alpha = \alpha_o \exp\left(\frac{h\nu}{E_U}\right) \quad (13)$$

Where α_o is pre-exponential constant. By plotting $\ln(\alpha)$ vs. $(h\nu)$, the values of the Urbach energy of the samples were determined from fits to the linear portions of the curves, as illustrated in Fig. 6(b). The Urbach energy of LCTO increased when compared to other nanoparticles (i.e. the degree of disorder in the structure increases). This increase of E_U can be illustrated as extensions of localized states, generating defect or impurity in the energy bands. High E_U can also be associated with the existence of a large number of oxygen vacancies. This leads to higher separation of the photo-generated supports. The values obtained of E_U are reported in Table 3.

The dispersion of linear refractive index in the material due to photo/thermal treatment is very much important for various applications in various sectors. This change is being analyzed on the basis of the Wemple–DiDomenico (WDD) single oscillator model [43,44], the following relationships:

$$n^2(h\nu) = 1 + \frac{E_d E_o}{E_o^2 - (h\nu)^2} \quad (14)$$

Where E_o and E_d are oscillator energy and dispersion energy. E_o is the average excitation energy for electronic transitions, it is also considered as the distance between the centers of gravity of the valence and conduction bands, and E_d is the energy of dispersion, which is a measure of the strength of inter-band optical transitions. The single-oscillator linear Eq.(15) can take the following form:

$$(n^2 - 1)^{-1} = \frac{E_o}{E_d} - \frac{1}{E_d E_o} (h\nu)^2 \quad (15)$$

However, Fig. 6(c) illustrates the fit of the $(n^2 - 1)^{-1}$ plot with respect to $(h\nu)^2$ which allowed us to determine directly the values of E_o and E_d from the intercept E_o/E_d and the slope $(E_d E_o)^{-1}$ successively. The values of the dispersion parameters E_o and E_d values for all samples are reported in Table 3. One can notice that the values of E_o and E_d vary depending on the used dopant. E_o is considered as an average energy gap to a close approximation; it scales with the optical band gap E_g^{Opt} , $E_o \approx 1.5 E_g^{Opt}$, as suggested by Wemple and Di-Domenico (WDD) model [44,45]. Additionally, the approximate values of the optical gap energy E_g^{Opt} can also be derived from the dispersion relationship of the WDD model using the expression $E_{g(Opt)}^{WDD} \approx 2/3$

E_o . From the values reported in Table 3, it is evident that the values of $E_{g(Opt)}^{WDD}$ calculated from the WDD model is in agreement to some extent with those determined from the Tauc model.

The values of E_o and E_d can also be used to estimate the static refractive index n_o by rewriting Eq. (15) and when $h\nu$ tends towards 0 giving:

$$n_o^2 = (1 + \frac{E_d}{E_o}) \quad (16)$$

The calculated values of static refractive index n_o are reported in Table 4. For example, the values of n_o related to the compounds LYTO and LCTO are 2.94 and 3.04, successively. These high values compared to the other compounds can be linked to the transition metal elements used for doping. The high-frequency dielectric constant ϵ_∞ has been determined from the relation: $\epsilon_\infty = n_o^2$. The linear optical susceptibility $\chi^{(1)}$ and the NL optical susceptibility $\chi^{(3)}$ involving E_o and E_d can be predicted from the following Miller generalized rule [46]:

$$\chi^{(1)} = \frac{(n^2 - 1)}{4\pi} \quad \text{and} \quad \chi^{(3)} \cong A[\chi^{(1)}]^4 \quad (17)$$

Where $A = 1.7 \times 10^{-10}$ esu. Within the long wavelength range when $(h\nu) \rightarrow 0$, the previous relationships become:

$$\chi_{min}^{(1)} = \frac{(n_o^2 - 1)}{4\pi} \quad (18)$$

$$\chi_{min}^{(3)} \cong A[\frac{(n_o^2 - 1)}{4\pi}]^4 \quad (19)$$

which is also in the form of

$$\chi_{min}^{(3)} \cong A[\frac{E_d}{4\pi E_o}]^4 \quad (20)$$

The NL refractive index n_2 is correlated with the third-order susceptibility $\chi^{(3)}$ by the following expression:

$$n_2 = \frac{12\pi\chi^{(3)}}{n_o} \quad (21)$$

The calculated values of n_o , n_∞ , $\chi^{(1)}$, $\chi^{(3)}$, and n_2 are reported in Table 4. It can be noticed that the value of the first and the third-order optical susceptibility $\chi^{(3)}$ varies randomly as a function of the gap energy, as shown in Figs.7(a) and 7(b). All studied compounds have too high values of $\chi^{(3)}$ and n^2 , making them candidates for interesting materials for NL optical devices.

4. Conclusion

In the present study, the nanoparticles LTO, LBTO, LCTO, and LYTO were successfully prepared by the sol-gel process and calcined at 1050 °C for 3 hours. X-ray diffraction (XRD) analysis revealed a monoclinic layered perovskite-like structure with space group $P2_1$. UV-visible diffuse reflectance spectroscopy was used to characterize the optical properties. The results show that in the visible region, the transmission is very high, inversely to the reflectance, there is also an inverse tendency in the UV range for all nanoparticles. By introducing Ce ion into the host structure, it was found that the gap energy decreased from 3.69 to 3.51 eV. This may be due to mixtures of the oxidation states (+3/+4) of Ce. It has also been shown that Ce doping causes a high degree of disorder in the structure. The low extinction coefficients in the visible region make these studied nanocrystals promising materials that could be used in the field of electro-optics. It should also be noted that all compounds have very high transmission in the visible and near-infrared, hence their transparency in these spectral regions, which may be useful in several applications that require transparent materials such as LED (light-emitting diode) lamps and UV filters.

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Fig. 1. (a) XRD patterns of all nanoparticles studied. (b) DRX Rietveld refinement for $x = 0.00$.

Fig. 2. (a) Reflectance, (b) Absorbance spectra versus wavelength λ .

Fig. 3. Plots of $(ah\nu)^2$ versus $(h\nu)$ for estimating the E_g values.

Fig. 4. (a) Refractive index n , (b) extinction coefficient k , (c) optical susceptibility χ_{opt} , and (d) optical polarization P_{opt} function ($h\nu$).

Fig. 5. (a) Variation of ϵ_1 and ϵ_2 as a function of $h\nu$. (b) Adjustment of $\tan(\delta)$. (c) Optical conductivity σ_{opt} versus $h\nu$.

Fig. 6. (a) Linear plots of $\ln(\alpha)$ versus $h\nu$. (b) Refractive index plot versus $(h\nu)^2$.

Fig. 7. (a) Linear and (b) Nonlinear susceptibility versus $(h\nu)^2$.

Table 1. Structural parameters from XRD of LTO, LBTO, LCTO, and LYTO powder calcined at 1050 °C

Sample	Ref.	Structural parameters					
		a (Å)	b (Å)	c (Å)	β (°)	V (Å ³)	D (nm)
LTO	[8]	7.8181	5.5457	13.0121		557.81	
	[10]	7.8081	5.5479	12.9993	98.636	556.73	
	[12]	7.8114	5.5474	13.0185	98.719	557.53	
	[24]	7.8120	5.5440	13.010		557.04	
LTO		7.8136	5.5478	13.0038	98.561	557.411	20.586
LBTO	this work	7.8021	5.5412	13.002	98.635	555.743	11.013
LCTO		7.8108	5.5465	13.011	98.551	557.401	15.324
LYTO		7.8101	5.5439	13.007	98.618	556.823	11.434

Table 2. Electronic configuration, oxidation states, as well as the ionic and atomic rays that form the studied nanoparticles.

Element	La	Bi	Ce	Y
Z	57	83	58	39
Elect. Conf.	[Xe] 6s ² 5d ¹	[Xe] 6s ² 4f ¹⁴ 5d ¹⁰ 6p ³	[Xe] 6s ² 4f ¹ 5d ¹	[Kr] 5s ² 4d ¹
Radii	195 pm	160 pm	185 pm	180 pm
Oxidation states	+3	+3 and +5	+3 and +4	+3
Ionic Radius	117.2 pm	117 pm (90 pm)	115 pm (101 pm)	104 pm

Table 3. The optical parameters of the studied nanoparticles.

Compounds	E_g^{opt} (eV)	E_U (eV)	E_o (eV)	E_d (eV)	E_g^{WDD} $E_{g(Opt)}$ (eV)
LTO	3.69	0.28	4.69	33.97	3.13
LBTO	3.65	0.17	4.54	32.81	3.03
LCTO	3.51	0.85	4.67	38.51	3.11
LYTO	3.87	0.29	4.65	35.45	3.10

Table 4. The optical parameters of the studied nanoparticles.

Compounds	n	n_0	ϵ_∞	$\chi_{min}^{(1)}$	$\chi_{min}^{(3)}$ ($10^{-11} esu$)	n_{2min} ($10^{-10} esu$)
LTO	1.58	2.87	8.24	0.58	1.89	2.48
LBTO	1.31	2.89	8.23	0.59	1.86	2.43
LCTO	2.15	3.04	9.25	0.65	3.15	3.91
LYTO	2.02	2.94	8.62	0.61	2.30	2.95

Figures

Figure 1

(a) XRD patterns of all nanoparticles studied. (b) DRX Rietveld refinement for $x = 0.00$.

Figure 2

(a) Reflectance, (b) Absorbance spectra versus wavelength λ .

Figure 3

Plots of $(\alpha h\nu)^2$ versus $(h\nu)$ for estimating the E_g values.

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