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Credit Author Statement

Isela Padilla-Rosales: Formal analysis, Investigation, Writing-Original Draft, Visualization. **Rigoberto López-Juárez**: Resources, Writing - Review & Editing. **Germán López-Pacheco**: Validation, Formal analysis, Visualization. **Ciro Falcony**: Resources, Investigation, Writing - Review & Editing. **Federico González**: Conceptualization, Methodology, Resources; Writing - Original Draft, Visualization.

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TOC



Sketch of the energy transfer from the $O^{2-} \rightarrow Ti^{4+}$ ligand-to-metal charge transfer state (LMCT) to the Yb³⁺ excited state via intrinsic defect levels.

Near infrared photon-downshifting in Yb³⁺-doped titanates: the influence of intrinsic defects

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Abstract

Powder samples of Yb³⁺-doped TiO₂ (0.5 mol%) -exhibiting anatase and rutile phases-CaTiO₃, SrTiO₃ and Na_{0.5}Bi_{0.5}TiO₃ were synthesized by the sol-gel and polymeric complex methods. The crystal structure, microstructure and optical properties of the powders annealed at 800 °C and 1000 °C for 1 h were investigated by X-ray diffraction, scanning electron microscopy, diffuse reflectance and photoluminescence spectroscopies, respectively. X-ray diffraction patterns show the presence of the expected crystalline phase for each compound. Reflectance spectra for all compounds exhibit a broad absorption band below 425 nm ascribed to the ligand-to-metal charge transfer (LMCT) O²⁻ \rightarrow Ti⁴⁺ fundamental state. The Yb³⁺ excitation spectra for all titanates show a broadband being also compatible with the LMCT O²⁻ \rightarrow Ti⁴⁺ state, indicating the energy transfer from the host to the Yb³⁺. Interestingly, the excitation band edges follow the same order as that of the optical bandgap energy of the investigated titanates. A conspicuous excitation band in the CaTiO₃:Yb³⁺ provides evidence about the importance of intrinsic defects in the energy transfer process from the host to Yb³⁺. Photoluminescence emission and diffuse reflectance

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spectra in the visible and NIR, reveal an emission band that overlaps with the absorption band of the Yb³⁺, explaining reasonably well the energy transfer process from the host to Yb³⁺. According to each compound, the integrated intensity of the Yb³⁺ emission follows the order Na_{0.5}Bi_{0.5}TiO₃ > CaTiO₃ > SrTiO₃ > TiO₂. Finally, it is shown that titanates may downshift photons from UV to wavelengths where a crystalline-silicon photovoltaic solar cell has its higher spectral responsivity.

Keywords

Oxide materials; Polymeric complex method; Optical properties; Yb³⁺-luminescence; NIR downshifting; X-ray diffraction

1. Introduction

The current environmental degradation associated, among other factors, with the energy consumption mainly provided from fossil fuels [1], is a matter of concern. Consequently, any approach pursuing the efficient use and saving of energy, as well as the improvement in harnessing the renewable and sustainable energy sources, is a research topic of paramount importance. One of those topics that falls into the realm of the energy-related light-based applications is the suitable transformation between photons of different energies. A prototypical example of an energy-related application using photon transformation is given by a phosphor-converted white light emitting diode (pc-WLED), where the light emitted by a LED at wavelengths ranging from near UV to blue, is subsequently converted by a phosphor to produce the emission of the desired white light [2-6]. Another energy-related potential application investigated in recent years involving transformation of photons is the solar spectrum adaptation to enhance the efficiency of photovoltaic (PV) solar cells [7-13]. In this regard, three mechanisms may participate in such adaptation, namely downshifting [7,11,13], downconversion [8,10,12,13] and upconversion [9,10,12,13]. The first process - which is similar to the operative mechanism in pc-WLED- involves transforming a high

Journal Pre-proof

energy photon, where the spectral responsivity of a PV cell is poor, into a lower-energy one for which the spectral responsivity is greater. Unlike downshifting, in downconversion one high energy photon is converted in two lower energy photons. Finally, upconversion is the opposite process to downconversion, i.e. two low energy photons not absorbed by the PV cell are added up to produce one higher energy photon, which at least possesses the energy of the PV cell's bandgap.

The most mature and economically competitive PV technology are cells made of (mono or multi) crystalline silicon (c-Si), which according to recent reports accounts for more than 95% of the commercial PV technologies production [14,15]. Photovoltaic cells based on c-Si have their maximum spectral response under irradiation of light at ~1000 nm (near to the c-Si-bandgap which is around 1.1 eV). Thus, to improve the efficiency of this type of PV cells, any of the three described processes should be focused on transforming the energy of photons coming from the sun into photons of around 1.1 eV. Lanthanide ions have been considered as the prime candidates to accomplish the conversion of photons. Among them, the energy associated with the Yb³⁺ ${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$ transition, which is around 1.2 eV, is comparable to the bandgap of the c-Si photovoltaic cell. Moreover, theoretical calculations have predicted an efficiency of 38.6% for a solar cell made of a semiconductor with a bandgap of 1.1 eV when a downconverter material is coupled to the cell. This efficiency represents an improvement over the theoretical value of 30.9% achieved with a conventional solar cell having the same bandgap.

Recently, we have shown the plausibility of downshifting photons from below 400 nm to near 1000 nm in Yb³⁺-doped SrTiO₃. The operative mechanism of the downshift process is ascribed to an energy transfer between the ligand-to-metal charge transfer state (LMCT) O^{2-}

 \rightarrow Ti⁴⁺ of the host, and the Yb³⁺ [16]. It is reasonable to assume that the same process should be present in other titanates, and the fingerprint to establish the presence of an analogue energy transfer process would be the correspondence between the fundamental transition, revealed in the absorption spectra, and the excitation spectra when the emission of Yb³⁺ is monitored. However, the effect of other extrinsic and intrinsic factors on the energy transfer process to Yb³⁺ in titanates should also be considered.

According to the literature, anatase (a-TiO₂), rutile (r-TiO₂), SrTiO₃, CaTiO₃ and Na_{0.5}Bi_{0.5}TiO₃ have optical bandgap energies in the blue, violet or the near UV, following the order: r-TiO₂ ~ 3.0 eV [17], a-TiO₂ ~ 3.2 eV [18], SrTiO₃ ~ 3.25 eV [19], Na_{0.5}Bi_{0.5}TiO₃ ~ 3.26 eV [20] and CaTiO₃ ~ 3.85 eV [21]. Apart from the band gap values, two other differences on the intrinsic properties among these titanates should be noticed. First, for all the compounds except TiO₂ [22], intrinsic luminescence (in some cases only observed at low temperature) has been assigned to a reverse Ti⁴⁺ \rightarrow O²⁻ transition, associated with a self-trapped exciton [22-24]. Second, for all compounds the valence band has fundamentally *O*-2*p* character, and the conduction band has essentially Ti-3*d* character [22,24-26], except for Na_{0.5}Bi_{0.5}TiO₃ where according to ab-initio calculations, the conduction band has a Ti-3*d* - Bi-6*p* admixture character, although the Bi-6*p* orbital contribution is rather minor [25,26].

Several works reporting on Er^{3+}/Yb^{3+} co-doped titanates emphasizing on the upconversion process have been published [27-31], and despite some works on the luminescent properties of Yb^{3+} single-doped titanates such as a-TiO₂ [32], SrTiO₃ [16], Na_{0.5}Bi_{0.5}TiO₃ [33], and CaTiO₃ [34,35] have also been published; in our opinion, the lack of a systematic understanding with a more general approach about these properties in the latter case remains as an important research topic. In this sense, in addition to some questions not fully understood and pointed below, it is not clear what of those Ti-based compounds may achieve a more efficient energy transfer from the LMCT $Ti^{4+} \rightarrow O^{2-}$ state to the Yb³⁺, nor what is the mechanism that gives rise to it. In TiO₂, there are at first glance two drawbacks for that energy transfer, the huge difference between the ionic size of Ti⁴⁺ and Yb³⁺ making difficult the incorporation of the latter into the TiO₂ crystal structure, and the fact that there is no evidence of the self-trapped exciton formation in TiO₂ even at low temperature [22]. On the other hand, in Yb³⁺-doped Na_{0.5}Bi_{0.5}TiO₃, surprisingly the research has been focused only on the upconversion but not into the Yb³⁺ emission when exciting trough the host [33]. Finally, in the Yb³⁺-doped CaTiO₃ so far, it is unclear the origin of an excitation band around 400 nm [34,35]. In the literature it is associated with impurities and defects, without clearly distinguishing between them, despite they have different implications.

This research aims to gain a more general insight into the influence of the physicochemical properties of the titanate host on the energy transfer process from the LMCT $O^{2-} \rightarrow Ti^{4+}$ state to the Yb³⁺, which may allow to assess the impact of some host intrinsic factors on photon downshifting from near UV-violet to the NIR. For this purpose, the Yb³⁺-doped (0.5 mol%) Ti- based compounds rutile, anatase, SrTiO₃, CaTiO₃ and Na_{0.5}Bi_{0.5}TiO₃ were synthesized by the polymeric complex and sol-gel methods. Their structural, morphological and optical properties were characterized by X-ray Diffraction (XRD); Scanning Electron Microscopy (SEM); diffuse reflectance and luminescent spectroscopies, respectively.

2. Experimental

2.1. Titanium compounds synthesis

For the synthesis of Yb-doped powders of rutile, anatase, SrTiO₃, CaTiO₃ and Na_{0.5}Bi_{0.5}TiO₃, the polymerizable complex and sol-gel methods were used. The starting reagents were titanium isopropoxide (97 %, Sigma-Aldrich), CaCO₃ (J.T. Baker), Sr(NO₃)₂ (99%, Sigma-Aldrich), Na₂CO₃ (99.5%, Sigma-Aldrich), Bi(NO₃)₃-5H₂O (98.9 %, Sigma-Aldrich), Yb(NO₃)₃-5H₂O (99.9%, Sigma-Aldrich), citric acid monohydrate (J.T. Baker), ethylene glycol (99.8%, Sigma-Aldrich), absolute ethanol (J.T. Baker) and deionized water. The Yb³⁺ molar concentration for all the samples was calculated to be 0.5 mol% on a total molar basis of the compounds. For the alkaline earths titanates, it was assumed the substitution of Ca²⁺ and Sr²⁺ by Yb³⁺, then in order to maintain the charge balance for every two lanthanide ions incorporated into the compound, three alkaline earth metal ions were removed from it. In Na_{0.5}Bi_{0.5}TiO₃, it was assumed that Bi³⁺ is substituted by Yb³⁺, while in titanium oxide, the assumption was that Ti⁴⁺ is directly replaced by Yb³⁺.

For Yb-doped calcium titanate, strontium and bismuth-sodium titanate with the nominal compositions $Ca_{1-1.5x}Yb_xTiO_3$, $Sr_{1-1.5x}Yb_xTiO_3$ and $Na_{0.5}Bi_{0.5-x}Yb_xTiO_3$ (x = 0.025), hereafter denoted as $CaTiO_3:Yb^{3+}$, $SrTiO_3:Yb^{3+}$ and $NBT:Yb^{3+}$, respectively, the polymerizable complex method was used. First, absolute ethanol was placed into a baker followed by the addition of titanium isopropoxide. After that, for avoiding titanium isopropoxide hydrolysis, citric acid was added immediately. Once the titanium was in solution, the other reagents were added, depending on the desired composition. Finally, ethylene glycol was poured into the solution (with a citric acid:ethylene glycol molar ratio = 1:4). The final solution was heated at 70 °C until complete evaporation of the solvent, and further at 90 °C for promoting the polymerization. The obtained resin was precalcined

at 370 °C for 45 min. Then, it was crushed in an agate mortar and calcined at 800 °C and 1000 °C for 1 h.

In the case of Yb-doped TiO₂, with the Ti_{1-y}Yb_yO₂ (y = 0.015) nominal composition and hereafter denoted as TiO₂:Yb³⁺, the sol-gel methodology was applied. The first stage is the same as for the polymerizable complex method. Then, Yb(NO₃)₃-6H₂O was added, and deionized water was slowly poured for gel formation. The gel was aged overnight and then dried at 90 °C, followed by milling and finally calcined at 450 °C for 3 h. Despite anatase was present at this synthesis stage, characterization on the Yb-doped anatase and rutile were performed on samples further annealed at 800 °C and 1000 °C during 1 h, respectively.

2.2. Structural characterization

The powders annealed were structurally characterized by X-ray diffraction in a Bruker D8 Advance with Cu K α radiation. The data were measured in the range from 15° to 108° in 2 θ with a step size of 0.020415°, for 76.8 s per point. Crystal structure of the compounds was refined by fitting the whole pattern as implemented in Topas Academic code (v. 4.2) using the fundamental parameters approach [36]. SRM-NIST 660b (LaB₆) [37] was used to determine the instrumental contribution to the X-Ray diffraction patterns. The morphology of the powders was observed by field emission scanning electron microscopy (JEOL JSM-7600F).

2.3. Optical characterization

The absorption spectra were obtained by using the diffuse reflectance technique and measured in a Cary 5 spectrophotometer equipped with a Praying Mantis (Harrick Scientific Products, Inc.) accessory, in the range from 200 nm to 1200 nm. The emission and excitation spectra were recorded with an Edinburgh Instruments FSP920 spectrofluorometer. Detection in the UV-VIS region (200 nm to 870 nm) was performed by a Hamamatsu R928P photomultiplier tube (PMT) that operates in single photon counting mode. For detection in the near-infrared (IR) region (900 nm to 1650 nm) a Hamamatsu G8605-23 InGaAs diode was used. Additional emission spectra in the red-NIR region were recorded with an Edinburgh Instruments FSP980 spectrofluorometer fitted with a Hamamatsu R5509-72 NIR-PMT All the excitation and emission spectra were corrected for the wavelength dependent responses of the Xe-lamp and the detector, respectively.

3. Results and discussion

3.1. Crystal structure and morphology

The XRD patterns of SrTiO₃:Yb³⁺, NBT:Yb³⁺, CaTiO₃:Yb³⁺ and TiO₂:Yb³⁺, are shown in Fig. 1. Samples annealed at 800 °C and 1000 °C for 1 h are depicted in Figs. 1(a) and 1(b), respectively. As it is observed in Fig. 1(a) corresponding to the compounds annealed at 800 °C, TiO₂:Yb³⁺ exhibits mostly anatase but rutile is also observed. Both crystalline phases match with the 00-021-1272 and 04-003-0648 PDF cards, respectively. Noteworthy is the fact that the incorporation of Yb³⁺ into TiO₂ stabilizes the anatase phase at 800 °C in comparison to the undoped sample which exhibits mostly rutile phase, as it can observed in Fig. S1 where the X-ray diffraction patterns of all undoped samples annealed at 800 °C and 1000 °C are shown. CaTiO₃:Yb³⁺ presents the same orthorhombic perovskite-like structure of CaTiO₃, matching well with the 04-007-5451 PDF card, but also it is possible to see the diffraction maxima associated with rutile (almost imperceptible). On the other hand, SrTiO₃:Yb³⁺ and NBT: Yb³⁺ exhibit single phases compatibles with the cubic and

rhombohedral perovskite-like structures of their corresponding undoped compositions. They match with the 04-007-0044 and 01-080-8493 PDF cards, respectively.

As it is seen in Fig. 1(b) the increase in the calcination temperature from 800 °C to 1000 °C promotes the formation of $Yb_2Ti_2O_7$ in the $TiO_2:Yb^{3+}$ and $SrTiO_3:Yb^{3+}$ samples. However, for CaTiO₃:Yb³⁺ and NBT:Yb³⁺, the crystalline phases observed are the same as those present in samples annealed at 800 °C.



Fig. 1 XRD patterns of SrTiO₃:Yb³⁺, NBT:Yb³⁺, CaTiO₃:Yb³⁺ and TiO₂:Yb³⁺ calcined at 800 °C (a) and 1000 °C (b). Appropriate marks for each crystalline phase in the samples presenting impurities are included.

In order to get quantitative data from the XRD patterns such as the cell parameters, average crystallite size and phase concentration, Rietveld refinement analyses were performed. For implementing the Rietveld analyses, we proceeded as follows. For TiO₂:Yb³⁺, anatase was modeled with the tetragonal symmetry described by the *I4*₁/*amd* space group, and a basis containing one Ti⁴⁺ and one O²⁻ at the relative coordinates (0, 0, 0) and (0, 0, z) with an initial z value of 0.2, respectively. Rutile was modeled with the tetragonal symmetry described by the *P4*₂/*mnm* space group, and a basis containing one Ti⁴⁺ at the relative coordinates (0, 0, 0) with initial z and cell parameters values as those reported in [38]. For CaTiO₃:Yb³⁺, the unit cell was modeled

with the orthorhombic symmetry described by the Pnma space group, and a basis containing one Ca^{2+} at the relative coordinates (x_{Ca} , $\frac{1}{4}$, z_{Ca}); one Ti⁴⁺ at the relative coordinates ($\frac{1}{2}$, 0, 0); and two O²⁻, one of them at the relative coordinates (x_{01} , $\frac{1}{4}$, z_{02}), and the other one at the relative coordinates (x_{02}, y_{02}, z_{02}) [39]. Details about the unit cell for the refinement analysis of the $SrTiO_3$: Yb³⁺ compound may be found in [16]. Regarding the bismuth sodium titanate there is no consensus about what structure adopts at room temperature, since in the literature it has been described with both rhombohedral and monoclinic symmetries. In our opinion, this lack of consensus is due to the intrinsic disorder associated with the presence of two cations in the A site of the perovskite-type structure, namely Na⁺ and Bi³⁺, whose ionic radii in dodecahedral coordination for an ideal perovskite are 1.39 Å and 1.45 Å (extrapolated), respectively [40]. Thus, for the refinement analysis of the NBT:Yb³⁺ the unit cell was modeled with the monoclinic symmetry described by the Cc space group, and a basis containing the corresponding fractions of Na⁺ and ${\rm Bi}^{3+}$ at the relative coordinates (x_{Na/Bi}, y_{Na/Bi}, z_{Na/Bi}) but maintaining fixed values of $x_{Na/Bi} = z_{Na/Bi} = 0$ and $y_{Na/Bi} = 1/4$ during refinements; one Ti⁴⁺ at the relative coordinates (x_{Ti}, y_{Ti}, z_{Ti}) ; and three O^{2-} at the relative coordinates (x_{Oi}, y_{Oi}, z_{Oi}) (i = 1, 2, 3). The initial cell parameters and relative coordinate values were those reported in [41]. However, we speculate that for the reasons presented previously, the fit between the experimental data and the calculated ones was not as good as those for the other titanium compounds. The results of the Rietveld refinement analyses such as concentration (wt%) for the phases present in each compound, average crystallite size, cell parameter and R_{wp} values, are summarized in Table 1. The equivalent data for the undoped compounds are shown in Table S1.

Fig. 2 shows representative plots from among all resulting refinement analyses corresponding to CaTiO₃:Yb³⁺ and NBT:Yb³⁺ annealed at 800 °C and 1000 °C, (similar plots for the undoped compounds are presented in Fig. S2). The figures of merit (R_{wp}) for these fits are given in Table 1. As it is seen in Fig. 2, the R_{wp} values < 10% are compatible with the good agreement between experimental and calculated data. We attribute the slightly higher R_{wp} value (~ 9.8%) for NBT:Yb³⁺ due to the local disorder in this phase.

800 °C							
Sample	Phases found	Concentrati on phase (wt. %)	Average crystallite size	a (Å)	b (Å)	c (Å)	R _{wp}
	Anatase	96.0(1)	27.8 (2)	3.78607 (15)	3.78607 (15)	9.50699 (43)	8.2
TiO_2 :Yb ³⁺	Rutile	4.0 (1)	22.1 (1)	4.5966 (13)	4.5966 (13)	2.9587 (18)	-
	CaTiO ₃	97.2 (1)	86.0 (7)	5.43896 (17)	7.64158 (23)	5.38164 (16)	8.0
CaTiO ₃ :Yb ³⁺	Rutile	2.8 (1)	31 (2)	4.59078	4.59078	2.95696	-
				(100)	(100)	(119)	
NBT:Yb ³⁺	NaBiTiO ₃	100	29.0 (5)	9.52010	5.48693 (26)	5.49162 (36)	9.3
				(101)			
SrTiO ₃ :Yb ³⁺	SrTiO ₃	100	41.2 (2)	3.90699 (6)	-	-	5.2
			1000 °C	,			
TiO ₂ :Yb ³⁺	Rutile	95.6 (1)	175 (1)	4.59284 (4)	4.59284 (4)	2.95934 (3)	8.3
	Yb ₂ Ti ₂ O ₇	4.4 (1)	66 (1)	10.03176	-	-	-
				(29)			
CaTiO ₃ :Yb ³⁺	CaTiO ₃	96.3 (1)	167(2)	5.43704 (11)	7.63993 (15)	5.38070(11)	8.0

 $\label{eq:constant} \textbf{Table 1} Lattice \ parameter, \ average \ crystallite \ size \ and \ R_{wp} \ of \ SrTiO_3: Yb^{3+}, \ NBT: Yb^{3+}, \ CaTiO_3: Yb^{3+} \ and \ States \ average \ States \ State$ $TiO_{\bullet} \cdot Yh^{3+}$ calcined at a) 800 °C and b) 1000 °C

On the other hand, comparison among data presented in Tables 1 and S1 (undoped samples) allows to demonstrate the Yb³⁺-doping effect on crystalline features of the titanates. It may be summarized as follows: for TiO_2 addition of Yb^{3+} stabilizes the anatase phase for the annealing at 800 °C (TiO2:Yb3+ possesses 96 wt% of anatase and 4 wt% of rutile, while TiO₂ is made of around 94 wt% of rutile and 6 wt% of anatase). The undoped samples (with the sole exception of CaTiO₃) do not have secondary crystalline phases,

102(5)

109(2)

75.7 (4)

35 (2)

4.58890 (35)

9.52022 (46)

3.90526(4)

10.0354 (13)

4.58890 (35)

5.48182 (11)

Rutile

SrTiO₃

NaBiTiO₃

Yb₂Ti₂O₇

NBT:Yb³⁺

SrTiO₃:Yb³⁺

3.7 (1)

98.0(1)

2.0(1)

100

2.95738 (34)

5.48856 (38)

9.8

5.6

while all doped samples have secondary phases, except for NBT:Yb³⁺ and SrTiO₃:Yb³⁺ annealed at 800 °C. Despite the thermodynamic equilibrium regarding the incorporation of lanthanide ions into transition metal oxides deserves research attention, this topic is out of the scope of this work. However, why in NBT:Yb³⁺ no secondary phases are formed is easy to understand. In this compound, the substitution of Bi³⁺ by Yb³⁺ is due to their physicochemical similarities, i.e., they have the same valence and similar size (ionic radii (both extrapolated) of 1.45 Å and 1.22 Å, respectively [40]). Regarding the average crystallite sizes Yb³⁺-doping leads to its reduction as has been previously reported for SrTiO₃ [16]. Finally, differences in the lattice parameters among undoped and Yb³⁺-doped samples in general, are not conclusive about the site occupancy of Yb³⁺ in the synthesized titanates, except for the NBT where the reduction in the crystal cell dimensions is compatible with the substitution of Bi³⁺ by Yb³⁺.



Fig. 2 Refinement plots of CaTiO₃:Yb³⁺ calcined at 800 °C (a) and 1000 °C (b), and NBT:Yb³⁺ calcined at 800 °C (c) and 1000 °C (d). The scatter crosses and the upper solid line correspond to the experimental and calculated data, respectively. The lower curve is the difference between them. The vertical marks on the bottom represent the Bragg reflections associated with the indicated crystalline phase.

In Fig. 3 are depicted the SEM micrographs of powder samples of TiO_2 :Yb³⁺, CaTiO₃:Yb³⁺ and NBT:Yb³⁺, annealed at 800 °C (Figs. 3 (a), (b) and (c)) and 1000 °C (Figs. 3 (d), (e) and (f)) for 1 h. As it can be seen the powders are made of particle agglomerates. For the samples of TiO_2 :Yb³⁺ and CaTiO₃:Yb³⁺annealed at 800 °C, the particles have a regular shape with a size smaller than 100 nm. Meanwhile for NBT:Yb³⁺, the particles have sizes around a few hundreds of nanometers and their shapes do not present any regularity. On the other hand, the only conspicuous feature of samples annealed at 1000 °C is the larger sizes

Journal Pre-proot

of the particles as compared with those annealed at 800 °C, but they are also in the nanometric scale. These findings are consistent with the results of the refinement analyses.



Fig. 3. SEM micrographs of powder samples of TiO_2 : Yb³⁺, CaTiO₃: Yb³⁺ and NBT: Yb³⁺, annealed at 800 °C ((a), (b) and (c)) and 1000 °C ((d), (e) and (f)), respectively.

3.2. Optical properties

3.2.1. Absorption

In order to get some insight into the optical properties of the titanium compounds, absorption spectra of $SrTiO_3:Yb^{3+}$, $NBT:Yb^{3+}$, $CaTiO_3:Yb^{3+}$ and $TiO_2:Yb^{3+}$ calcined at 800 °C and 1000 °C were recorded by the diffuse reflectance technique (for the spectra of undoped samples see Fig. S3). The absorption spectra are shown in Fig. 4 and all of them exhibit a conspicuous broadband between 200 nm and 400 nm, corresponding to the host absorption, which is ascribed to a ligand-to-metal charge transfer (LMCT) state $O^{2-} \rightarrow Ti^{4+}$ according to previous works. Furthermore, as previously reported in oxides including

titanium in its composition, such as TiO₂, CaTiO₃, SrTiO₃ and NBT, the valence and conduction bands have fundamentally O-2*p* and Ti-3*d* character, respectively [22,24-26]. From Fig. S3, it is observed that the addition of Yb³⁺ into titanates does not have a perceptible effect on the edge and shape of these broad and intense bands associated with the absorption of the O²⁻ \rightarrow Ti⁴⁺ LMCT state but with the absorption tails extending towards larger wavelengths. This result seems to indicate that the fundamental electronic structure of the hosts is little disturbed by the Yb³⁺ doping, being more significant the generation of electronic states within the bandgap due to defects induced by the Yb³⁺ addition. Also, shown in greater detail in the inset of Fig. 4(a), the absorption peaks ascribed to the Yb³⁺ *f*-*f* transition ${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$ are observed.



Fig. 4 Absorption spectra of SrTiO₃:Yb³⁺, NBT:Yb³⁺, CaTiO₃:Yb³⁺ and TiO₂:Yb³⁺ calcined at a) 1000 °C and b) absorption spectra in the 200-450 nm region of titanates annealed at 800 °C and 1000 °C.

3.2.2. Luminescence

The normalized excitation spectra of SrTiO₃:Yb³⁺ ($\lambda_{em} = 980$ nm), NBT:Yb³⁺ ($\lambda_{em} = 978$ nm), CaTiO₃:Yb³⁺ ($\lambda_{em} = 998$ nm) and TiO₂:Yb³⁺ ($\lambda_{em} = 1002$ nm) calcined at 1000 °C are presented in Fig.5. The wavelength (energy) of the broad excitation bands maxima

observed between 300 nm and 425 nm, are 416 nm (2.98 eV) for $CaTiO_3:Yb^{3+}$, 383 nm (3.24 eV) for NBT:Yb³⁺, 356 nm (3.48 eV) for SrTiO_3:Yb³⁺, and 404 nm (3.07 eV) for TiO_2:Yb³⁺. Noticeably, the values for those maxima agree reasonably well with the bandgap energy values calculated from the reflectance spectra depicted in Fig. 4 and Fig. S3 (presented in Table S2) for each compound, except for CaTiO_3:Yb³⁺. However, for this last compound the maximum whose value is consistent with the bandgap energy is that one clearly defined at 330 nm (3.76 eV). The origin of the excitation peak at 416 nm in CaTiO_3:Yb³⁺ will be discussed later.



Fig. 5 Luminescence spectra of $SrTiO_3$: Yb^{3+} , NBT: Yb^{3+} , $CaTiO_3$: Yb^{3+} and TiO_2 : Yb^{3+} calcined at 1000 °C. (a) Normalized excitation spectra, and (b) emission spectra.

The emission spectra (Fig. 5 (b)) were recorded exciting with light corresponding to the excitation peak for each case, namely 356 nm for SrTiO₃:Yb³⁺, 383 nm for NBT:Yb³⁺, 416 nm for CaTiO₃:Yb³⁺, and 404 nm for TiO₂:Yb³⁺. In all samples emission bands in the range from 900 nm to 1100 nm corresponding to the ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ transition of Yb³⁺ are observed. Thus, the excitation and emission spectra in Fig. 5 demonstrate that, in all these titanium compounds, not only in SrTiO₃:Yb³⁺ as showed recently [16], some energy transfer process

is being operative between the LMCT $O^{2-} \rightarrow Ti^{4+}$ state of the host and the Yb³⁺ electron energy states. Regarding this result, the intriguing fact is why despite the large difference between the LMCT $O^{2-} \rightarrow Ti^{4+}$ state energy (3.07 eV to 3.76 eV) and the excitation energy of the Yb³⁺ (\Box 1.27 eV) that energy transfer occurs. Also, from Fig. 5(b) it is noticed that the Yb³⁺ emission intensity depends on the host. In Fig. 6 the integrated emission intensity for each compound annealed at 800 °C and 1000 °C is shown. As it is observed, when the annealing temperature increases the integrated emission intensity also increases and, depending on the host, it follows the order $I_{Yb}^{3+}(NBT:Yb^{3+}) > I_{Yb}^{3+}(CaTiO_3:Yb^{3+}) >$ $I_{Yb}^{3+}(SrTiO_3:Yb^{3+}) > I_{Yb}^{3+}(TiO_2:Yb^{3+})$. Since it is well known that defects on the surface of crystallites contribute to the luminescence quenching, the reduction of those defects due to the crystallite growth with increasing calcination temperature, and supported by the refinement analyses results, is consistent with that rising of the integrated emission intensity.

In relation to the dependence on the Yb³⁺ emission intensity with the host, according to previous experimental and theoretical reports, it is possible to speculate about different reasons: the degree of the delocalization-localization of the LMCT $O^{2-} \rightarrow Ti^{4+}$ state [22]; the subtle additional contributions to the LMCT state arising from the weak hybridization between O-2p, Ti-3d orbitals with Ca-4s, Sr-5s, Na-2s, Na-2p, Bi-6s and Bi-6p orbitals. Moreover, the strong hybridization between the O-2p and Ti-3d orbitals within the valence and conduction bands being mainly O-2p in character the former and Ti-3d in character the latter [22,24-26,42]. Finally, electronic defects within the band gap.

Regarding the first proposed reason, since the intrinsic luminescence is assigned to a reverse $Ti^{4+} \rightarrow O^{2-}$ transition (when present in titanates at low temperature), the formation

of an exciton, i.e. a localized state, could favor the energy transfer between the LMCT $O^{2-} \rightarrow Ti^{4+}$ state and the Yb³⁺. However, no intrinsic luminescence is observed in r-TiO₂ [22], and the Stokes shifts between the maxima of excitation and emission are 0.9 eV for SrTiO₃ [22], 1.29 eV for CaTiO₃ [38], and although no information about the Stokes shift value at low temperature has been reported for NBT, its room temperature value seems to be very small [28]. Those Stokes shifts are far from matching the energy to bring the Yb³⁺ from its ${}^{2}F_{7/2}$ ground state to its ${}^{2}F_{5/2}$ excited state. Thus, this evidence does not convincingly answer the question about how the energy transfer process LMCT \rightarrow Yb³⁺ proceeds.



Fig. 6 Integrated emission intensity of $SrTiO_3$: Yb^{3+} , NBT: Yb^{3+} , $CaTiO_3$: Yb^{3+} and TiO_2 : Yb^{3+} calcined at 800 °C (black line) and 1000 °C (red line) excited via the LMCT $O^{2-} \rightarrow Ti^{4+}$ state. Open squares represent the integrated emission intensity of $CaTiO_3$: Yb^{3+} exciting at 416 nm. It should be noticed the vertical scale is logarithmic.

All the reported experimental information above-mentioned agrees with the theoretical calculations which indicate that the additional contributions of the Ca-4s orbital in CaTiO₃

and Sr-5*s* orbital in SrTiO₃ to the valence and the conduction bands are negligible and there being no other electronic state associated with them within the bandgap whose energies could contribute to the energy transfer from the host to the Yb³⁺ [42]. But even in NBT where Bi-6*s* and 6*p* orbitals have a more significant contributions to those fundamental electronic bands, the general electronic structure is not so different to the other titanates reported here which may explain the host-Yb³⁺ energy transfer process.

Since neither the modifications to the intrinsic electronic structure of the compounds due to changes in the chemical composition nor the delocalization-localization degree of the LMCT $O^{2-} \rightarrow Ti^{4+}$ state can explain per se the energy transfer mechanism LMCT $\rightarrow Yb^{3+}$ and its efficiency, we decided to explore the third option. In this regard, the excitation spectrum of CaTiO₃:Yb³⁺ gives important clues.

Similar excitation bands as that seen in Fig. 5(a) at 416 nm when monitoring the Yb³⁺ emission at 998 nm, have already been reported in Yb³⁺-doped CaTiO₃ [34,35]. Because there is some ambiguity about their origin, being associated with impurities [34] or with intrinsic defects [35], X-ray fluorescence spectroscopy was performed on CaTiO₃:Yb³⁺ annealed at 1000 °C and no trace of any element that may give place to such excitation band was detected (See Fig. S4). Moreover, we synthesized Yb³⁺-doped CaTiO₃ again but with a 2.5% mol deficiency of Ti⁴⁺ having a nominal composition Ca_{0.9625}Yb_{0.025}Ti_{0.975}O₃ (for further details about synthesis, XRD patterns and their whole fitting (Fig. S5) as well as the absorption spectra (Fig. S6) see Supplementary Information). The excitation and emission spectra of this sample together with those ones corresponding to the compensated-in-charge Ca_{0.9625}Yb_{0.025}TiO₃, i.e., sample denoted as CaTiO₃:Yb³⁺ are presented in Fig. 7. Even though the excitation spectra exhibit a broad and intense band that grows when the

annealing temperature increases, spectral features that make important differences between them are also observed. In the Ti⁴⁺-deficient sample an intensification in the luminescence, as well as a shift in the excitation maxima towards lower wavelengths for both annealing temperatures (maxima at 404 nm and 408 nm for samples annealed at 800 °C and 1000 °C, respectively) in comparison with the compensated-in-charge sample are seen. A subtler difference between both samples is the less pronounced excitation band associated with the LMCT $O^{2-} \rightarrow Ti^{4+}$ state in the Ti^{4+} -deficient compound. Interestingly, the emission maxima ascribed to the ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ Yb³⁺ transition for both samples and annealing temperatures is the same: 998 nm. Therefore, this excitation band should be assigned to CaTiO₃ intrinsic lattice defects, which are expected to be affected by the stoichiometry. This result is also supported by a previous investigation [21]. On the other hand, the integrated emission intensity is almost twice compared to that one observed in the CaTiO₃:Yb³⁺ sample.



Fig. 7. Luminescence spectra ((a) excitation and (b) emission) of the two samples of $CaTiO_3$: Yb^{3+} with different stoichiometry annealed at 800 °C and 1000 °C. Continuous lines correspond to the compensated-in-charge $Ca_{0.9625}Yb_{0.025}TiO_3$ sample, while the dashed ones correspond to the Ti^{4+} -deficient $Ca_{0.9625}Yb_{0.025}Ti_{0.975}O_3$ sample.

In our opinion, defects play an important role in the activation of the Yb^{3+} luminescence in all the titanates presented here, and they may explain in a reasonable way how to overcome

the huge difference between the LMCT state energy and that one required to excite Yb³⁺. In order to validate our hypothesis, emission spectra in the visible and NIR ($\lambda_{em} \leq 900$ nm) of all the Yb³⁺-doped titanates (see Fig. S7) and the undoped CaTiO₃ and NBT NIR ($\lambda_{em} \leq 1150$ nm) (see Fig. S8) annealed at 1000 °C when exciting at representative wavelengths close to the LMCT O²⁻ \rightarrow Ti⁴⁺ state and at the defect level in CaTiO₃:Yb³⁺ were recorded. Fig. 8 shows the absorption spectra of CaTiO₃:Yb³⁺ and NBT:Yb³⁺ and the emission spectra of CaTiO₃ and NBT. In these figures the overlapping between a wide emission band centered at around 850 nm and the Yb³⁺ absorption band is seen. That emission band should be originated from energy levels ascribed to the host but not to the reverse Ti⁴⁺ \rightarrow O²⁻ transition, which is generally quenched at room temperature or, if present, it would be expected to possess a higher energy. Instead, it is possible to associate the emission band centered at around 850 nm with defects within the bandgap. Also supporting the presence of these defects are the tails in the long wavelength region of the diffuse reflectance spectra.

From the previous results it is plausible to assume that defects having energy values close to the energy required to excite Yb^{3+} would be responsible for the activation of its luminescence. In this way we think it is possible to explain the operating mechanism allowing to match processes as dissimilar in energy as those corresponding to the LMCT $O^{2-} \rightarrow Ti^{4+}$ and the Yb^{3+} excited states. Analogous findings also compatible with the abovementioned mechanism and supported on excitation and emission luminescence spectra for all the investigated Yb-doped titanates are presented in Fig. S7. Furthermore, as it is observed from Figs. 5(b) and S8, the intensity of the emission in the visible and the closets NIR correlates with the Yb^{3+} emission intensity for the CaTiO₃ and NBT: the higher the former is, the higher the latter is.

21



Fig. 8. Emission and absorption spectra of CaTiO₃:Yb³⁺ ($\lambda_{ex} = 416$ nm) and NBT:Yb³⁺ ($\lambda_{ex} = 383$ nm) annealed at 1000 °C. The overlap between both spectra is indicated. Dashed lines are incorporated only as a visual guide.

Fig. 9. schematically illustrates the energy transfer process from the LMCT $O^{2-} \rightarrow Ti^{4+}$ state to the Yb³⁺ via the defect-related energy levels within the bandgap. Once the system gains energy via the LMCT state it gradually loses its energy through sequential steps in the defect levels until it reaches one of the lower levels from which energy transfer to Yb³⁺ may occurs. The cut-off in the absorption spectra shown in Fig. 8 support this conjecture since no significant defect levels are present just above the energy required to excite the Yb³⁺, thus avoiding additional energy losses through those levels and favoring the Yb³⁺luminescence activation.

Regarding the defects it is not obvious their origin. In perovskite-like titanates A^{2+} -site and Ti⁴⁺ acceptor vacancies as well as fivefold coordinated TiO₅ defects have been reported [21, 44, 45]. Therefore, in order to determine the detailed nature of the defects present in our titanates, further experimental and theoretical work is necessary.



Fig. 9. Sketches of energy levels and defects within the bandgap and different de-excitation pathways in $CaTiO_3$: Yb³⁺ and NBT: Yb³⁺.

Finally, it is worth noting that compounds such as those investigated in this work offer the possibility to downshift photons from the most energetic region of the solar spectrum towards wavelengths where a c-Si photovoltaic cell possesses its higher spectral responsivity. In Fig. 10 it is schematically shown the whole downshifting photon conversion process considering the relevant properties of the standardized solar spectrum (AM1.5 G) and the c-Si photovoltaic cell. Although more research is required to clarify what is the nature of defects mediating the energy transfer process between the LMCT $O^{2-} \rightarrow Ti^{4+}$ /host state(s) and the ${}^{2}F_{5/2}$ excited level of Yb³⁺, we have presented evidence of the importance of those intrinsic defects in downshifting photons from near UV-violet spectral region to the NIR (950 nm-1050 nm).



Fig. 10. Adapted AM1.5G solar spectrum, c-Si-PVC spectral response and the superimposed excitation and emission spectra for $SrTiO_3:Yb^{3+}$ (ST), NBT: Yb^{3+} (NBT), $CaTiO_3:Yb^{3+}$ (CT) and rutile- $TiO_2:Yb^{3+}$ (r- TiO_2) annealed at 1000 °C. Also, spectrum of anatase- $TiO_2:Yb^{3+}$ (a- TiO_2) annealed at 800 °C is shown.

4. Conclusions

Several Yb³⁺-doped titanate powders of TiO₂ (anatase and rutile) CaTiO₃, SrTiO₃ and Na_{0.5}Bi_{0.5}TiO₃ were synthesized by the sol-gel and polymeric complex methods. After annealing treatment at 800 °C and 1000 °C for 1 h, all they exhibit crystal structures corresponding to those expected for the undoped compounds. The estimated average crystal sizes is in the nanometric range for all compositions and annealing temperatures but smaller for those annealed at 800 °C. Absorption and luminescent excitation spectra are dominated by the presence of an LMCT $O^{2-} \rightarrow Ti^{4+}$ state, except in CaTiO₃:Yb³⁺ for which an intense band ascribed to intrinsic defects dominates the excitation spectrum. Luminescent emission spectra in the NIR when exciting through the fundamental LMCT $O^{2-} \rightarrow Ti^{4+}$ state (or at 416

nm in CaTiO₃:Yb³⁺ ascribed to intrinsic defects) present maxima (978 nm $\leq \lambda_{em_max} \leq 1002$ nm) assigned to the ²F_{5/2} \rightarrow ²F_{7/2} Yb³⁺ transition. Due to the large difference in the involved energies of those states, further luminescence experiments, also when exciting titanates through the host, but recording the emission in the visible and the closest NIR (480 nm-900 nm) were performed. Surprisingly, they reveal broad emission bands that overlap the Yb³⁺ absorption band, thus supporting an energy transfer process between the LMCT O²⁻ \rightarrow Ti⁴⁺ state and the Yb³⁺ excited state mediated by host intrinsic defects that allows to overcome the huge energy difference between them. This finding was additionally corroborated by changing the stoichiometry in a sample of Yb³⁺-doped CaTiO₃ in order to have a deficiency of Ti⁴⁺, and as expected the features of excitation and emission luminescent spectra of the Yb³⁺ when the sample was monitored at and excited through the band ascribed to the intrinsic defects of the host; namely, the change in the wavelength (energy) of the excitation maxima and the increase on the Yb³⁺ emission intensity, demonstrating beyond a reasonable doubt the effect of intrinsic defects on the near infrared photon-downshifting in Yb³⁺-doped titanates,

The Yb³⁺ integrated emission intensity for each compound follows the order Na_{0.5}Bi_{0.5}TiO₃ > CaTiO₃ > SrTiO₃ > TiO₂. Finally, it is possible to say that the fundamental understanding of the energy transfer processes in titanates may lead to the increase of the efficiency in c-Si photovoltaic cells by downshifting photons from the most energetic region of the solar spectrum towards wavelengths where a c-Si photovoltaic cell possesses its higher spectral responsivity

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.ios (Cát ine X-ray fluorescence)

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Highlights

- Yb³⁺-doped anatase, rutile, CaTiO₃, SrTiO₃ and (N_{a0.5}, Bi_{0.5})TiO₃ are synthesized.
 Yb³⁺-emission excited through the O²⁻ → Ti⁴⁺ state in the five titanates is present.

Near infrared photon downshifting from near UV-violet to 1000 nm is achieved.
The energy transfer between the O²⁻ → Ti⁴⁺ state and Yb³⁺ is mediated by intrinsic defects.

• Stoichiometric changes on Yb³⁺-doped CaTiO₃ support that energy transfer mechanism.

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Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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