Structural and optical characterization of crystals obtained via solid state reactions in the In_2O_3 – TiO_2 – Al_2O_3 pseudoternary system

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Abstract

In this article, a synthesis of the compound In_2O_3 – TiO_2 – Al_2O_3 (molar relation 3:4:1 and 5:8:1) at 1350 °C by solid-state reactions is described. The compounds were obtained after heat treatment at 1350 °C for two days. X-ray diffraction patterns indicate that the synthesized samples belong to the monoclinic crystal system with the space group C 2/m. An agglomeration of the crystals was observed by scanning electron microscopy for the heat-treated samples of either composition (S1HT and S2HT). Atomic quantitative analysis showed variations of the two compositions presented and TEM analyses confirmed that $\text{In}_3\text{Ti}_2\text{AlO}_{10}$ crystals were formed. Partial nanocrystallization and irregularities can be observed in the micrographs. Both samples were polymorphic and presented chain discontinuities attributed to oxygen vacancies and/or distortions in the structure. UV–vis measurements were performed obtaining a band gap ~ 3.2 eV for all the samples analyzed. XPS analysis for S1HT and S2HT confirmed the expected oxidation of the compounds.

Keywords Ternary system · Pseudobinary systems · XPS · X-ray · SEM · TEM

1 Introduction

New crystalline materials with novel combinations of physical properties are of great importance for new as well as for existent applications. Pursuing this quest for inorganic systems often means the design and preparation of new or modified existing compounds that provide a sought after combination of certain properties. For example, the fabrication and characterization of nanostructures in inorganic matrices needs to be studied in more depth to improve our knowledge of the underlying mechanisms so that new designs can be developed [1]. With the emergence of nanostructured materials, a new dimension is opened for phase diagrams, as the particle size should now be considered as well [2]. New properties that are related to such

small length scale lead to a wide range of scientific and technological advances [3].

Metal oxides, such as indium oxide (In_2O_3), belong to the important group of transparent conductive oxides (TCO), with properties such as transparency in the visible range and high electric conductivity at room temperature [4]. Titanium dioxide, on the other hand, is considered a material with good characteristics for photocatalysis [2]. Three types of crystalline polymorph phases are possible to obtain for TiO_2 : anatase, rutile, and brookite [5]. Properties and characteristics can be varied between these phases such as photoactivity [5, 6], phase stability [6], strong oxidizing power of the photogenerated holes, chemical inertness, non-toxicity [2], low cost, band gap of 3.2 eV [7], which in turn make it a very interesting material.

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Moreover, metal oxides like alumina (aluminum oxide) add other advantageous properties, such as hard hardness, high corrosion resistance, as well as chemical inertness. The one stable phase of alumina is the α - Al_2O_3 phase and this phase can partially be stabilized by doping with transitions metal oxides as Cr_2O_3 , Fe_2O_3 and TiO_2 [8].

A wide variety of applications for these metal oxides such as solar cells, optoelectronic devices of solid state, UV–vis lasers, detectors and gas sensors [9], hydrogen generation, dye-sensitized solar cells, semiconductors, photocatalysis, self-cleaning and antimicrobial and antifungal activity is now open to these new materials [7].

In the decade of 1970, more unusual oxide states and coordination numbers were studied based on the effective ionic radii and as a result, certain types of structures are developed such as rock salt, spinel, perovskite and pyrochlore [10]. Recently, the synthesis of $\text{R}_2\text{Ti}_2\text{O}_7$ having a pyrochlore-type structure has been achieved [11]. However, discrepancies in the synthesis to obtain this phase were reported [12, 13] and for this reason, new compounds were synthesized based on the pseudoternary system In_2O_3 – TiO_2 – $\text{M(III)}_2\text{O}_3$ (M(III): Al, Cr, Mn, Fe, or Ga) as well as In_2O_3 – TiO_2 – $\text{M(II)}\text{O}$ (M(II): Mg, Mn, Co, Ni, Cu, or Zn) [4]. Studies of the pseudobinary system InAO_3 – $\text{In}_2\text{Ti}_2\text{O}_7$ revealed that two types of layered composite crystals were formed [4, 11, 14]. These studies suggested the possibility of the formation of solid solution along “ InAO_3 ”–“ $\text{In}_2\text{Ti}_2\text{O}_7$ ” system. The solid solution obtained presented two related crystal structures to the pyrochlore structure that is a monoclinic and orthorhombic structure [11].

In the current work, synthesis as well as structural and optical characterization of inorganic compounds of the In_2O_3 – TiO_2 – Al_2O_3 system were performed for materials prepared in the molar ratios: 3:4:1 and 5:8:1. The molar composition In_2O_3 – TiO_2 – Al_2O_3 of 3:4:1 represents the intersection of the “ InAO_3 ” and “ $\text{In}_2\text{Ti}_2\text{O}_7$ ” line in the aforementioned pseudobinary. The molar ratio In_2O_3 – TiO_2 – Al_2O_3 of 5:8:1, was chosen to as closest pseudobinary of the solid solution of the “ InAO_3 ” and “ $\text{In}_2\text{Ti}_2\text{O}_7$ ” line to the known compound $\text{In}_3\text{Ti}_2\text{AlO}_{10}$ [4]. Structural and microscopic studies revealed the monoclinic structure of the compounds and their nanocrystallization after heat treatment. XPS studies were conducted for the compounds S1HT and S2HT in order to obtain the oxidation state of the elements. TEM analysis showed the variations between both samples studied. Nanocrystallization as well as the irregularities in these compounds are reported.

2 Experimental details

Two In_2O_3 – TiO_2 – Al_2O_3 samples were prepared in the molar ratio 3:4:1 and 5:8:1 for S1 and S2, respectively. Before synthesis, the respective oxide powders of the

raw materials were heated for a period of 24 h at 850 °C under air atmosphere to obtain the dry oxide powders. The oxides were then mixed for 30 min in an agate mortar, here, acetone was added for improved homogenization. For the solid-state reaction: the homogenized mixtures were pelletized, each pellet was weighted and placed in an alumina crucible before heating for 2 days at 1350 °C in an electric Thermolyne furnace model 46100 (Thermo Scientific, Wilmington, DE, USA). Heating was conducted under air atmosphere and after completion of the fixed heating periods were the pellets rapidly cooled and weighted once more. Both heat treated samples S1 and S2 showed phase stability of the synthesized samples after an analogue second heat treatment period of 2 days at 1350 °C. These products will be named S1HT and S2HT in this paper (Scheme 1).

Scheme 1 Diagram of the preparation process of In_2O_3 – TiO_2 – Al_2O_3 compounds S1, S2, S1HT and S2HT by solid state reaction

All the samples were pulverized to obtain X-ray diffractograms using a Rigaku D/Max-B Geigerflex diffractometer (Tokyo, Japan) with a Cu K α line. The detector was of the scintillator type (NaI doped with Thallium) using the following grating DS: 1°, SS: 1°, RS: 0.15 mm, RSm: 0.6 mm and a glass holder. The range extended from 5° to 100° with a step size of 0.02° (2 θ) and the scan speed was 2°/min (2 θ). All the diffractograms were measured in the continuous mode.

XPS measurements for the samples S1HT and S2HT were carried out in a PerkinElmer PHI 5100 photoelectron spectrometer (Eden Prairie, MN, USA) with an Mg anode generating a nonmonochromatic K α radiation of 1253.6 keV, these samples were carried out with 15 kV and 20 mA. The pressure in the analysis chamber was maintained approximately at 10⁻⁹ Torr during each measurement. For all the samples, a wide range of surveys was taken at a pass energy of 71.55 eV and a step size of 0.5 eV in 5 sweeps. The high-resolution spectra of C 1s, In 3d, Ti 2p and Al 2p were performed at a pass energy of 22.36 eV and a step size of 0.025 eV for each region. All binding energies were referenced to adventitious carbon C 1s at 284.8 eV. The In 3d, Ti 2p, and Al 2p spectra were fit using a Voigt1 function to determine center, full width at half-maximum (FWHM) and integrated area of each peak.

The optical absorption was characterized by using a spectrophotometer PerkinElmer Lambda 20 (CT, USA) within the range of 380–800 cm⁻¹. SEM micrographs were obtained using a JEOL JSM-5410LV microscope (Tokyo, Japan) and Energy Dispersive X-ray (EDS) analysis was performed using a JEOL JSM-5410LV equipped with an INCA system and an EDS microanalysis detector Oxford X-Max (Buckinghamshire, UK) operated at 20 kV. The TEM micrographs of the samples S1HT and S2HT were obtained using a JEOL TEM-2010F electron microscope (Tokyo-Japan) operating at 200 kV. For TEM characterization, a drop of 10 μ l of the S1HT and S2HT sample suspension was deposited on a carbon-coated copper grid (300 mesh).

3 Results and discussion

3.1 X-ray characterization

The X-ray diffraction patterns for the sample S1, S2 and S1HT, S2HT are shown in Fig. 1 within the 2 θ range from 5° to 100°. Heat treatment was performed to stabilize the compound, sharper diffraction patterns emerged after heat treatment and the intensities in some planes increased. The analyzed samples correspond to the diffraction pattern of aluminum indium titanium oxide (In₃Ti₂AlO₁₀), a monoclinic crystal system with a space group of C 2/m (ICDD PDF card No. 00-053-0383) from

the primary reference N. Kimizuka, Hermosillo, Sonora, México, Private Communication, (2001) [4]. S2 and S2HT presented the rutile phase of TiO₂ in solid solution (ICDD PDF card No. 96-900-7532) [15]. It is apparent from Fig. 1a that the preferred orientation of the sample S1 is (0 0 2) which corresponded to the peak at 2 θ = 29.58° and for the heat treated sample 2 θ = 29.62°. For the sample S2, the preferred orientation was at ($\bar{1}$ 1 1) with 2 θ = 32.06° and at 2 θ = 32.08° for S2HT. Comparing both samples (S1 and S2), some differences are evident. As can be observed from Fig. 1, the peaks at 2 θ = 30.72° and 2 θ = 32.20° from the sample S1 show a shoulder at around 2 θ = 31.04° and 2 θ = 31.64°, respectively, the sharpness of these peaks decreased for the sintered material. For sample S2, sharper peaks at these positions were obtained and no shoulders are evident as in the case of S1 (see also magnification in Fig. 1b). In general, comparing the samples S1, S2, S1HT and S2HT, the intensities of the peaks varies between the different samples as seen in Fig. 1, shifts and/or higher intensities of some peaks are evident and these changes are easier to observe after 2 days of heat treatment. As seen in Fig. 1b, the peaks related to the monoclinic structure can be identified at ~36.4° and ~39.5° (2 θ) for all samples in agreement with the lattice parameters obtained in this work and the literature [16]. An interesting behavior is apparent for samples S1 and S1HT with the appearance of the peaks at ~34.1° and ~43.1° (2 θ). It should be noted, that these two samples also show the characteristics peaks of the monoclinic phase, this is indicative for a phase transition to the orthorhombic phase after heat treatment [16]. The formation of such a phase will be discussed later in more detail in Sect. 3.5 and Fig. 8 HRTEM. Also, X-ray diffraction patterns present the intensive peak at 27.44° for rutile TiO₂. The variation of the intensity of this peak can be taken as indicator for the stability of the solid phase for sample S2HT as observed in the HTEM comparing this sample with S1HT, respectively.

Similar XRD results were presented by Wenjie et al. and therefore were compared with the samples reported in this work. Wenjie et al., obtained shifts of the X-ray diffraction peaks, demonstrating the incorporation of In³⁺ by substituting Ti⁴⁺ ions in TiO₂ crystal lattice. A shift of the peaks position to a lower angles was also observed in this work and might be attributed to the same substitution due to the larger ionic radius of In³⁺ ion (0.81 Å) compared with Ti⁴⁺ ions (0.68 Å) and as a result, an increment of the lattice parameters and the interplanar distance can be presented as a shift of diffraction peaks leading to the lattice expansion [17]. Moreover, Benjaram M. Reddy et al. suggested that Ti partially can be substituted by Al in the octahedral sites during the synthesis of the compounds due to a slight difference of charges between these cations and similar

Fig. 1 **a** X-ray diffraction patterns of the samples: S1, S2, and S1HT, S2HT in the range 5° to 100° (2θ). **b** Magnification of the X-ray diffraction patterns for the same samples for the range 29° to 44° (2θ)

size, as the ionic radius of octahedrally-coordinated Ti(VI) is 0.605 Å and for the octahedrally-coordinated Al(III) ions is 0.53 Å. It is interesting to mention that for this cation substitution one site should remain vacant and for an instant the diffusion of the smaller aluminum ions might be favored by the heat treatment received [18]. Furthermore, is important to remark that a rapid way for diffusion can be provided through the grain boundaries [19] and while at the same time, impurities and defects can also originate from diffusion [20].

The Bragg's diffraction formula [21, 22] was used to obtain the interplanar spacing (*d*). This equation can be used to determinate the lattice constants *a*, *b* and *c* from the value 2θ of the X-Ray Diffraction, with the interplanar spacing (*d*) and Miller indices (*h k l*). The lattice constants *a*, *b* and *c* for monoclinic crystal system of ($\text{In}_3\text{Ti}_2\text{AlO}_{10}$) presented in the compounds were obtained with the interplanar spacing (*d*) of the monoclinic structure [23] and it was calculated substituting the value (*d*) using the adequate equation with the first order approximation,

$n = 1$ [22] in the Bragg's diffraction equation. The lattice constant (*a*) for (3 1 0) plane was calculated from the substitution of the Miller indices *h*, *k*, *l* in the appropriate equation of the monoclinic structure for the interplanar spacing (*d*) and the Bragg diffraction formula. The same procedure was applied to obtain the lattice constant (*b*) and (*c*) using the plane (0 2 0) and (0 0 1), respectively. The results of the lattice constants *a*, *b*, *c* of the monoclinic phase of ($\text{In}_3\text{Ti}_2\text{AlO}_{10}$) were: *a* = 5.8407 Å, *b* = 3.3703 Å and *c* = 6.3350 Å (S1), *a* = 5.8644 Å, *b* = 3.3865 Å, *c* = 6.3522 Å (S2), *a* = 5.8382 Å, *b* = 3.3703 Å, *c* = 6.3350 Å (S1HT) and *a* = 5.8600 Å, *b* = 3.3853 Å, *c* = 6.3522 Å (S2HT) confirming the results with the ICDD PDF card No. 00-053-0383.

The cell volume was calculated with the equation of the monoclinic structure [23] and the results obtained were: 118.687 Å³ (S1), 120.067 Å³ (S2), 118.636 Å³ (S1HT) and 119.934 Å³ (S2HT). Similar results were found in the ICDD PDF card No. 00-053-0383. The decrement of the oxygen occurred in the samples with the heat treatment applied and it can be due to an oxygen substitution [24].

Although the Scherrer's equation presents a restriction for average sizes up to 100–200 nm [25], the crystallite size (D_{hkl}) in the direction perpendicular to the lattice planes hkl can be calculated using the Scherrer's equation [25–27] with the Full Width at Half Maximum (FWHM) of the X-ray diffraction peak in radians, $K=0.9$ as a good approximation in absence of the detailed shape information, λ as the wavelength of the X-rays (1.5406 Å) and θ is the Bragg angle [25, 26]. The values calculated for the crystallite size for the samples analyzed were: 52.42 nm (S1), 48.20 nm (S2), 53.19 nm (S1HT) and 46.82 nm (S2HT).

3.2 XPS spectra

The XPS spectra of the samples S1HT and S2HT show the core level peaks of indium, titanium, oxygen, carbon, and aluminum. The X-ray induced Auger lines from the named elements were C KVV, In MNN and O KLL as can be observed in the Fig. 2. The peak C 1s ascribed to adventitious carbon was detected at 284.8 eV. Impurities were not detected in the XPS spectra for any of the two heat treated samples. The main elements from the photoelectron peaks were the spin–orbit doublet of In 3d (~444 eV), Ti 2p (~458 eV), In 3p (~666 eV). Also, the peaks of O 1s, Al 2p and In 4d were located at ~530 eV, ~75 eV and ~18 eV, respectively. Moreover, as apparent from Fig. 2, the relative intensities of the elements for the samples S1HT and S2HT are very similar to each other. The spin–orbit doublet of the Ti 2p and In 3d as well as its satellite as mentioned in the literature [28] are displayed in the insert of the Fig. 2 and as can be observed, the intensity of the sample S1HT presented a little more intensive photoelectron peak for

the spin–orbit doublet of In 3d compared to the sample S2HT. Even though the molar relation is higher for the sample S2HT, this can be due to the metal oxidation of the compounds.

3.2.1 In 3d spectra

The high resolution XPS spectra of In 3d for the samples S1HT and S2HT are presented in Fig. 3a and have been fitted for the range from 455 to 440 eV. The spectra of both samples show comparable results. The spectrum of S1HT for the In $3d_{3/2}$ could be deconvoluted into one peak reflecting the oxidation state of indium. For the sample S1HT the position $U_0^*=451.82$ eV and the spin–orbit doublet $3d_{5/2}$ at $U_0=444.21$ eV were assigned to In^{3+} such as in $In_3Ti_2AlO_{10}$ [28–32]. A similar value of the peak mentioned before was reported by Detweiler et al. [33] they found the binding energy of the oxidized species (In^{3+}) at 444.8 eV and related values by Jiayong Gan et al. were found for the In 3d and its spin–orbit doublet attributed to In^{3+} in the main product. In agreement on what is reported in this work for the samples S1HT and S2HT, it can be observed (Fig. 3a) that the chemical state of In does not present a considerable change [34] when comparing the two samples with each other, similar behavior was observed and corroborated with the X-ray diffraction patterns (Fig. 1).

The spectrum of the sample S2HT for the In $3d_{3/2}$ was deconvoluted into one peak centered at $U_0^*=451.68$ eV and their spin–orbit doublet $3d_{5/2}$ at $U_0=444.04$ eV. Both samples (S1HT and S2HT) presented the same peak assignments but the binding energies of the In

Fig. 2 XPS general spectra of the samples S1HT (top) and S2HT (bottom)

Fig. 3 High-resolution spectra of **a** In 3d spin-orbit doublet and **b** Ti 2p spin-orbit doublet for the samples S1HT (left) and S2HT (right)

3d and its spin-orbit doublet showed small differences between them. Comparing both samples as it can be seen in Fig. 3a, the sample S1HT presented a slight shift to higher energies for the peak U₀^{*} and its spin-orbit doublet U₀. This small shift can be related by the oxidation state due to the incorporation of In³⁺ by substitution of Ti⁴⁺ [17]. A shift to higher energies might indicate higher electron density due to the oxidation state presented [33].

3.2.2 Ti 2p spectra

The peaks of the sample S1HT and S2HT for the core level Ti 2p and their spin-orbit doublet are depicted in Fig. 3b. Fitting of two peaks for the high resolution was realized for both samples in the range from 468 to 455.0 eV. The binding energies for the sample S1HT for Ti 2p_{1/2} and Ti 2p_{3/2} were centered at U₀^{*}=463.70 eV and U₀=458.00 eV, respectively and they were attributed to Ti⁴⁺ as in In₃Ti₂AlO₁₀ [29, 35–37] as well as S2HT with U₀^{*}=463.65 eV and U₀=457.87 eV.

3.2.3 Al 2p spectra

The spectrum of the sample S1HT and S2HT was deconvoluted in one peak as shown in Fig. 4a. The peak of the spectrum S1HT for the Al 2p core level at U₀=73.50 eV was assigned to Al³⁺ as in In₃Ti₂AlO₁₀ [29, 38, 39]. However, it is noteworthy that at high-temperature α-Al₂O₃ is obtained in more proportion as mentioned in the literature [40]. Even though a high temperature was used in this work, this phase was not observed in the X-ray diffraction patterns. Besides, the peak at U₀=73.45 eV of the sample S2HT (Fig. 4b) was attributed to the same component as the sample S1HT. A comparison of the sample S1HT in contrast to the sample S2HT was presented. The same molar relation was involved in both samples analyzed, but the intervention of the Ti⁴⁺ as mentioned before by Reddy et al. [18] might be an influence in the Al 2p and oxidation occurred to both samples as observed in Fig. 4.

Fig. 4 High-resolution spectra of **a** Al 2p core level for the sample S1HT (left, **a**) and **b** Al 2p core level for the sample S2HT (right, **b**)

Fig. 5 Normalized absorbance spectra of samples S1HT with a thickness of 2.54 mm, S2HT with a thickness of 3.12 mm, the inset shows the direct band gap determination by Tauc plots

3.3 UV–vis spectra

Figure 5 shows the absorbance of the samples S1HT and S2HT. The band gap edge as seen in Fig. 5 is located for these samples around 385 nm. The thickness of the sample S1HT was 2.54 mm and 3.12 mm for S2HT. As observed in Fig. 5, the background of the samples S1HT and S2HT is low, and a better transmission of the samples is obtained with heat treatment. The equation proposed by Tauc and Menth [41] to calculate the optical band gap (E_{opt} or also denominated E_g or E_g^{opt}) depends on the type of the electronic transition, $m = 2$ for indirect allowed transition [42]

and $m = 1/2$ for direct band gap [43, 44]. Otherwise, the absorbance can be used to determinate the band gap energy and as mentioned in the literature [45], where $A \approx 1 - (1 - OD) = OD$ for low optical density [45], the spectra of both samples were fitted to a linear equation for direct transition and it was calculated as following [46]:

$$(OD * E)^2 = A(E - E_g) \quad (1)$$

where OD is the optical density, $E = h\nu$ is the energy of the incident photon, A is a constant and E_g is the energy band gap [46]. The band gap was obtained by extrapolation

plotting [43] of the graphic $[(\text{Absorbance})^2 \cdot (h\nu)^2]$ versus the photon energy $h\nu$ as shown in the insert of the Fig. 5.

Indium oxide (In_2O_3) is reported with a direct band gap of 3.6 eV [47, 48] and an indirect band gap of 2.8 eV [49]. Alumina has a band gap of 9 eV and it is considered an insulator [50]. The band gap for TiO_2 is 3.2 eV for anatase and 3.0 eV for rutile [51]. The insert of the Fig. 5 presented good linearity over a wide range of the photon energies corroborating the direct band gap [42]. The band gap obtained for S1HT was 3.23 eV and for S2HT was 3.27 eV. As can be observed, the values between the samples S1HT and S2HT are quite similar. It may be due to the slight differences in the X-ray diffraction pattern. Ayeshamariam et al. point out that the band gap depends on its crystalline structure [52]. A shift to the blue and visible ranges (3.17–3.24 eV) can occur when TiO_2 is doped with Al_2O_3 or other oxides such as In_2O_3 based on the type of dopant and the size crystalline [53]. This shift to blue can be expected when low polarizable oxides are added (Al_2O_3) and a shift to red (3.5 eV) can occur when highly polarizable oxides are added (In_2O_3), this related to polarizability as well as optical basicity mentioned by Dimitrov et al. [54], Rodríguez-González et al. [55].

Similar values of the band gap were obtained by other researchers. Ayeshamariam et al. [52] states a value of $E_{\text{opg}} = 3.268$ eV for a comparable sample that has not been heat-treated. Also, the researchers Tahir and Amin [56] realized compounds of In-doped TiO_2 and they obtained a band gap of 3.22 eV for one of their samples, similar results to our work. The band gaps reported in the literature for In_2O_3 were in the range between 2.3 and 3.8 eV [57].

3.4 SEM and EDS measurements

SEM micrographs and EDS analyses were obtained for samples S1, S2, and S1HT, S2HT. The SEM micrographs are shown in Fig. 6. Sample S1 (Fig. 6a1) presents agglomeration of crystals and shows a low degree of porosity and similar observations are made for sample S2 (Fig. 6a2). Similitudes in SEM characterization by Castillón-Barraza et al. [16] are apparent, they reported a low degree of porosity in all their compounds obtained (ITAM, ITAZ, ITGM, and ITGZ) at 1573 K. Agglomeration of the crystals and irregular particles are also present for the sample S1HT as seen in Fig. 6a3. Particle aggregation can be caused by grinding during the preparation of the compounds [17]. Moreover, it is possible to induce recrystallization during heat treatment and this might occur on the crystal surface as the surface acts as nucleus [58]. The micrograph of the sample S2HT (Fig. 6a4) also depicts agglomerates of crystals and a diffused hexagonal crystal shape is apparent [59]; this agglomeration of crystallization for both samples can contribute to more pronounced grain boundary effects [60]. New sites can be produced, dependent on the detailed nature of the grain boundary [61]. The low porosity for samples S1HT and S2HT confirms a well-sintered morphology for these compounds [16].

EDS characterization was performed for samples S1, S2, and S1HT, S2HT. Elemental oxygen, aluminum, titanium, and indium were detected, and the atomic percentages for the samples are presented in Table 1. As can be observed from the comparison of all the results obtained in EDS analyses, the variation of the atomic percentage of the elements was quite small. A slight variation of the titanium amount for S2HT was associated with the augmentation of the molar relation. The high atomic percentage for the oxygen shown in Table 1 likely was due to residual oxygen contamination in the chamber and also was from the oxide of the alumina, indium, and titanium presented in the compound.

Fig. 6 a1, a2, a3, a4 Micrographs of samples S1, S2, and S1HT, S2HT, respectively

Table 1 Energy dispersive spectroscopy analysis (EDS) from the samples S1, S2, and S1HT, S2HT

Sample	Oxygen (at.%)	Aluminum (at.%)	Titanium (at.%)	Indium (at.%)
S1	76.32	4.00	7.06	12.62
S2	77.39	2.08	9.13	11.41
S1HT	76.55	3.87	7.16	12.42
S2HT	76.51	1.97	10.13	11.40

Fig. 7 TEM analysis of the sample S1HT (**a1**) and S2HT (**a2**) with a scale bar of 100 nm

Fig. 8 High resolution TEM analysis of the sample S1HT (**a1**) and S2HT (**a2**). Simulated FFT (Fast Fourier Transform) was realized for the micrograph in the selected area to obtain the interplanar distances of the material for the sample S1HT (**b1**) and S2HT (**b2**)

3.5 TEM measurements

Figure 7 shows the TEM micrographs of the sample S1HT and S2HT at 100 nm. Similarities were found for both samples as observed in the SEM micrographs. Both samples show crystallization and the shape of the crystals appears similar. Figure 8 presents high-resolution TEM micrographs for samples S1HT and S2HT. Simulated FFT (Fast Fourier Transform) was realized in order to obtain the interplanar distances of the material. Electron diffraction patterns are evident in Fig. 8b1 and b2 for each sample and are highlighted in selected areas as indicated by a white square in Fig. 8a1 and a2. The presence of an electron diffraction pattern of aluminum indium titanium oxide ($\text{In}_3\text{Ti}_2\text{AlO}_{10}$) is confirmed through a simulated FFT analysis, filtering and

IFFT (Inverse Fast Fourier Transform) on the high-resolution TEM micrographs, as indicated in Fig. 8a1 and a2. The electron diffraction pattern observed of the simulated FFT in Fig. 8b1 for sample S1HT confirmed the crystallinity of the compound presented in the selected area of the micrograph (Fig. 8a1). The interplanar distances were determined from the simulated IFFT for samples S1HT and S2HT and they were: $d = 2.8810 \text{ \AA}$ ($\bar{1}10$), $d = 2.7880 \text{ \AA}$ and $d = 2.7950 \text{ \AA}$ ($\bar{1}11$), $d = 2.4570 \text{ \AA}$ (111), $d = 1.9630 \text{ \AA}$ (112), $d = 1.7880 \text{ \AA}$ and $d = 1.7930 \text{ \AA}$ ($\bar{1}13$), $d = 1.6850 \text{ \AA}$ (020), $d = 1.6690 \text{ \AA}$ (plane was not indicated in the ICDD PDF card No. 00-053-0383) and the lowest interplanar distance observed was $d = 1.6330 \text{ \AA}$ (310) and for the sample S2HT were: $d = 3.3870 \text{ \AA}$ (plane was not indicated in the ICDD PDF card No. 00-053-0383), $d = 3.2090 \text{ \AA}$ (plane was not indicated in the ICDD PDF card No. 00-053-0383), $d = 2.7760 \text{ \AA}$ ($\bar{1}11$), $d = 2.0720 \text{ \AA}$ (plane was not indicated in the ICDD PDF card No. 00-053-0383) and $d = 1.6880 \text{ \AA}$ (020). Both samples S1HT and S2HT presented interplanar distances that can be attributed to the monoclinic crystal system of $\text{In}_3\text{Ti}_2\text{AlO}_{10}$ (ICDD PDF card No. 00-053-0383) and also these samples presented polymorphism as mentioned in the literature [4] and are evident in X-ray diffraction patterns. In contrast, the interplanar distances obtained by TEM analysis for the sample S2HT showed at least for some instances a slight shift which can be due to the irregularities of the structure. Due to the fact that an orthorhombic transition or the intervention of rutile (TiO_2) phase for the samples analyzed cannot be excluded, it is not always possible to attribute each plane to a certain morphology. Some interplanar distances observed in the HRTEM micrographs through the filtering of IFFT cannot be assigned the plane belongs due to the similitudes of them.

For sample S1HT, the micrograph indicates a clear orientation of the crystallization compared to sample S2HT. Also, it is important to mention that the micrographs of Fig. 8a1 and a2 of both samples present chain discontinuities of the crystals, which might be attributed to oxygen vacancies and/or distortions in the structure. Moreover, the discontinuities can be associated with the bulk compounds. Otherwise, Al atoms might be playing a fundamental role in the crystallization process at the nanoscale [26, 62]. Comparing both samples analyzed by HRTEM (High-Resolution Transmission Electron Microscopy) (Fig. 8a1 and a2), both present irregularities in the structure and they may be related to the variation of the crystal size. In contrast to the X-ray diffraction patterns, sample S2HT shows sharper peaks than sample S1HT, and this may be due to variations of the bulk compound at a micrometric scale. In addition, the affinity to form nanocrystals might depend on the chemical nature of the materials, structure [63] and also of grain boundaries [62]

and the variation of the crystal sizes can be influenced by the concentration of the raw materials [62] and the affinity to donate oxygen vacancies [64].

The compound obtained in this work shows a distortion of the structure and this can be associated to partial nanocrystallization and for this reason, oxygen vacancies and/or distortions are present in the atomic structure. Similar behavior was reported by A. Ayeshamariam et al. [64] in their research as In_2O_3 nanoparticles are capable to supply conducting electrons in these oxide nanoparticles from the donor sites associated with oxygen vacancies. Moreover, the distortion of the structure can be associated with polymorphism. Bereciartua et al. [65] mentioned that the composition of a solid solution can be varied from x ($\text{InFe}_{1-x}\text{Ti}_x\text{O}_{3+x/2}$) in the range from 0.5 to 0.69. In this range, it is possible to obtain not only the orthorhombic phase but subsequently also the monoclinic phase. In our current study the parameter x for sample S1HT was $x = 2/3$, which is within the reported range and confirms the transition of metastable phase for S1HT to the orthorhombic phase. For the sample S2HT, $x = 4/5$. While the compositional parameter x is outside the reported range, it does coincide with the monoclinic phase [65]. In this compositional range of the solid solution (0.5–0.69), phase variations are expected as x approaches the limits of the range mentioned before. This was for example observed by Bereciartua et al. and therefore, it is difficult to predict the structure [65]. Such phase variations, can be observed in the HRTEM (Fig. 8) and are noteworthy, as the phases observed for S2HT can be metastable due to the TiO_2 phase the latter having been confirmed for this structure in the X-ray diffraction patterns as seen in Fig. 1.

4 Conclusions

In summary, synthesis of the compound was successfully conducted at 1350 °C via a solid state reaction. Crystal structures were obtained for the samples S1, S2, S1HT, and S2HT and all of them corresponded to the X-ray diffraction pattern of the monoclinic phase of aluminum indium titanium oxide ($\text{In}_3\text{Ti}_2\text{AlO}_{10}$). The transition to the orthorhombic phase is possible and was successfully obtained in sample S1HT after heat treatment of sample S1. The excess TiO_2 in composition S2 resulted in the formation of a TiO_2 phase for which the highest intensity peak can be observed for the samples S2 and S2HT. The shift in the XRD peaks for $\text{In}_3\text{Ti}_2\text{AlO}_{10}$ was attributed to the substitution of In^{3+} ions to Ti^{4+} ions due to larger ionic radius of In^{3+} ion and as a consequence of it, an increment of the lattice parameters and interplanar distances was associated with the lattice expansion cell. Moreover, Ti can be partially substituted by Al, resulting in the creation of vacancies. As

a result, the diffusion of smaller aluminum ions may occur along the grain boundaries during the heat treatment and can result in impurities and defects. The binding energy for the deconvoluted peak of the $\text{In } 3d$ core level and its spin–orbit doublet of the sample S1HT and S2HT was attributed to In^{3+} , as in $\text{In}_3\text{Ti}_2\text{AlO}_{10}$ (U_0^* and U_0). The peak for the $\text{Ti } 2p$ core level and the spin–orbit doublet for the sample S1HT and S2HT was assigned to Ti^{4+} , as in $\text{In}_3\text{Ti}_2\text{AlO}_{10}$ (U_0^* and U_0) and $\text{Al } 2p$ core peaks for both samples analyzed were assigned to Al^{3+} , as in $\text{In}_3\text{Ti}_2\text{AlO}_{10}$ (U_0). The Indium and TiO_2 interaction can promote the formation of oxygen deficient/rich species. The band gap of the samples S1HT and S2HT was calculated using the equation proposed by Tauc and Menth based on the type of the electronic transition, in this case, $m = 1/2$ for direct band gap was applied to obtain the values. The band gap for all the samples was around 3.22 eV and with it was based on the dependence of the crystalline structure. Heat treatment did reduce the background scattering and improved the transparency of the samples. SEM micrographs for samples analyzed (S1, S2, and S1HT, S2HT) showed the agglomeration of crystals, indicating more grain boundary effects and recrystallization for enlargement of the crystal. A low degree of porosity was visible for samples S1, S2, and S1HT, S2HT evidencing a well-sintered morphology of the compounds. EDS characterization confirmed the amounts of oxygen, aluminum, titanium, and indium elemental with a small variation of the atomic percentage of the elements. The electron diffraction pattern of aluminum indium titanium oxide ($\text{In}_3\text{Ti}_2\text{AlO}_{10}$) and the crystallinity of the compound were confirmed by TEM micrographs for the sample S1HT and S2HT. The occurrence of an orthorhombic transition, S1HT, or the intervention of rutile (TiO_2) phase, S2HT, cannot be excluded and resulted in variations of some interplanar distances. Some interplanar distances observed in the HRTEM micrographs through the filtering of IFFT cannot be assigned to a certain plane due to the similarity between them. Both samples are polymorphic and present chain discontinuities attributed to oxygen vacancies and/or distortions in the structure. The irregularities in the structure of both samples characterized are related to the size of the crystal and depend on the chemical nature of the materials, structure and also on the grain boundaries. Nanocrystallization occurred in both samples analyzed by HRTEM, these are not homogeneous and thus contributed to obtaining oxygen vacancies product of distortions in the atomic structure.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interests.

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