

Temperature effect on the structural and the optical properties of sol gel CdTiO₃ nanopowders

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Sol gel processed cadmium titanate (CdTiO₃) ceramic has been characterized by X-ray diffraction (XRD), infrared (IR) and Raman techniques. The results confirm that CdTiO₃ crystallizes in the pure hexagonal ilmenite phase at 900 °C and undergoes a transition to the pure orthorhombic structure above this temperature. Furthermore, it was showed that a post-annealing at the temperature of 1100 °C leads to a transition to a new phase with Pbn21 as space group, with the following lattice parameters: $a = 5.30 \text{ \AA}$, $b = 5.43 \text{ \AA}$ and $c = 7.57 \text{ \AA}$. UV-Vis spectroscopy results show that CdTiO₃ band gap energies are strongly affected by the crystallite size and structural properties. The obtained band gap values of ilmenite and perovskite phases are higher than those reported in the literature, whereas that of Pbn21 is slightly lower than that related to Pbnm, probably due to the distortion of Pbnm structure or to the presence of TiO₂ structure.

Key words: CdTiO₃, Sol-gel, Ilmenite, Perovskite, Diffuse reflectance.

Introduction

Cadmium titanate (CdTiO₃) materials have long found many applications in polycrystalline form due to their electro-optical properties [1-3]. CdTiO₃ crystallizes in non-ferroelectric ilmenite or ferroelectric perovskite orthorhombic phase depending on the method of synthesis and/or post-growth annealing temperature [3]. Recent studies have shown that below 1000 °C CdTiO₃ crystallizes in the ilmenite structure and above 1050 °C in distorted orthorhombic perovskite structure [4]. It should be noticed that some previous works based on structural refinements and Raman analysis related to CdTiO₃ crystals concluded that CdTiO₃ structure belongs to the Pbnm space group, ruling out the possibility of existence of the Pbn₂₁ structure [5], or to the Pnma space group [6]. The CdTiO₃ compound has been prepared using different methods such as conventional solid state reaction, sol gel, hydrothermal or the coprecipitation method [1-3]. Several forms were produced as powder, nanofibers, and nanoplate. It however was reported that difficulties to synthesize CdTiO₃ were encountered principally due to volatilization of CdO during the process of preparation [4]. The experimental studies on CdTiO₃ in

the perovskite phase revealed some difficulties and controversies in determining the symmetry group of its orthorhombic structure at room temperature. In order to clarify and understand the properties of the different proposed structures for the CdTiO₃ in the perovskite form, many theoretical studies have been made [7]. The theoretical calculations, using the Full-Potential Linearized-Augmented-Plane-Wave (FLAPW) method, concluded that the proposed Pbnm structure form of CdTiO₃ is stable, contrary to Pbn₂₁ [7]. Comparatively to other perovskite compounds, cadmium titanate has been poorly studied in the powder form [6].

In this study, CdTiO₃ was synthesized using the sol-gel method through the destabilization of colloidal solution (DSC). The structural and optical properties of the CdTiO₃ were examined at different annealing temperatures in order to study the transition between its possible structural forms. The resulting powders were characterized by X-ray diffraction (XRD), Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR). The optical properties of the synthesized powders were determined by ultraviolet-visible (UV-Vis) reflectance spectroscopy.

The sol gel process has been used to prepare the studied samples due to its many advantages in particular the possibility to product pure mixed oxides at relatively low temperature associated to the excellent control of the stoichiometry and the good homogeneity [8-9].

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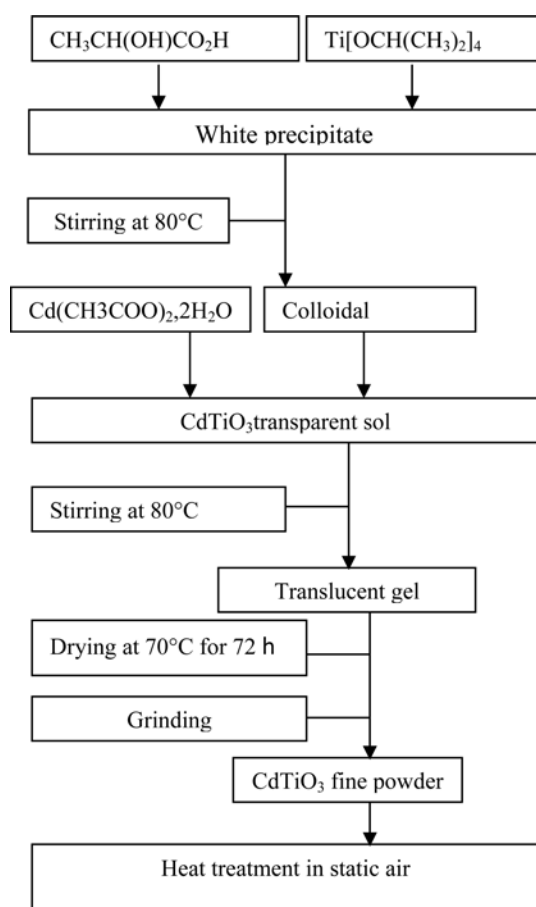


Fig. 1. Procedure to synthesize CdTiO_3 powders.

Experimental Details

CdTiO_3 powders were prepared by the sol-gel method through the destabilization of colloidal solution (DSC). The cadmium acetate ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, Aldrich, 97%) and titanium alkoxide ($[\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$, Aldrich, 97%) have been used as a precursor, the lactic acid ($\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H}$, Aldrich, 90%) as a peptizer and distilled water as a solvent. First, the titanium alkoxide was added to lactic acid aqueous solution under a continuous stirring at 80 °C. After 12 hrs of reaction, the obtained white precipitate is transformed into clear solution. In a second step was added to this colloidal solution the cadmium acetate in a stoichiometric amount. The obtained powders were annealed in static air for 2hrs at 500, 600, 800, 900, 1000 and 1100 °C with a heating rate of 5 °C/min with a systematic dwelling time at 400 °C for 2 hrs in order to eliminate the organic species. The procedure to synthesize CdTiO_3 is presented in the synoptic shown in Fig. 1.

Results and Discussions

The XRD analysis of the samples was realized at room temperature in the Bragg-Brentano geometry

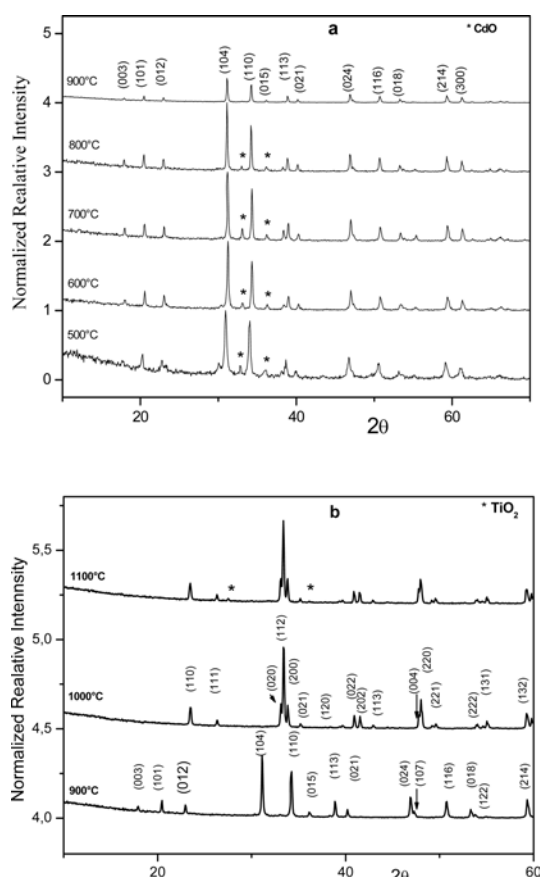


Fig. 2. XRD spectra of CdTiO_3 at different temperatures: (a) at 500-900 °C, (b) at 900-1100 °C.

using $\text{CuK}\alpha$ (1.5406 Å) radiation. The XRD patterns of the annealed powders recorded at different temperatures are presented in Fig. 2. Fig. 2(a) shows the corresponding XRD patterns of powders annealed at temperatures from 500 °C to 900 °C. It is clearly observed that the crystallization of CdTiO_3 in ilmenite phase (space group $R\bar{3}$) begins at 500 °C with the presence of CdO structure. When the temperature increases, the intensity of the peaks related to CdO decreases progressively and the resolution of the peaks corresponding to the ilmenite phase is ameliorated. At 900 °C, the powder is found in a pure ilmenite structure without any secondary phases such as CdO or anatase/rutile TiO_2 ; the obtained ilmenite structure matches well with the JCPDS card n° 00-029-0277. It should be noted that most of the time, the CdTiO_3 structure is formed inseparably of the CdO and/or TiO_2 secondary phases [2].

At 1000 °C (Fig. 2(b)), the CdTiO_3 structure changes from ilmenite to orthorhombic (perovskite) structure with Pbnm as space group in good agreement with the JCPDS Card n. 01-078-1014) without any secondary phase. The estimated lattice parameters of this phase were: $a = 5.29$ Å, $b = 5.42$ Å and $c = 7.57$ Å. This structural change was also reported in the literature [1]

but sometimes at higher temperatures.

As shown in Fig. 2(b), when the temperature reaches 1100 °C the CdTiO₃ Pbnm phase undergoes a slight distortion to orthorhombic phase belonging to the Pbn21 space group in the presence of some traces of rutile TiO₂ (JCPDS, Card n. 01-073-1765). The corresponding lattice parameters are: $a = 5.30 \text{ \AA}$, $b = 5.43 \text{ \AA}$ and $c = 7.57 \text{ \AA}$ which matches well with the JCPDS card n. 01-078-1015. This distortion appears on the diffraction diagram by the broadening and the shifting of the peaks positions (the peak, (retated to reflection (220), located at $2\theta = 48.0635^\circ$ shifts to $2\theta = 48.0293^\circ$) and by a fluctuation in their relative intensities. The presence of traces of TiO₂ observed in the XRD of the sample heated at 1100 °C is due to the volatilization of CdO [4].

Bersani et al. [4] have prepared CdTiO₃ samples and obtained the ilmenite phase at 800 °C with the presence of traces of rutile. A heat treatment of the samples at 1100 °C, revealed the presence, on the corresponding XRD spectrum, of a phase, with some traces of rutile, which they identified as orthorhombic phase, without specifying its space group, and what they called a new phase; the latter corresponds to distorted orthorhombic phase (space group Pbn21) which we have obtained from our study. These authors [4] have not performed a heat treatment at temperatures below 1100 °C so they

have not observed the orthorhombic phase (space group Pbnm).

It is reported through first principles calculations, that CdTiO₃ might have a symmetric Pbnm and a non-centrosymmetric Pbn21 space groups [7], whereas according to theoretical studies it was more suitable to assign the space group Pbnm to CdTiO₃ [7]. The average crystallite size D was estimated from XRD data using Scherrer's equation. Table 1 gives the annealing temperature, the estimated crystallite size, the unit lattice parameters and the phase structure of CdTiO₃. As

Table 2. Comparison of unit cell parameters of CdTiO₃ with the literature.

Phase	Unit cell parameters (Å)			Forme	References
	a	b	c		
Ilmenite	5.23	5.23	14.84	Powder	[1]
	5.23	5.23	14.81	Powder	This work
	5.30	5.42	7.61	Powder	[1]
Pbnm	5.29	5.42	7.57	Powder	This work
	5.24	5.38	7.57		[9]
	5.28	5.40	7.59		[9]
Pbn21	5.23	5.37	7.61		[9]
	5.30	5.43	7.57	Powder	This work

Table 1. Crystallite size, structure phase and unit cell parameters of CdTiO₃ versus temperature.

Annealed temperature (°C)	Crystallite size (nm)	Phase	Unit cell parameters (Å)		
			A	b	c
500	26,59	Ilmenite	—	—	—
600	39,20		—	—	—
700	41,34		5,22	5,22	14,81
800	45,49		5,24	5,24	14,81
900	46,06		5,24	5,24	14,84
1000	43,47	perovskite	5.29	5.42	7.57
1100	35,58		5.30	5.43	7.57

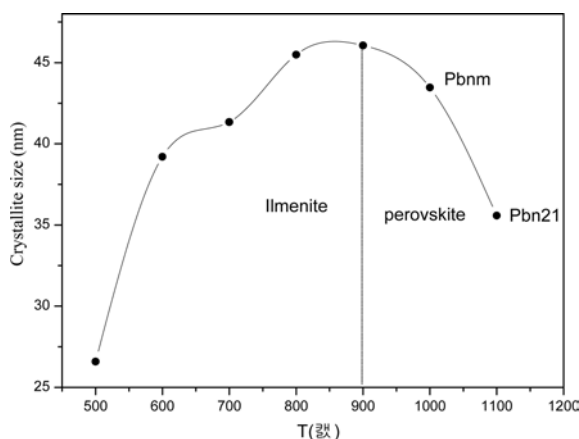


Fig. 3. Crystallite size and structure phase of CdTiO₃ versus temperature.

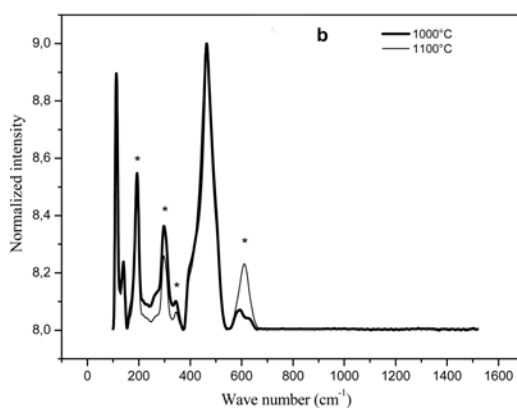
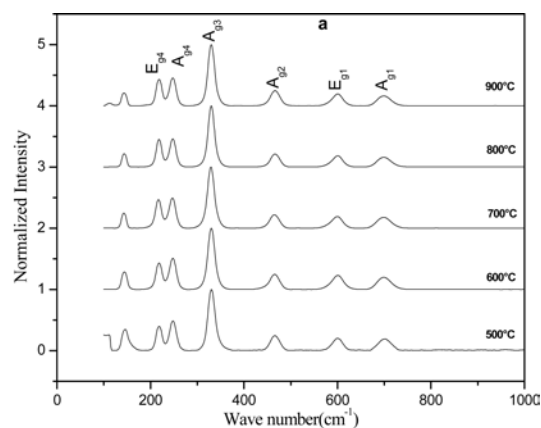


Fig. 4. Raman spectra of CdTiO₃ at different temperatures: (a) at 500 -900 °C, and (b) at 1000-1100 °C.

it is clearly illustrated in this table and in Fig. 3 the crystallite size increases with increasing temperature until 900 °C and then decreases. This result is due to the change of the lattice parameters (i.e change in the crystalline structure). (We know that the grain size increases as function of temperature, and since in our case, it decreases from 1000 °C which shows that environmental gains change (ie., structural change).

Table 2 shows that the estimated lattice parameters of ilmenite and orthorhombic phases of CdTiO₃ are in good agreement with the reported ones [1]. It is worth noticing that the determined lattice parameters for Pbn21 perovskite phase are also in good agreement with the calculated ones [10].

The room temperature Raman spectra of CdTiO₃ powders as functions of the annealing temperature are displayed in Figs. 4(a) and 4(b) within the frequency range of 100-900 cm⁻¹. According to the group factor analysis, the CdTiO₃ ilmenite phase shows six Raman active modes of vibration in the range of 200-700 cm⁻¹ [1], viz:

$$\Gamma = 4 A_g + 2 E_g \quad (1)$$

Raman frequencies for all studied samples are gathered in Tables 3(a), 3(b) and 3(c). By comparison with the previous published Raman spectra of ilmenite phase (Table 3(a)) [11, 15], the obtained Raman bands showed in Figs. 4(a) and 4(b) are assigned to ilmenite modes. The additional peak observed at 143 cm⁻¹ was also reported by Bersani et al, but at 148 cm⁻¹. For powders annealed at temperatures below 1000 °C (Fig. 4(a)), the improvement of peaks intensity following the increase in temperature indicates that the structural evolution is in good accordance with X-ray diffraction results.

However, the Raman spectrum of the prepared powder at 1000 °C (Fig. 4(b)) reveals nine vibrational bands located around 112, 141, 193, 298, 344, 394, 464, 592 and 622 cm⁻¹. Based on the literature and as illustrated in Table 3(b), these frequencies are assigned to B_{2g}, B_{3g}, A_g, A_g, B_{2u}, B_{1u}, A_g, B_{2u} and B_{3u} modes respectively characteristic of the orthorhombic perovskite structure of CdTiO₃ [7, 12]. Moreover, these recorded Raman modes agree well with those calculated [12, 13]. When the temperature increases to 1100 °C, a new peak appears at 611 cm⁻¹ whereas the peaks located at 592 and at 622 cm⁻¹ disappear, this result indicates the existence of Pbn21 or TiO₂ rutile phases.

These available experimental data are compared in Table 3(c) [13] with the calculated frequencies by considering a distortion of the orthorhombic lattice of Pbn21. This comparison points out an agreement between calculated and experimental data and confirms that the sample undergoes a distortion of its orthorhombic structure Pbn21.

Table 3. (a) Comparison of Raman spectra frequencies of CdTiO₃ in ilmenite phase with the literature.

This work	Experiment [4]	Experiment [1]	Experiment [9]	Raman mode
143	148	-	-	-
217	216	216	214	E _{g4}
246	246	246	246	A _{g4}
329	325	325	327	A _{g3}
465	460	461	463	A _{g2}
599	598	598	599	E _{g1}
700	700	694	700	A _{g1}

Table 3. (b) Comparison of Raman spectra frequencies of CdTiO₃ in perovskite Pbnm phase with the literature.

This work	Experimental values		Calculated values		Raman mode
	[11]	[1]	[11]	[12]	
112	-	-	117	-	B _{2g}
141	141	-	140	142	B _{3g}
193	190	-	195	196	A _g
298	295	279	295	290	A _g
344	342	326	353	347	B _{1g}
394	390	400	414	390	B _{1u}
464	461	444	449	-	A _g
592	-	578	-	605	B _{2u}
622	-	-	-	640	B _{3u}

Table 3. (c) Comparison of Raman spectra frequencies of CdTiO₃ in perovskite Pbn21 phase with the literature.

This work	112	141	193	298	344	394	464	611
[12] Theo	117	144	193	298	351	396	466	610
Raman mode	A ₁	A ₁	B ₂	B ₂	B ₁	B ₁	B ₁	B ₁

It is reported that the peaks located at 298, 344, 592 and 622 cm⁻¹ are related to O-Ti-O and Ti-O respectively [1]. Taking into account the XRD results (presence of TiO₂ rutile) one can confirm that Pbnm structure undergoes a distortion towards non-centrosymmetric Pbn21 phase with appearance of traces of TiO₂ rutile phase [14] and that this distortion affects the TiO₆ octahedron. To our knowledge, this result was not reported experimentally in the literature and agrees well with the theoretical work showing that the distortion of CdTiO₃ from Pbnm into Pbn21 is due to the distortion of TiO₆ [6].

The IR curves of the heat treated samples at different temperatures are shown in Figs. 5(a) and 5(b). The spectrum related to the sample annealed at T = 500 °C reveals bands located at 500 cm⁻¹ and around 1390 cm⁻¹, which were assigned [15] to stretching vibration of M-O (Ti-O and Cd-O) and of CO₃²⁻ (residue of precursor in ilmenite phase) (figure 5(a)) respectively. Indeed one can observe the broad band around 660 cm⁻¹, which can probably be due to the existence of one of both M-O (sh face) or M-O (unsh face) (M= Cd and Ti) [16] or

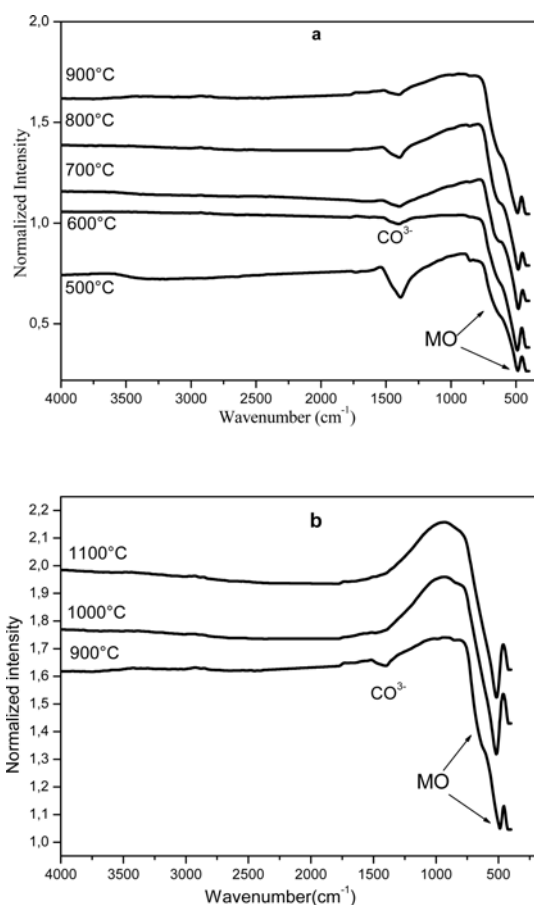


Fig. 5. FT-IR spectra of CdTiO₃ at different temperatures: (a) at 500 -900 °C and (b) at 900-1100 °C.

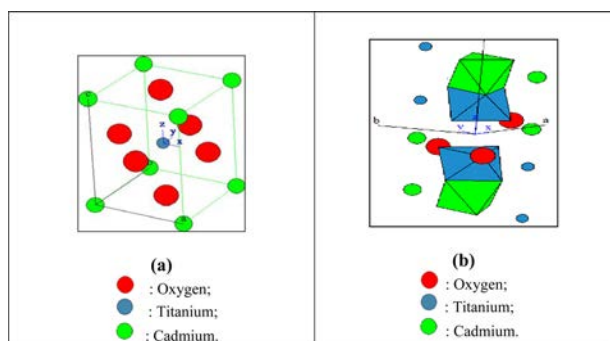


Fig. 6. (a) Perovskite structure and (b) Ilmenite structure of CdTiO₃.

to in-plane bending vibrations of CO₃²⁻ [17]. However, Raman spectra did not show the band at 760 cm⁻¹ related to CO₃²⁻ [18], which confirms that the band located around 660 cm⁻¹ may be related to MO sh or unsh face.

For temperatures above 900 °C (Fig. 5(b)), the bands located at 1390 cm⁻¹ and at 660 cm⁻¹ disappear. The disappearance of the last band may be due to the structural change of CdTiO₃ from ilmenite phase to perovskite one; at 1000 °C in the perovskite phase the faces (M-O) are regular contrarily to ilmenite structure

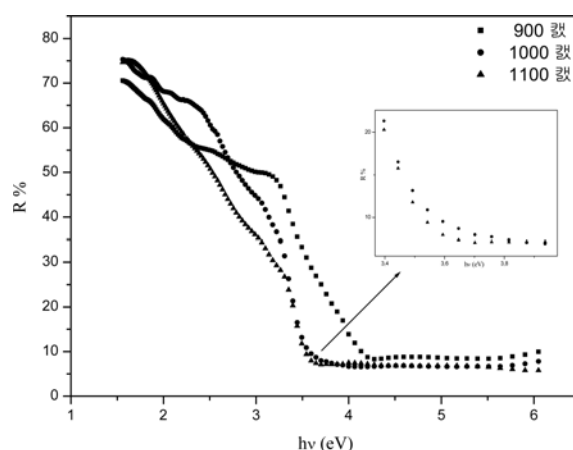


Fig. 7. UV-Vis reflectance spectra of CdTiO₃ at different temperatures.

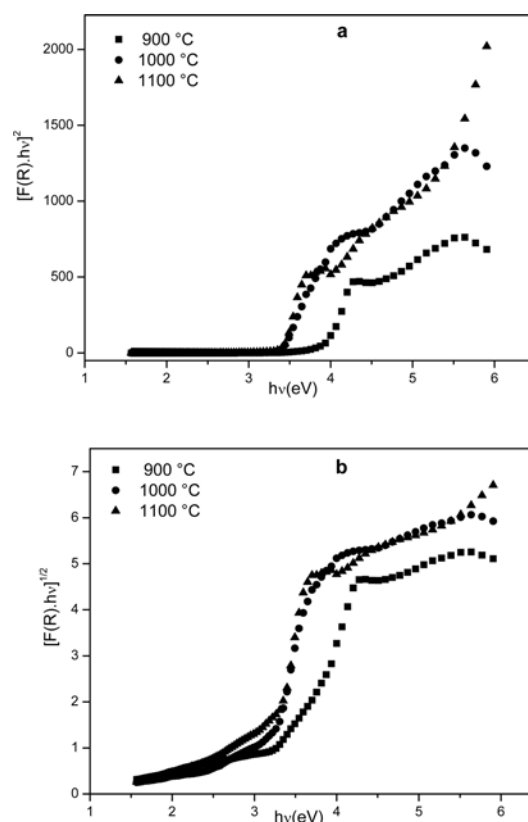


Fig. 8. (a) (F(R)·hv)² and (b) F(R)·hv^{1/2} versus hv of CdTiO₃ at different temperatures.

which have the irregular faces (MO sh or unsh face), as shown in Figs. 6(a) and 6(b). The Infrared results are in a good agreement with XRD and Raman ones. It is important to mention, that up to our knowledge, such infrared results have not been reported.

UV-Vis spectroscopies of the CdTiO₃ annealed for 2 hrs in air at 900, 1000 and 1100 °C, were carried out for wavelengths varying from 200 nm to 800 nm. The diffuse reflectance spectra (DRS) of these samples are shown in Fig. 7. DRS show clearly that the band gap of the samples is shifted to lower energies when the

temperature increases from 900 °C to 1000 °C, and then exhibits the slightly shift at 1100 °C as illustrated in Fig. 7.

The direct and indirect band gaps of CdTiO₃ annealed at different temperatures are determined from the Tauc plot of $[F(R) \cdot hv]^2$ and $[F(R) \cdot hv]^{1/2}$ versus photon energy (hv) (Figs 8(a) and 8(b)) respectively. F(R) is the Kubelka-Munk function:

$$F(R) = (1-R)^2/2R \quad (2)$$

R is the reflectance. The values of direct and indirect band gaps of CdTiO₃ obtained by extrapolation of $[F(R) \cdot hv]^2$ and $[F(R) \cdot hv]^{1/2}$ value to F(R) = 0 respectively, are given in table 4. Figs. 9(a) and 9(b) illustrate the determination of the direct and indirect band gaps for CdTiO₃ annealed at 1000 °C.

Values given in Table 4 show that the change from ilmenite to perovskite phases caused by the change in temperature from 900 °C to 1000 °C decreases the direct band gaps; the latter increases slightly when the temperature is raised to 1100 °C, temperature at which appeared the Pbn21 phase. The bands gap value variation may be explained by the symmetry of crystal: ilmenite structure is less symmetric than that of orthorhombic, thus the band gap value decreases; and when the crystal undergoes a distortion, to Pbn21, it increases slightly.

Table 5 gives values of the direct and indirect band gaps of CdTiO₃, in the ilmenite and perovskite phases in different forms (powder, nanoplate, nanofibers, nanostructure, thin film, etc.) elaborated through different methods. It is

observed that values of direct band gap of the powdered samples given in ref [1] are lower than those corresponding to the samples under nanoplates [19] nanostructure [20] nanofibres [15] and thin films [21] forms. Values of the latter determined for the ilmenite phase are lower than those calculated for our powder samples.

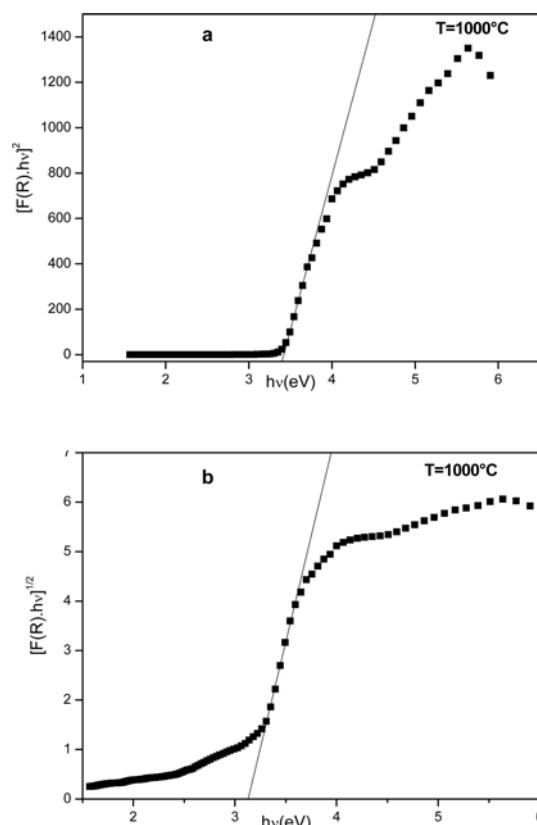


Fig. 9. Tauc-plots calculated from the UV-Vis diffuse reflectance for: (a) direct band gap energy and (b) indirect band gap calculations of CdTiO₃ at 1000 °C.

Table 4. Direct and indirect band versus temperature.

Annealed temperature (°C)	Direct band (eV)	Indirect band (eV)
900	3.86	2.86
1000	3.42	3.12
1100	3.43	3.19

Table 5. Comparison of the band gap energy and method of preparation of CdTiO₃ in different forms with those of the literature.

Form of compound	Method	Phase	Direct band gap (eV)	Indirect band gap (eV)	References
Powder	Co-precipitation	Ilmenite	2.90		[1]
		Perovskite	2.80		
Nanostructure	Sol-gel	Ilmenite	3.56	3.27	[18]
Thin film	Sol-gel	Ilmenite	3.9		[19]
Nanofiber (150–200 nm) diameter	Electrospinning	Ilmenite	3.26		[13]
Nanoplate (150–200 nm)	Solide state	Ilmenite	3.90		[17]
Powder	Sol-gel	Ilmenite	3.86	2.86	This work
		Pbmnn	3.42	3.12	
		Pbn21	3.43	3.19	

Conclusions

Powders of CdTiO₃ perovskite materials have been successfully prepared by using the sol gel process. Annealed at 900 °C, their XRD spectra showed the presence of ilmenite phase without any secondary phase. A further treatment at 1000 °C gave rise to a structural change from the (rhombohedral) ilmenite structure to the pure orthorhombic structure (space group Pbnm) without any secondary phase (CdO or TiO₂). The observed phase transformation was also detected and followed via FT-IR analysis. Indeed, the latter also confirmed that of XRD analysis, as observed through the gradual change in the recorded spectra in the temperature range 900 to 1000 °C. In particular the disappearance of the band may be linked to the phase change from the ilmenite to the perovskite structure.

When heat treated at 1100 °C a slight distortion occurred, as observed on the calculated cell parameters determined from the corresponding XRD spectrum, which gave rise to the orthorhombic perovskite phase (space group Pbn21). The room temperature Raman spectra of CdTiO₃ powders revealed the presence at 900 °C of the ilmenite phase, and at 1000 °C that of the perovskite phase (space group Pbnm). The new aspect of the spectrum annealed at 1100 °C may indicate the phase transformation from Pbnm to Pbn21 in agreement with XRD analysis. To our knowledge, such detailed analysis of the structural change in CdTiO₃ has not been reported.

UV-Vis measurements showed the effect of structural change from ilmenite to perovskite of CdTiO₃ on band gap values. In particular, our gap energy values are higher than those reported in Ref [1] for powdered samples, and are quite similar to those obtained for thin films, nanofibres and nanoplates samples.

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