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Intermediate phases formation during the synthesis of $Bi_4Ti_3O_{12}$ by solid state reaction

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Abstract

In this work, the formation of $Bi_4Ti_3O_{12}$ by solid state reaction from Bi_2O_3 and TiO_2 starting powders has been studied. The $Bi_4Ti_3O_{12}$ formation occurs through an intermediate $Bi_{12}TiO_{20}$ sillenite phase formed at temperatures sligthly over 300 °C. This sillenite phase is stable up to ~750 °C, but in the presence of TiO_2 reacts to form $Bi_4Ti_3O_{12}$ at temperatures >500 °C. Raman spectroscopy has been used to evidence the amorphization of TiO_2, demonstrating that the $Bi_4Ti_3O_{12}$ formation occurs through the reaction of sillenite $Bi_{12}TiO_{20}$ and TiO_2.

Keywords: (A) Powders: solid state reaction; (D) TiO_2; Raman Spectroscopy; Bi_2O_3

1. Introduction

$Bi_4Ti_3O_{12}$ (BIT) has attracted considerable interest as a promising material for high temperature piezoelectric applications, due to its high Curie temperature (about 675 °C) [1–3]. Nowadays, most of the piezolectric applications at high temperature are based on quarzt crystals, which show nearly temperature independent properties up to 573 °C, where an alotrophic phase transition takes place [4]. Quartz has its low piezoelectric coeficients and electromechanical coupling factors as major drawbacks. Moreover, BIT shows a high transparency on the visible and near infrared, making it a good candidate for optical switching applications [5].

BIT is an intermediate compound of the binary Bi_2O_3–TiO_2 system with a layered Aurivilius structure [6–8]. This structure is formed by a stacking of layers of $(Bi_2O_2)^{+2}$ tetraedrons and pseudo-perovskite layers of $(Bi_2Ti_3O_{10})^{-2}$. This structure presents a preferential conductance direction along the $(BiO_2)^{2+}$ layer, making it difficult to obtain a high polarization on the material.

BIT has been prepared by different methods, as chemical methods (Hidrothermal synthesis [9], sol–gel [10], co-precipitation [11], etc.), mechanoquemical activation [12] or solid state reaction [13,14]. One of the major drawbacks of this material is the difficulty of preparation, due to the appearance of secondary phases that produce exagerated grain growth and affect the material density and properties [15], making it to develop a reliable industrial process to prepare the material.

Among the different preparation methods, the synthesis by solid state reaction is one of the most implanted industrial metodologies since ceramic pieces with different shapes can be prepared at low cost. Some authors have proposed that BIT can be formed by solid state reaction following the direct reaction $2Bi_2O_3 + 3TiO_2 \rightarrow Bi_4Ti_3O_{12}$ [16]. Nevertheless, some other authors have observed the appearance of secondary phases, as the sillenite phase $Bi_{12}TiO_{20}$ [17] or the $Bi_2Ti_2O_7$ [18]. These secondary phases reduce the piezoelectric properties of the material. In order to avoid the appearance of these phases it will be neccesary to study the solid state reaction process to fully characterize the formation of the material. Recently, it was reported in this system the formation of the different phases at high temperature [19], which occurs via a transient liquid phase that promotes grain growth and induces the occurrence of secondary phases, but the nature of this transient liquid was not established.

In this work we study the solid state reaction of Bi_2O_3 and TiO_2 to from BIT, demonstrating that it takes place through an intermediate sillenite phase.

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2. Experimental

Rutile TiO_2 (Alfa Aesar, mean particle size 1.04 μm) and α-Bi_2O_3 (Aldrich, particle size 11.89 μm) with 99.9% purity were used as starting materials. The appropriate stoichiometric amounts of the starting materiales were mixed in an attrition mill with 1.2 mm ZrO_2 balls in water for 3 h. A 0.6 wt.% of T5003 Rohm&Haas dispersant was added to improve homogeneization. The powders were overnight dryed at 75 °C and sieved through a 0.1 mm mesh and calcined at different temperatures, 600 and 800 °C, for 2 h with constant heating and cooling rates of 3 °C/min. The calcined powders were again attrition milled on water adding a 0.6 wt.% of dispersant T5003 Rohm&Haas and dispersed by a high shear Ika Ultraturraz T50 for 10 min at 4000 rpm. The powders have been dryed again and shieved through a 0.1 mm mesh. The resultant powder was characterized by XRD (Cu Kα radiation on a Siemens D5000, Kristalloflex diffractometer), DTA-TG (Netzsch STA 409) and dilatometry (Netzsch 407/E).

Sillenite powders were prepared by calcining for 2 h at 600 °C a stoichimetric mixture of Bi_2O_3 and TiO_2. The resultant powder shows an average particle size of 1.14 μm. These powders were pressed at 200 MPa and sinterized at 800 °C for 2 h. The pellet shows a density of 8.0 g/cm^3 and the XRD confirms the formation of the sillenite phase.

Raman spectroscopy has been employed to study the presence of both crystalline and amorphous phases on the samples. The Raman scattering was excited using 514 nm radiation from an Ar^+ laser operating at 10 mW and it was collected by a microscopic Raman spectrometer (Renishaw Micro-Raman System 1000) in the 100–1100 cm^{-1} range at room temperature.

3. Results and discussion

Fig. 1a shows the DTA/TG of the milled stoichimetric mixture of $2Bi_2O_3$ and $3TiO_2$ starting powders. Six exothermic peaks are observed at temperatures of about 240, 335, 470, 590, 670 and 750 °C. The exothermic peaks occuring at temperatures below 600 °C are accompained by weigth losses on the TG, whereas those at higher temperatures do not show any weight variation, indicating that they are associated to phase changes and/or formation of new phases on the system Bi_2O_3–TiO_2. The total weigth loss is ∼0.6%, which agrees with the amount of dispersant, indicating that the exothermic peaks observed at temperatures below 600 °C mainly correspond to the burnout of the dispersant. Fig. 1b shows the dilatometry of $2Bi_2O_3$ and $3TiO_2$ mixed starting powders. An expasion of about 0.03% is observed at 740 °C. This expansion can be associated to the exothermic peak observed on DTA of the mixed powders and could be attributed in principle to the formation of the BIT phase. At temperatures >800 °C the densification process takes place, showing a local maximum of densification speed at ∼830 °C.

In order to study the effects associated to the exothermic peak occurring at 750 °C and the related expansion, thermal treatments have been carried out in air for 2 h at temperatures of 600 and 800 °C, which will be called on the following 6BIT and 8BIT, respectively. The DTA/TG of these samples are shown in Fig. 2a. As in the case of the mixed powders, the exothermic peaks observed at temperatures below 600 °C correspond to the burnout of the dispersant. Sample 6BIT shows a broad exothermic peak at ∼750 °C accompained by a shoulder at ∼680 °C, resembling the peaks observed on the DTA of the materials mixture (Fig 1a) indicating by that BIT formation processes have not been completed at the 600 °C for 2 h thermal treatment. On the other hand, the sample 8BIT does only show a clear endothermic peak at 673 °C, that can correspond to the ferroelectric to paraelectric phase transition of BIT [20]. The dilatometry curves of 6BIT and 8BIT are shown in Fig. 2b. The sample 6BIT shows a shrinkage dilatometric behaviour similar to that of the stoichiometric powders mixture, with an expansion at ∼740 °C and a shrinkage at higher temperatures, though the maximum shrinkage speed occurs at higher temperature (1000 °C). On the other hand, the sample 8BIT is free of the expansion process.

The X-ray diffraction patterns of samples 6BIT and 8BIT are shown in Fig. 3. The samples calcined at 800 °C (8BIT) present only the diffraction peaks corresponding to the BIT phase, withouth any traces of the starting material or secondary phases. The sample 6BIT shows the presence of BIT phase togheter with a majoritary sillenite phase, $Bi_{12}TiO_{20}$, with no traces of the starting materials. The sillenite phase has been previously observed on BIT samples as a secondary phase [17]. These results indicate that the BIT phase starts to form at temperatures below 600 °C, but only by thermal treatment at

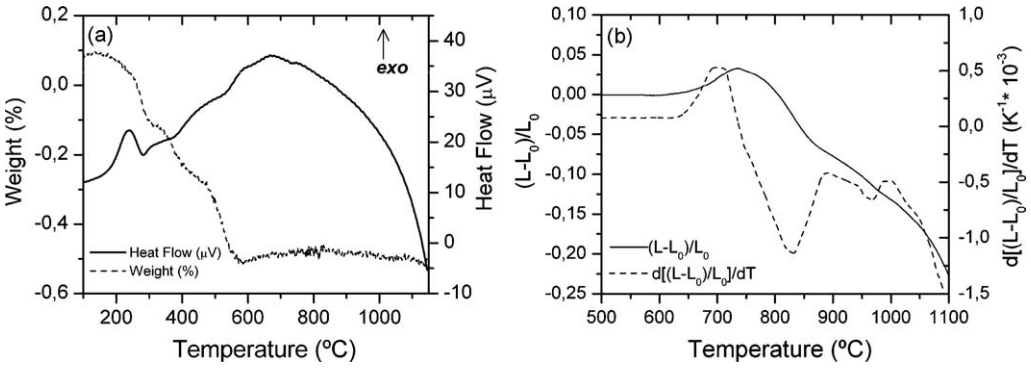

Fig. 1. (a) TG–DTA and (b) dilatometry curves of the stoichiometric mixture.

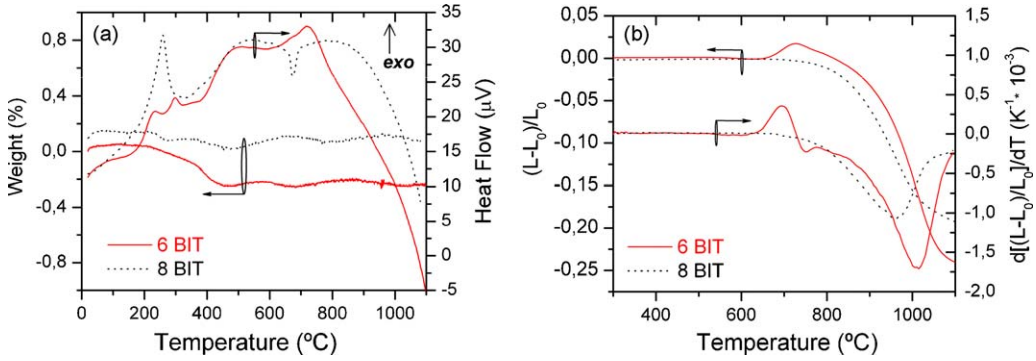

Fig. 2. (a) TG–DTA and (b) dilatometry curves of the powders thermal treatment at 600 and 800 °C (namely 6BIT and 8BIT, respectively).

temperatures well over it the Aurivilius phase becomes the unique crystalline phase present in the calcined samples.

Taking into account the previous results, a formation process of the BIT from Bi_2O_3 and TiO_2 can be proposed that occurs through the formation of a secondary, sillenite phase, following the reaction:

$$6Bi_2O_3 + 9TiO_2 \rightarrow Bi_{12}TiO_{20} + 8TiO_2 \rightarrow 3Bi_4Ti_3O_{12} \quad (1)$$

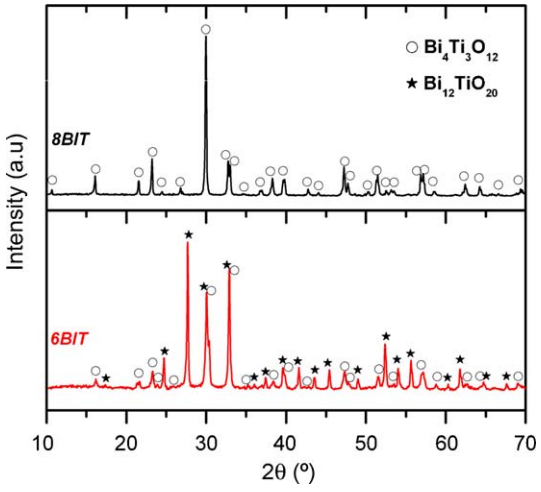

Fig. 3. XRD patterns of the 6BIT and 8BIT powders.

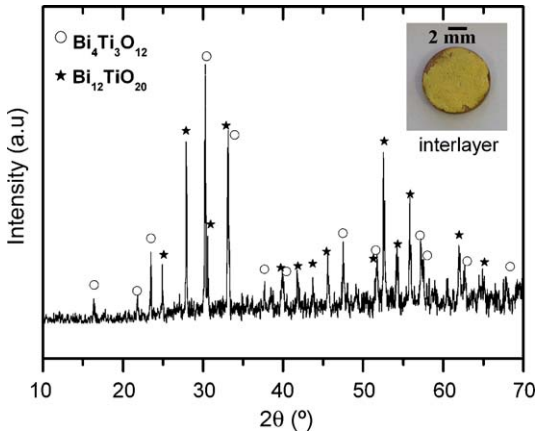

Fig. 4. XRD patterns of the interlayer between sillenite phase and TiO_2 phase. The inset shows the sample after the thermal treatment.

The formation of the sillenite phase occurs at temperatures below those of the formation of BIT. The reaction of sillenite and TiO_2 could thus be responsible for the observed expansion at ~740 °C in the dilatometric measurement in both the stoichiometric mixture of powders and the 6BIT sample. This two steps process is more complex than the proposed formation of BIT by a direct reaction between Bi_2O_3 and TiO_2 [16].

In order to corroborate this reaction process a diffusion pair composed by pellets of TiO_2 and sillenite was prepared. The diffusion pair was thermally treated at 750 °C for 12 min and the interlayer structures were characterized by XRD. The XRD diffraction pattern observed on the side of the sillenite pellet

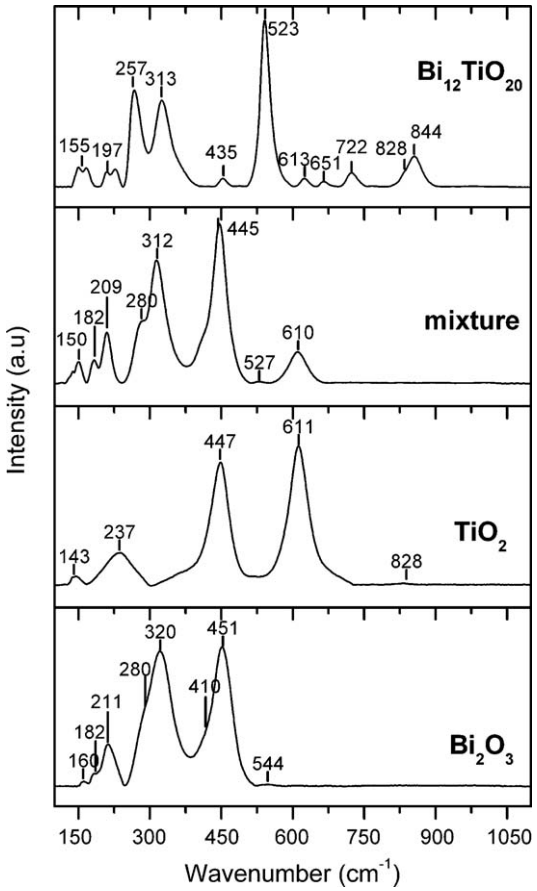

Fig. 5. Raman spectra of the raw materials (α-Bi_2O_3 and TiO_2), the stoichiometric mixtures and the $Bi_4Ti_3O_{12}$ (BIT) at room temperature.

shows the presence of both sillenite and BIT (see Fig. 4). This indicates that the sillenite phase is stable at temperatures over 740 °C, though it transforms into BIT phase in the presence of TiO_2 at this temperature. This would be in accordance with the reaction process proposed in (1), where the Bi_2O_3 is first consumed to form the sillenite phase and this phase is later transformed into BIT in the presence of TiO_2.

The XRD patterns of samples calcined at 600 °C for 2 h presented in Fig. 3 do only show the sillenite and BIT Aurivilius phases on the samples. It has been observed that the sillenite phase is stable up to temperatures of 800 °C, but it tranforms into BIT in the presence of TiO_2. Then, there must be some quantity of TiO_2 present in the sample in agreement with the employed stoichoimetric. This TiO_2 can be in the form of nanoparticles, much smaller than those observable by XRD (about 5 nm on our case), or as an amorphous phase. Raman spectroscopy has been used to study the presence and evolution of this phase, since this technique measures the chemical bonds between atoms, being then able to observe both crystalline and amorphous phases.

The Raman spectra of Bi_2O_3, TiO_2 and pure sillenite have been obtained and are shown in Fig. 5 and the principal peaks of each material are identified in Table 1. The Raman spectra of the starting powders allow the identification of the α-Bi_2O_3 and rutile TiO_2 polimorphic phases, in good agreement with the results obtained by XRD.

The sillenite phase has been previously studied in both monocrystal [21] and ceramic [22,23] form. The face centered cubic phase of sillenite (point group 123) should present 8A + 8E + 24F Raman modes, among which only 12 are observed on our work (see Table 1). Hardcastle and Wachs [23] have determined that the Raman mode at 251 cm^{-1} is characteristic of the sillenite phase. The modes at 262 and 320 are characteristic of the BiO_n polihedron on the sillenite phase and are very sensitive to geometry changes [21]. The peak observed at 722 cm^{-1} has been asigned to pyroclore phases of the type $Bi_2Ti_2O_7$ [24] and is not present on BIT structure [24–29]. Thus, there are three peaks, at 139, 651 and 844 cm^{-1}, that cannot be associated to Bi_2O_3, TiO_2 or sillenite phase, that should correspond to a small amount of BIT phase present in the sample, as observed by XRD.

Table 1
Main Raman modes observed on TiO_2, α-Bi_2O_3 and sintered $Bi_{12}TiO_{20}$ sillenite phase. The intensity of the peaks are marked from very low to very intense. (l: low; m: medium; s: strong; v: very).

Materials	Raman shift (cm^{-1})	Intensity (a.u.)	References
TiO_2 (rutile phase)	143 (B_{1g})	m	[29,30]
	237(E_g)	m	
	447 (E_g)	vs	
	611 (A_{1g})	vs	
	828 (B_{2g})	l	
α-Bi_2O_3	160 (B_g)	m	[22]
	182	m	
	211($A_g + B_g$)	m	
	280($A_g + B_g$)	vl	
	329 (bending modes of BiO_6 octahedral symmetry)	vs	
	410($A_g + B_g$)	vl	
	451($A_g + B_g$)	vs	
	454 ($A_g + B_g$)	m	
$Bi_{12}TiO_{20}$	139 (A)	vs	[20,22,25]
	155 (A)	vs	
	197 (F)	m	
	257 (A)	vs	
	313 (A)	vs	
	435 (E)	m	
	523 (A)	vs	
	613 (E)	m	
	722 (A)	m	
	828 (FTO; Anty-symmetric streching of TiO_4 tetrahedra)	m	

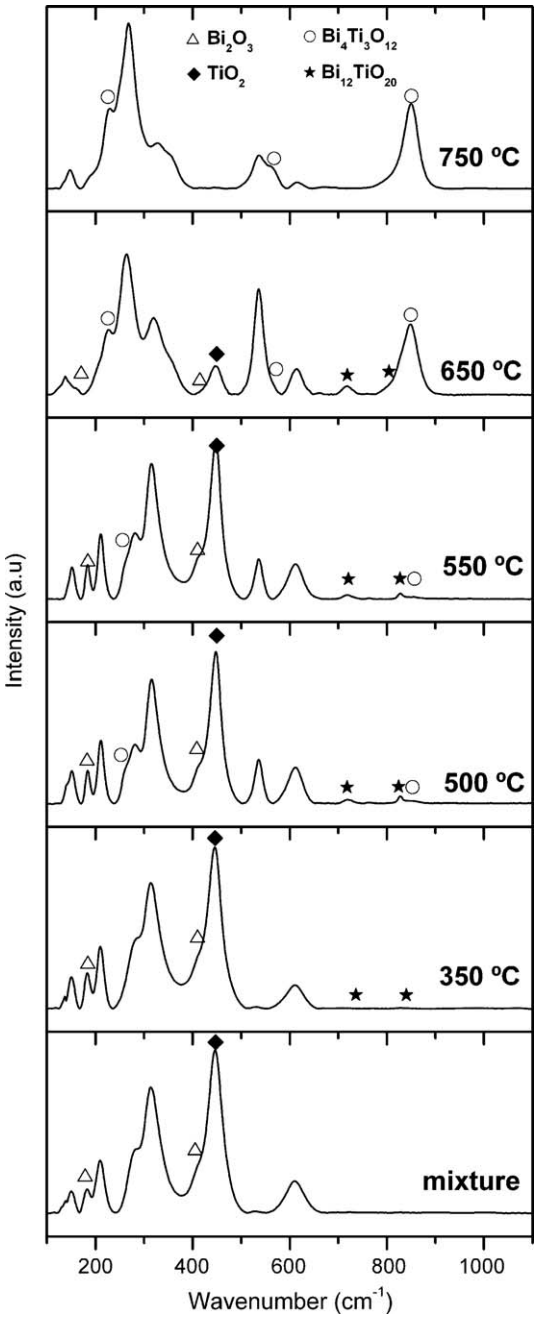

Fig. 6. Raman spectra of the stoichiometric mixture powders and materials calcined at different temperatures.

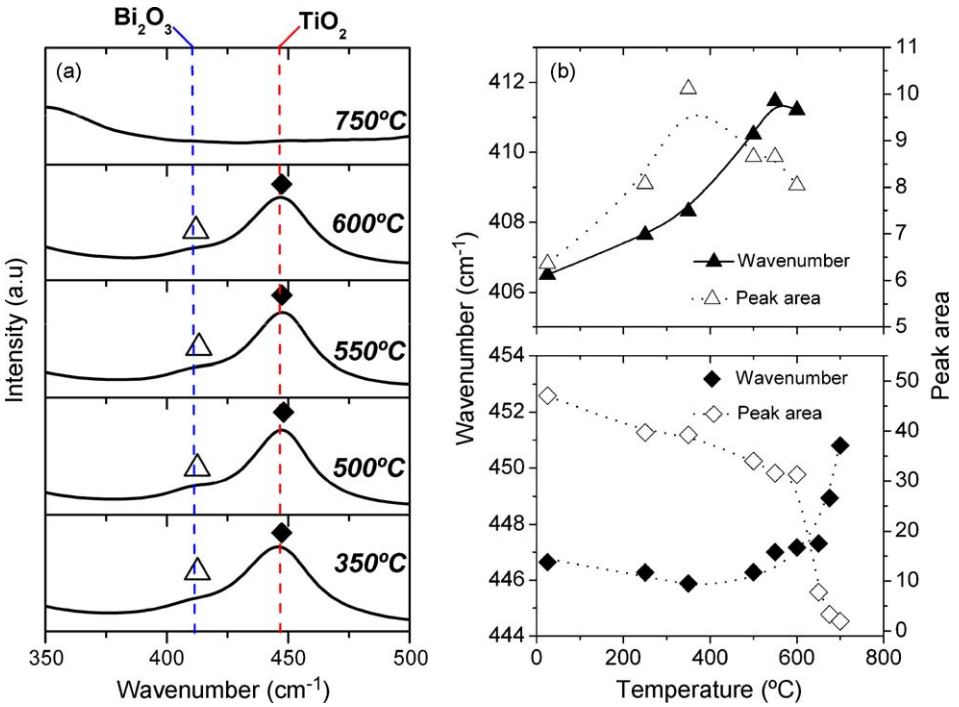

Fig. 7. (a) Magnified Raman spectra in the ranges of the wavenumber from 350 to 500 cm^{-1} as function of the composition and Lorentzian fits of the individual peaks of the α-Bi_2O_3 (△) and TiO_2 (◆) amorphous phase Raman modes. Evolution of Raman modes area (b) and wavenumber in function of calcinations temperature is also shown for α-Bi_2O_3 and TiO_2.

In order to study the existence and evolution of amophous (or nanocrystalline) phases in the Bi_2O_3/TiO_2 system, samples have been prepared by thermal treatment during 12 min at different temperatures. Their Raman spectra are shown in Fig. 6. At thermal treatment temperatures below 300 °C the spectra correspond to a combination of the Raman spectra of TiO_2 and Bi_2O_3, indicating that there is still material that has not reacted up to this temperature. At 350 °C new peaks appear at 261, 718 and 827 cm^{-1} and some other shift in position. The new peaks correspond to the sillenite phase, indicating that the formation of sillenite starts at temperatures below 350 °C. At temperatures above 550 °C, the peak at ∼850 cm^{-1} strongly increases in intensity and a new peak appears at 229 cm^{-1}, accompained by a reduction on the intensities of raw materials peaks. These new peaks are characteristic of the BIT phase [24–29] and indicate that this phase starts to form at temperatures of about 550 °C, in good agreement with the XRD results previously shown, although the formation of BIT is not completed at this temperature.

It should be noted that peaks at 182, 414 and 447 cm^{-1} appear on every spectrum. The two first peaks are characteristic of bismut oxide and do not appear on sillenite or BIT, so they could be associated to a Bi-rich oxide amorphous phase, since no crystalline Bi-oxide phases were observed by XRD at any calcination temperature over 300 °C. The last peak, 447 cm^{-1}, can be associated to O–Ti–O bond vibrations, indicating the presence of a TiO_2 amorphous phase. In Fig. 7a and b we show the evolution of 414 and 447 cm^{-1} peak areas, toghether with their Raman shift. As can be seen, the 447 cm^{-1} peak area decreases only slighty up to 600 °C, where it starts to sharply decrease. This could be explained by the reaction of the TiO_2 amorphous phase with the sillenite to form BIT, that has been previously observed to occur at temperatures well over 500 °C. On the other hand, the 414 cm^{-1} peak shows an increase of area followed by a decrease starting at ∼300 °C, Fig. 7b, when the sillenite phase starts to form. From these results we can propose that the sillenite formation starts at ∼300 °C and the formation of BIT occurs by a reaction between this sillenite phase and an amorphous TiO_2 phase at temperatures over 600 °C.

Moreover, we can evaluate the formation of sillenite and BIT phases by following the peaks at about 830 and 850 cm^{-1}, which are characteristic of each phase. In order to perform a depth analysis of the reaction mechanism and the role of the amorphous phase, a quantitative analysis of the Raman spectra was done. Peak position, area and width of the Raman peaks at 830 and 850 cm^{-1} were determined from the mathematical fit of the Raman data. The evolution of these peaks togheter with the peaks positions are shown in Fig. 8a and b.

The peak area (Fig. 8b) exhibits different trends. As can be seen, the formation of sillenite phase starts at about 350 °C (concomintantly with the reduction of BiO rich amorphous phase) and the corresponding area increases with the thermal treatment temperature up to temperatures of 600 °C. Over this temperature the peak area reduces and finally disappears at temperatures of 650 °C. The area of the peak corresponding to the BIT phase is visible at temperatures over 550 °C, and reaches a maximum at temperatures of ∼675 °C.

In summary, Raman spectroscopy proves to be a powerful tool to study the mechanism of the reaction between Bi_2O_3 and TiO_2 at low temperatures. This reaction consists on the

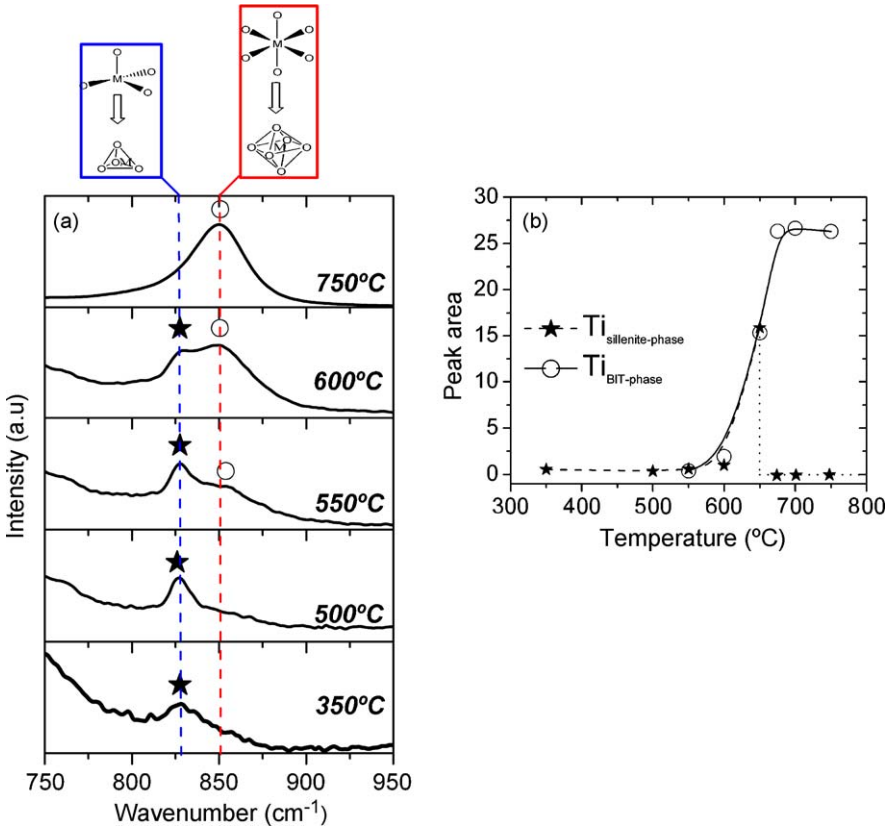

Fig. 8. (a) Magnified Raman spectra in the ranges of the wavenumber from 750 to 950 cm^{-1} as function of the composition and Lorentzian fits of the individual peaks of the stretching modes (O–Ti–O) corresponding with the sillenite phase (★) and BIT phase (○) Raman modes. Evolution of Raman modes area (b) in function of calcinations temperature is also shown.

formation of an intermediate phase with sillenite structure, $Bi_{12}TiO_{20}$, and the subsequent diffusion of TiO_2 in the $Bi_{12}TiO_{20}$ grains to form $Bi_4Ti_3O_{12}$.

4. Conclusions

The formation of BIT by solid state reaction from Bi_2O_3 and TiO_2 starting powders has been studied. It has been demonstrated that the BIT formation occurs through the formation of an intermediate sillenite phase. This sillenite phase starts to form at temperatures sligthly over 300 °C, and is stable up to temperatures of 750 °C. Nevertheless, in the presence of TiO_2 the sillenite phase reacts to form BIT at temperatures over 500 °C. Raman spectroscopy has been used to prove the existence of TiO_2 amorphous phase on the system and study its evolution, demonstrating that the BIT formation occurs through the reaction of sillenite $Bi_{12}TiO_{20}$ and TiO_2.

Acknowledgements

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