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Optical properties of $Bi_{12}SiO_{20}$ (BSO) and $Bi_{12}TiO_{20}$ (BTO) obtained by mechanical alloying

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Mechanical alloying has been used successfully to produce nanocrystalline powders of BTO and BSO. The milled BTO and BSO were studied by x-ray powder diffraction, DTA, infrared and Raman scattering spectroscopy. After 7 hours of milling the formation of BTO and BSO was confirmed by x-ray powder diffraction. The infrared and Raman scattering spectroscopy results suggest that the increase of the milling time lead to the formation of ferroelectric BTO and BSO, as seen by x-ray diffraction analysis. These materials are attractive for various electro-optical devices, including optical data processing. They present a number of attractive features as reversible recording materials for real-time holography and image processing applications. This milling process presents the advantage, that melting is not necessary, and the powder obtained is nanocrystalline with extraordinary mechanical properties. The material, can be compacted and transformed in solid piezoelectric ceramic samples. The high efficiency of the process, opens a way to produce commercial amount of nanocrystalline piezoelectric powders. Due to the nanocrystalline character of this powder, their mechanical properties have changed and for this reason a pressure of 1 GPa is enough to shape the sample into any geometry.

1. Introduction

$Bi_{12}SiO_{20}$ (BSO), $Bi_{12}GeO_{20}$ (BGO) and $Bi_{12}TiO_{20}$ (BTO) are attractive materials for various optical devices [1–3] including optical data processing [4]. They are closely related materials and having quite similar properties. They present a number of attractive features as reversible recording materials for real-time holography and image processing applications. Specifically, BSO and BGO have been used for real time intensity inversion [5], subtraction [5] and image correlation with four wave mixing techniques [2]. These materials have the same body-centered structure [6], belong to the group of sillenites from the γ phase of Bi_2O_3. Point group symmetry is m3. Crystals of BSO have been grown from the melt by the Czochralski method. Melting temperatures are 895°C (BSO), 930°C (BGO) and 880°C (BTO). For BTO, flux and hydrothermal methods have been successfully used [6]. Their structure is described by the space group T^3(I23). These compounds exhibit a number of remarkable properties: they are piezoelectric, electrooptical, elasto-optical, optical active, and photoconductive. A relevant optical property of BSO, BGO and less intense for BTO is the rotatory power [7]. Crystals with both clockwise and counter clockwise rotation senses have been reported [7]. The rotatory power at $\approx$5893 Å is $\approx$25°/mm for BGO and BSO; this is to be compared with 3.13°/mm at the same wavelength, for sodium clorate, a well known crystal of the same group symmetry [8]. Consistent with their symmetry, they are piezoelectric. Indeed, strong piezoelectricity was reported for BSO, BGO and BTO [9]. Piezoelectric coefficient $d_{14} = 8.5 \times 10^{-7}$ statcoulomb/dyn, was reported for BGO, being one order of magnitude larger than that of zinc blend [8]. Thus BGO, BSO and BTO are of high interest in view of their unusual optical and electro-optical properties.

In recent years there has been an increasing academic and technologic interest in glasses containing ferroelectric crystals and ferroelectric ceramics as nonlinear optical materials [10, 11]. These studies have shown the possibility to obtain piezoelectric ceramics from the melt-quenching technique. Mechanical alloying is a powerful technique to obtain any quantity of powder with controlled microstructure [12]. Nowadays the technique is used in a large of commercial products, moreover, most of these applications are on metallic domain. The mechanical alloying technique was already used, by our group, to obtain nanocrystalline ferroelectric ceramicas of lithium niobate LN ($LiNbO_3$) [13]. Lithium Niobate-LN is a ferroelectric material with a trigonal crystal structure, with melting point at 1253°C and Curie temperature at 1210°C. It is characterised by a large pyroelectric, piezoelectric, electro-optic, photo-elastic coefficients and is naturally birefringent. Furthermore the technique is very effective to produce nanocrystalline piezoelectric ceramics.

In this work we report the application of mechanical alloying technique to produce a polycristalline piezoelectric material (BTO and BSO), from elementary powders. The advantage of this procedure remains on the fact that melting is not necessary, the powders are nanocrystalline and exhibits extraordinary mechanical properties [14]. It can also be easily shaped (injected, compacted, etc) into any geometry. The production, and the study of the properties of the BTO and BSO ceramics is important in view of possible applications as reversible recording materials for real time holography and image processing applications. In this paper we propose a new method to obtain the BTO and BSO ceramic. The milled BTO and BSO were strudied by x-ray powder diffraction, DTA, infrared and Raman scattering spectroscopy.

2. Experimental procedure

2.1. Sample preparation

Commercial bismuth oxide (Bi_2O_3) and titanium oxide (TiO_2) was used in the BTO preparation. For BSO, TiO_2 was substituted by SiO_2. The material was ground on a Fritsch Pulverisette 5 planetary mill with the proportionality of $6Bi_2O_3$-TiO_2 for BTO and $6Bi_2O_3$-SiO_2 for BSO. Milling was performed in sealed stainless steel vials and balls under air, with 350 rpm as rotation speed. The powder mass to the ball mass ratio used in all the experiments was near 1/6. To avoid excessive heat the milling was performed in 30 min milling steps with 10 min pauses. Mechanical alloying was performed for 1, 4, 7, 10, 54 hours of milling.

2.2. XRD

The X-ray diffraction (XRD) patterns were done using a Siemens D5000 equipment with K_α-Cu radiation in a Bragg-Brentano geometry at room temperature (300 K) by step scanning using powdered samples. We used five seconds for each step of counting time, with a Cu-K_α tube at 40 kV and 25 mA.

2.3. Infrared spectroscopy

The infrared spectra (IR) were measured using KBr pellets made from a mixture of powder for each glass composition. The pellet thickness varied from 0.5–0.6 mm. The IR spectra were measured from 400–1400 cm^{-1} with a Nicolet 5ZPX FT-IR spectrometer.

2.4. Raman spectroscopy

Raman spectra were measured with a triple monochromator micro-Raman spectrometer (Dilor XY), equipped with a CCD detector and using the 5145 Å exciting line of the Arlaser. The Raman scattering was measured in a back scattering geometry directly from the powder.

2.5. DTA analysis

The DTA analysis was obtained at a heating rate of 10°C min^{-1} using a DTA-50 Shimadzu apparatus. The measurements were performed using a Platinum crucible in N_2. A constant sample weight of 40 mg was used for all measurements.

3. Results and discussion

Fig. 1 presents the XRD pattern of $6Bi_2O_3 + SiO_2$ powder at different milling times compared with the diffraction peaks of crystalline BSO obtained from the literature [15]. As can be observed the $6Bi_2O_3 + SiO_2$ mixture becomes BSO, as a result of grinding, as indicated by XRD. XRD in Fig. 1 indicates that after 1 hour of milling the presence of Bi_2O_3. After 4 hours the BSO phase is already present. After 7 hours the BSO phase is easily identified. After 54 hours the phase is still present showing good stability. In Fig. 2 one has the DTA analysis of the samples with 1, 4 and 7 hours of milling. Data from the literature gives the melting temperature

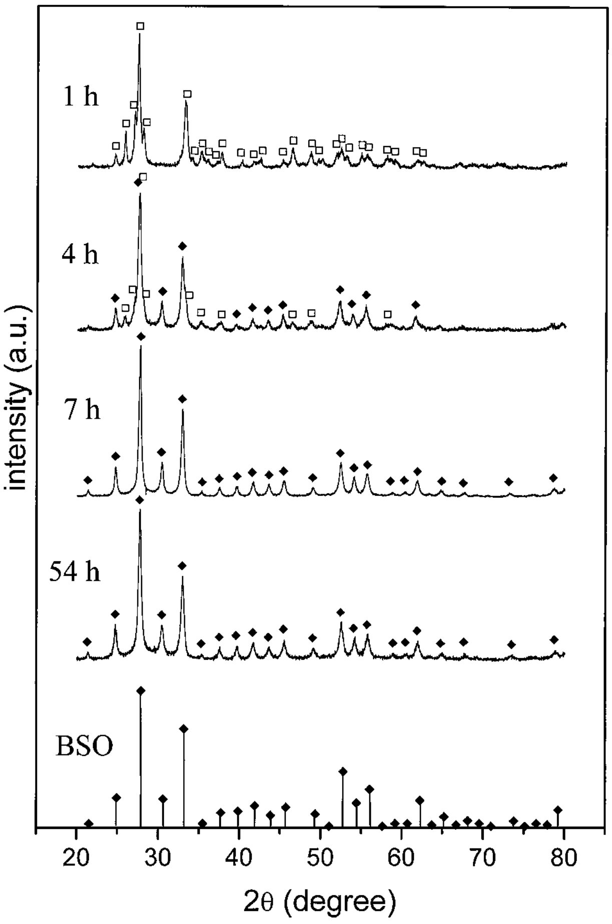


Figure 1 XRD patterns of $6Bi_2O_3 + SiO_2$ milled for 1, 4, 7, 54 hours and crystalline BSO [15] with (□) Bi_2O_3 and (◆) BSO.

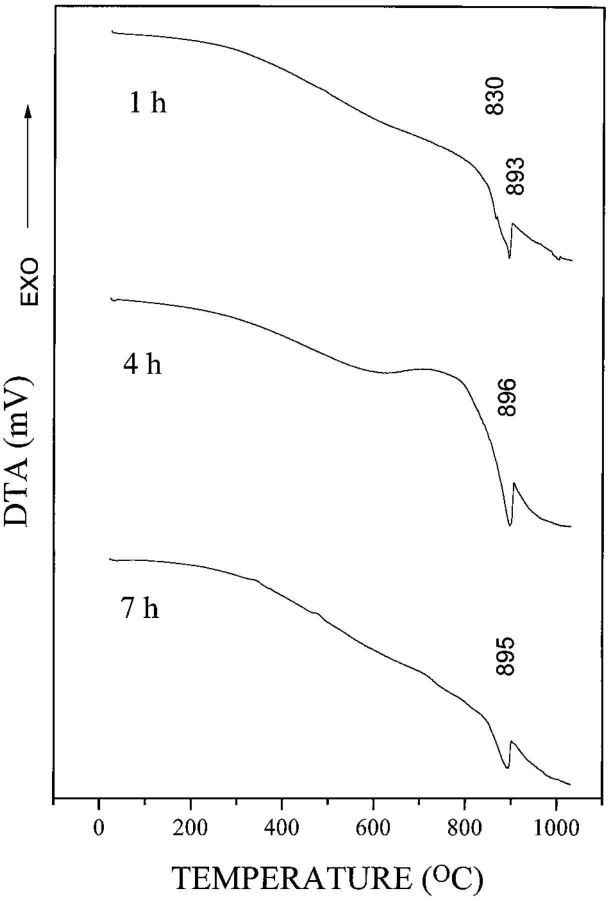
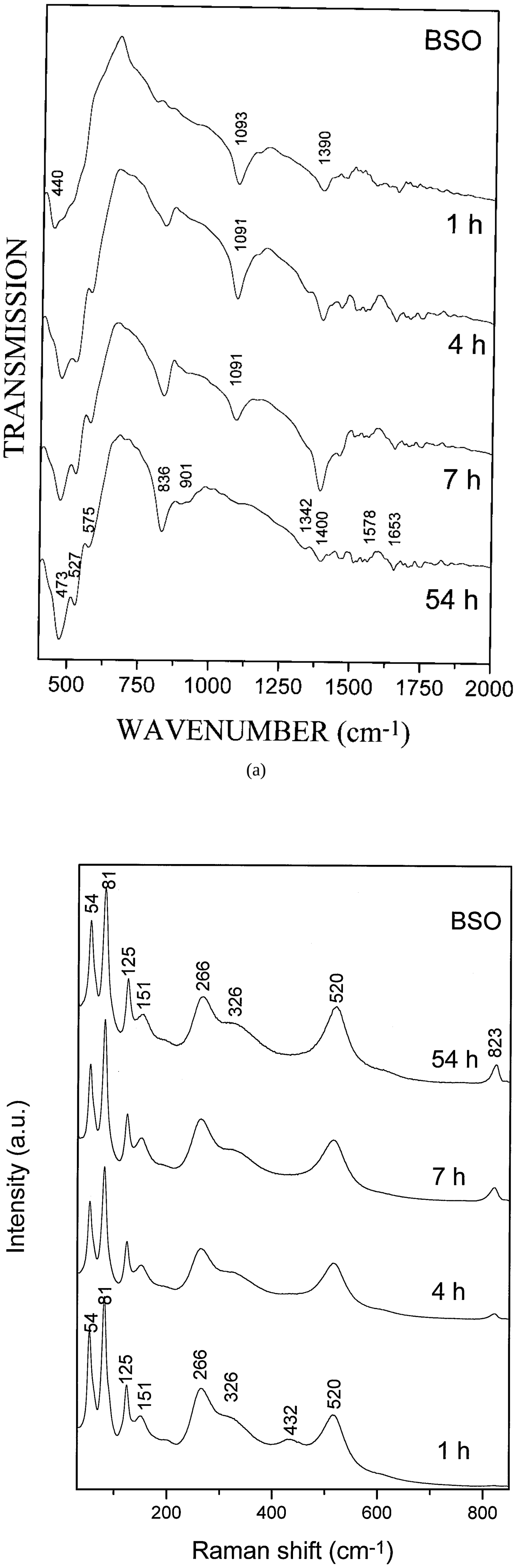


Figure 2 DTA curves of $6Bi_2O_3 + SiO_2$ milled for 1, 4, 7 hours.

for BSO (895°C), Bi_2O_3 (825°C). In Fig. 2, for 1 hour of milling, one can observe two transition temperatures at 830°C and 893°C. The first one should be associated to the melting temperature for Bi_2O_3. The second critical temperature should be associated to the start of production of BSO which is already present after 1 hour of milling. However the volume of BSO is very low, for this sample, which is confirmed in Fig. 1. After 4 hours of milling the peak associated to Bi_2O_3 is no more detectable and the peak at 896 °C (BSO) is dominant. For 7 hours of milling the critical temperature associated to the fusion of BSO is quite clear. In Fig. 3 have the IR and Raman spectra of samples of $6Bi_2O_3 + SiO_2$ with 1h, 4h, 7h and 54h of milling. The IR absorption spectra of the sample with one hour of milling (see Fig. 3a) could be directly associated with the spectra of Bi_2O_3. Where IR absorptions around 440, 1093 and 1390 cm^{-1} is observed. A noticeable change is observed after milling. In Fig. 3a and b we have the IR and Raman spectra of the sample with 54 hours of milling. We expect to have a good agreement with the IR and Raman spectra of the crystalline BSO. Assignment of the IR and Raman spectral features to the crystalline BSO and BTO has been reported previously [16–18]. In Table I one has the IR absorption lines and the Raman lines associated to the samples of 54 hours of milling, obtained from Figs 3a and b (BSO) and 6a and b (BTO) compared with the data obtained from the literature. The infrared spectra and Raman spectra are in good agreement with the data reported in the literature. The major lines associated to BTO and BSO was identified



(a)

(b)

Figure 3 (a) Infrared spectra of samples with 1, 4, 7 and 54 hours of milling (BSO) (see Table I). (b) Raman spectra of the samples of Fig. 3a (see Table I).

TABLE I IR lines and Raman lines obtained from the samples with 54 hours of milling*, data from Figs 3a, b, 6a, b compared with data of references 16–18

IR*/cm^{-1} This paper	BSO (54 hours) [Reference 16]/cm^{-1}	Raman*/cm^{-1} This paper	[Reference 17–18]
473	453	54	53.5
527	526	81	87.7
575	580	125	131.2
836	833	151	148.7
901		266	252
1342	1375	326	330.8
1400	1415	520	527.4
1578	1598	823	827.4
1653	1650		

IR*/cm^{-1} This paper	BSO (54 hours) [Reference 16]/cm^{-1}	Raman*/cm^{-1} This paper	[Reference 17–18]
467	457	52	51
524	518	80	85.5
585	589	121	126.5
667	661	148	147.5
848		252	
1330	1330	306	302.8
1393	1380	515	523.8
1454		820	

in our samples. For the BSO sample, the IR absorption at 901 cm^{-1} was not identified. For the BTO sample the IR absorption modes at 848 and 1454 cm^{-1} and the Raman modes at 252 and 820 cm^{-1} were not identified. We have to emphasize that the data from the literature was obtained from IR absorption and Raman scattering using single crystals. Our measurements were done in powdered polycrystalline samples. This could explain the large bandwidth of the optical lines associated to polycrystalline characteristic of the samples (Figs 3a, b, 6a and b).

Fig. 4 presents the XRD pattern of $6Bi_2O_3 + TiO_2$ powder at different milling times compared with commercial BTO. As can be observed the $6Bi_2O_3 + TiO_2$ mixture becomes BTO, as a result of grinding, a indicated by XRD. In Fig. 4, for 1 hour of milling, Bi_2O_3 is present and dominant. After 7 hours the BTO phase is easily identified. After 10 and 54 hours the BTO phase is present showing good stability and the diffraction pattern are similar. In Fig. 5 one has the DTA analysis of the samples with 1, 4, 7 and 10 hours of milling. Data from the literature gives the melting temperature for BTO (880°C), Bi_2O_3 (825°C). In Fig. 5, for 1 hour of milling, one can observe a transition temperature at 863°C. The first transition associated to the melting of Bi_2O_3 was not clearly identified for this sample. The second critical temperature (≈863°C) should be associated to the start of production of BTO which is already present after 1 hour of milling. The melting temperature observed for the nanocrystalline ceramic (BTO) is lower (863°C) compared to the BTO monocrystal (880°C). We believe that the reason for that is in the phase-diagram of the system Bi_2O_3-TiO_2, that does not present a clear solid solution region for BTO in contrast with BSO and BGO [6, 7]. After 4 hours of milling the peak associated to BTO is present (≈861°C) and

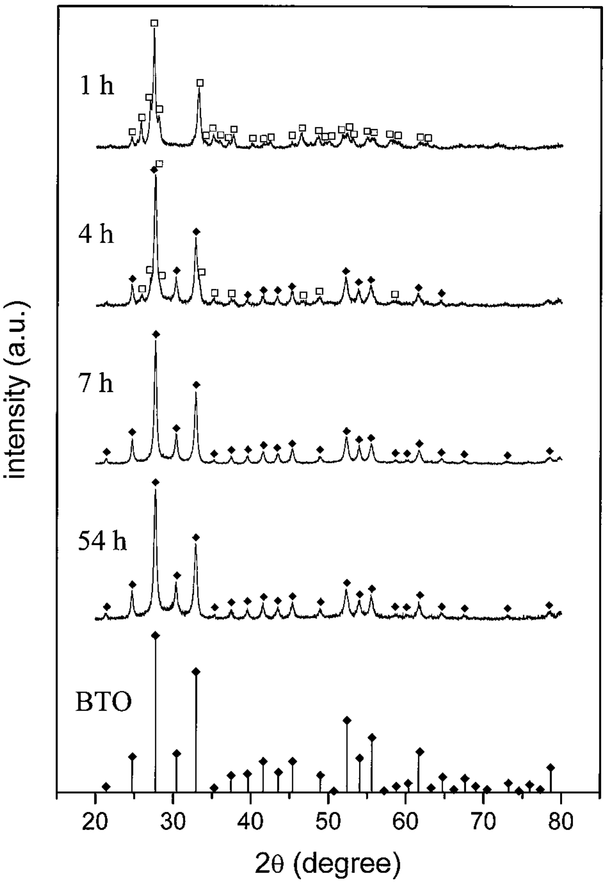


Figure 4 XRD patterns of $6Bi_2O_3 + TiO_2$ milled for 1, 4, 7, 54 hours and crystalline BTO [15] with (□) Bi_2O_3 and (♦) BTO.

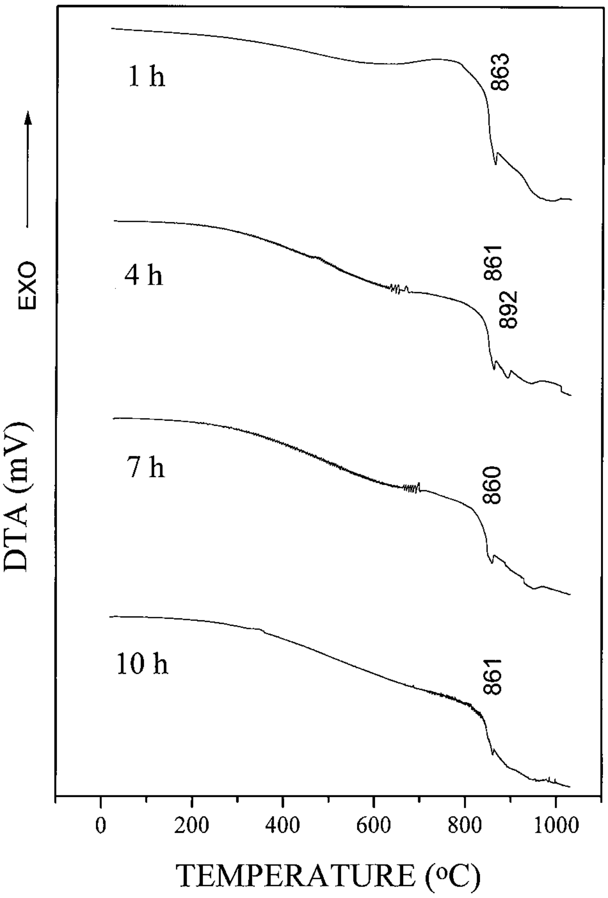


Figure 5 DTA curves of $6Bi_2O_3 + TiO_2$ milled for 1, 4, 7, 10 hours.

a second peak at 892 °C appears. This phase was not present in the X-ray diffraction analysis. This is an indication that this phase is in a very low proportion compared to BTO phase. For 10 hours of milling the critical temperature associated to the fusion of BTO is quite clear.

In Fig. 6a and b we have the IR and Raman spectra of the sample with 54 hours of milling. We expect to have a good agreement with the IR and Raman spectra of the crystalline BTO. Assignment of the IR and Raman spectral features to the crystalline BTO has been reported previously [16–18]. In Table I one has the IR absorption lines and the Raman lines associated to the samples of 54 hours of milling, obtained from Fig. 6a and b (BTO) compared with the data obtained from the literature. The infrared spectra and Raman spectra are in good agreement with the data reported in the literature. The major lines associated to crystalline BTO and BSO was identified in our samples. However we have to emphasize that the data from the literature was obtained from IR absorption and Raman scattering using single crystals, and our measurements were done in powdered polycrystalline samples. This could explain the large bandwidth of the optical lines associated to polycrystalline samples (Figs 3a, b, 6a and b).

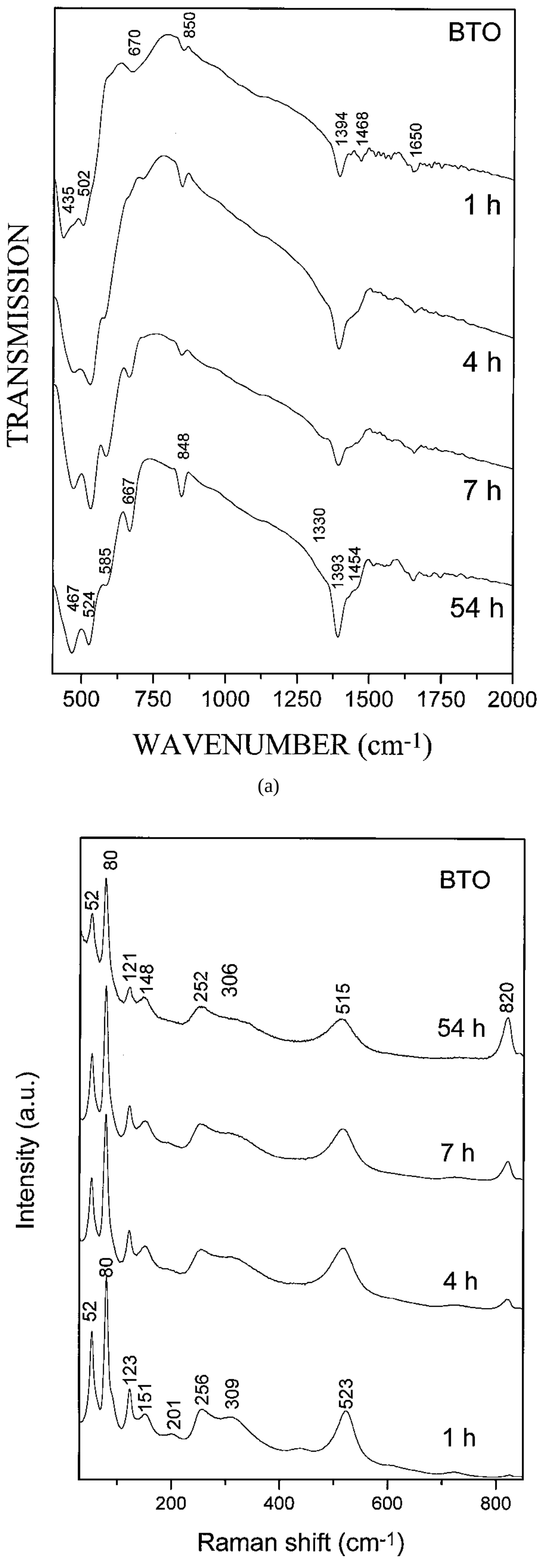
In fact XRD and DTA analysis indicates that after 7 hours, the reaction is finished, both techniques point out to the fact that the produced BTO and BSO are quite stable up to 54 hours of milling. The other important point observed was the high velocity of the production of BTO and BSO. For both cases the reaction is finished after 7 h. For $LiNbO_3$ after 42 hours we still had a little fraction of the starting material.

In conclusion, mechanical alloying has been used successfully to produce nanocrystalline powders of BTO and BSO. These materials are attractive for various electro-optical devices, including optical data processing. They present a number of attractive features as reversible recording materials for real-time holography and image processing applications. This milling process presents the advantage that melting is not necessary and the powder obtained is nanocrystalline with extraordinary mechanical properties. The material, can be compacted and transformed in solid piezoelectric ceramic samples. The reaction occurring during milling can be summarised as:

$$6Bi_2O_3 + SiO_2 \xrightarrow{\text{IMPACTS}} Bi_{12}SiO_{20}$$

$$6Bi_2O_3 + TiO_2 \xrightarrow{\text{IMPACTS}} Bi_{12}TiO_{20}$$

The high efficiency of the process, opens a way to produce commercial amount of nanocrystalline piezoelectric powders. Due to the nanocrystalline character of this powder, their mechanical properties have changed and for this reason a pressure of 1 GPa is enough to shape the sample into any geometry. Comparison of the piezoelectric properties between classical BSO and BTO ceramics and mechanical alloyed ones will be carried out in our laboratory.



(a)

(b)

Figure 6 (a) Infrared spectra of samples with 1, 4, 7 and 54 hours of milling (BTO) (see Table I). (b) Raman spectra of the samples of Fig. 3a (see Table I).

4. Conclusions

In conclusion, mechanical alloying has been used successfully to produce nanocrystalline powders of BTO and BSO. The milled BTO and BSO were studied by x-ray powder diffraction, DTA, infrared and Raman scattering spectroscopy. After 7 hours of milling the formation of BTO and BSO was confirmed by x-ray powder. The infrared and Raman scattering spectroscopy results suggest that the increase of the milling time lead to the formation of ferroelectric BTO and BSO, as seen by x-ray diffraction analysis. These materials are attractive for various electro-optical devices, including optical data processing. They present a number of attractive features as reversible recording materials for real-time holography and image processing applications. This milling process presents the advantage that melting is not necessary and the powder obtained is nanocrystalline with extraordinary mechanical properties. The material, can be compacted and transformed in solid piezoelectric ceramic samples. The high efficiency of the process, opens a way to produce commercial amount of nanocrystalline piezoelectric powders. Due to the nanocrystalline character of this powder, their mechanical properties have changed and for this reason a pressure of 1 GPa is enough to shape the sample into any geometry. Comparison of the piezoelectric properties between classical BSO and BTO ceramics and mechanical alloyed ones will be carried out in our laboratory.

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