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Photoluminescence of nanostructured PbTiO$_3$ processed by high-energy mechanical milling

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This letter reports on a process to prepare nanostructured PbTiO$_3$ (PT) at room temperature with photoluminescence (PL) emission in the visible range. This process is based on the high-energy mechanical milling of ultrafine PbTiO$_3$ powder. The results suggest that high-energy mechanical milling modifies the particle's structure, resulting in localized states in an interfacial region between the crystalline PT and the amorphous PT. These localized states are believed to be responsible for the PL obtained with short milling times. When long milling times are employed, the amorphous phase that is formed causes PL behavior. An alternative method to process nanostructured wide-band-gap semiconductors with active optical properties such as PL is described in this letter. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1362200]

The development of semiconducting materials with active optical properties such as photoluminescence (PL), electroluminscence, or nonlinear optical properties is of great scientific and technological interest. Amorphous or nanostructured semiconductors can replace single crystals in a variety of optoelectronic applications, particularly in large devices or in cases where cost is an important factor. Much interest has been evinced in the study of PL in amorphous or nanostructured materials since visible PL at room temperature has been observed in porous silicon.[1]

In crystalline form, the ATiO$_3$ compound (A=Ba, Sr, Ca, and Pb) is a typical wide-band-gap semiconductor (3.0–4.5 eV) with interesting nonlinear optical properties,[2] although other active optical properties, such as PL, are not normally observed.[3] Amorphous ATiO$_3$ materials such as Pb(Zr,Ti)O$_3$ and BaTiO$_3$ have recently attracted a good deal of attention due to their ferroelectric and electro-optical properties.[4] Despite extensive studies of this class of amorphous materials, PL at room temperature is not usually reported. Nonetheless, Pizani *et al.*[5] recently reported intense visible PL at room temperature in amorphous ATiO$_3$ compounds prepared by the sol–gel method.

In this letter, we report on an alternative method to process nanostructured wide-band-gap semiconductors, specifically PbTiO$_3$ (PT), showing PL at room temperature. This method is based on high-energy mechanical milling of ultrafine PbTiO$_3$.[6] High-energy mechanical milling is a well-known process employed in the preparation of nanostructured metals and alloys,[7] which has now become quite popular in ceramic materials processing.[8,9]

Ultrafine PbTiO$_3$ powder was mechanically milled in a high-energy attrition mill for varying lengths of time and the amorphization process was followed by x-ray diffraction (XRD) and UV–vis spectroscopy. Photoluminescence was measured using a U1000 Jobin–Yvon double monochromator coupled to a cooled GaAs photomultiplier and a conventional photon-counting system. The 488.0 nm exciting wavelength of an argon-ion laser was used, with the laser's maximum output power kept within 200 mW. All the measurements were taken at room temperature.

An XRD analysis of the PT powder milled for different lengths of time showed a progressive amorphization process. Figure 1(a) shows the XRD pattern of the powder milled for 10 and 200 h (inset). As can be observed, there is a typical amorphous (disordered) band centered at $2\theta = 29.7$. Figure 1(b) presents a high-resolution transmission electron microscopy (HRTEM) image of the powder milled for 200 h. The HRTEM image demonstrates that the specimen consists of an amorphous region (amorphous PT phase) and nanocrystalline particles, which characterize a nanostructured material. The HRTEM observations were performed using a JEM 3010 ARP.

Considering peak (101) and the broad amorphous peak, the amorphous fraction (AF) was calculated following Eq. (1):

$$AF = [I_A / (I_A + I_{(101)})] \times 100, \tag{1}$$

where I_A is the integrated amorphous peak area and $I_{(101)}$ is the integrated (101) peak area.

Figure 2(a) shows the evolution of the AF as a function of time (t). A rapid increase can be observed in the amount of AF up to 50 h. A small increase in this amount was observed when milling times of more than 50 h were employed,

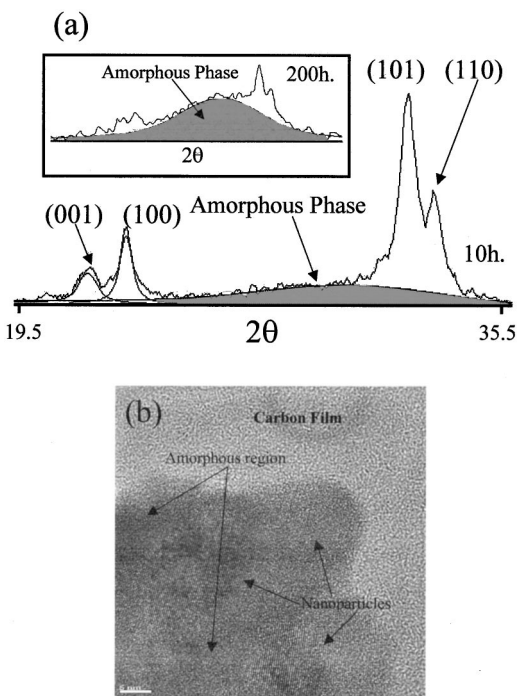[a]Electronic mail: derl@power.ufscar.br

FIG. 1. (a) XRD pattern of the ultrafine PbTiO₃ powder milled during 10 h. Inset shows the XRD pattern of the PbTiO₃ powder milled during 200 h; (b) HRTEM image of the powder milled during 200 h. For the HRTEM study, a drop of the powder suspension was deposited on a carbon-covered grid.
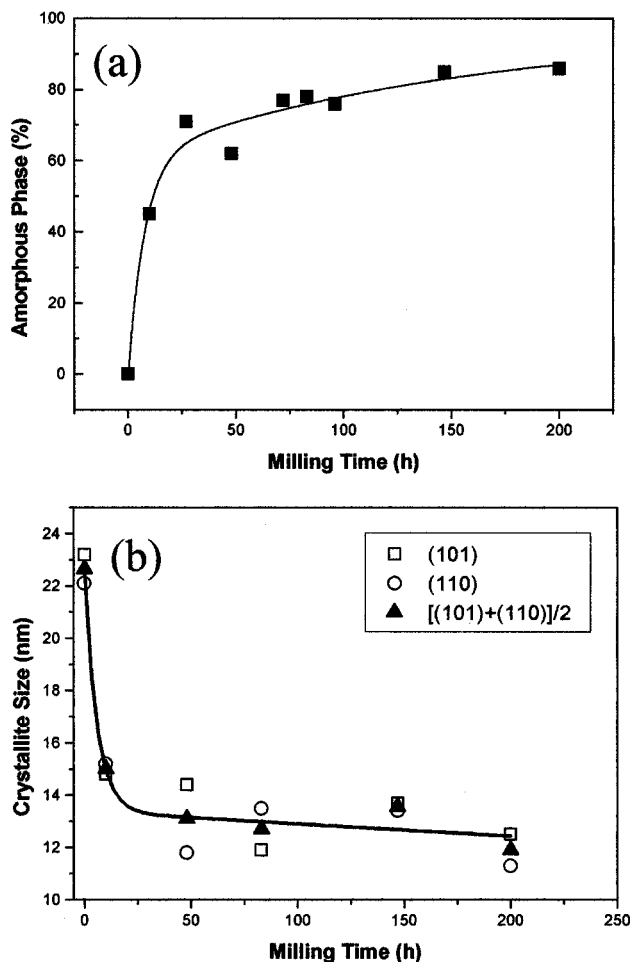

FIG. 2. (a) Evolution of the AF as a function of milling time (t); (b) evolution of the crystallite size as a function of the milling time.
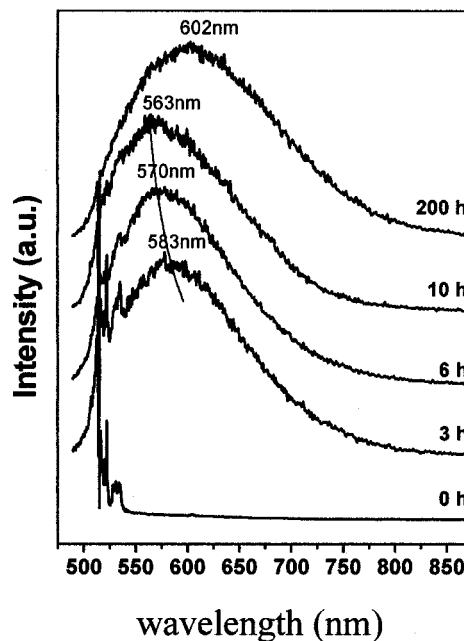

FIG. 3. PL spectrum for the amorphized PbTiO₃ compound after different milling times and for the ultrafine PbTiO₃ starting powder.

while a total AF of 87% was found after 200 h of milling. The best fit for the experimental data was a double-exponential growth equation

$$AF = -0.249 + 61.348(1 - \exp^{(-t/7.73)}) + 35.96(1 - \exp^{(-t/155.53)}). \qquad (2)$$

The decrease in crystallite size according to the milling time employed showed an exponential decay, as illustrated in Fig. 2(b). The crystallite size of the powder was determined based on the diffraction peak of the (110) and (101) PbTiO₃ planes and the Scherrer equation. In this study, the diffraction peak profile was fitted using a pseudo-Voigth function to calculate the full width at half maximum. A rapid decrease in crystallite size was observed in the first step of the amorphization process (first 50 h of milling). A crystallite size of 11 nm was reported after 200 h of milling.

These results suggest that the amorphization process and the decrease in the crystallite size are related. The decrease of the amorphization rate, for long milling time, can be related to the decrease of the crystallite size.

Figure 3 shows the PL spectrum for the amorphized PbTiO₃ compound after different milling times and for the ultrafine PbTiO₃ starting powder. The PL spectrum of the powder milled for 3, 6, and 10 h showed a broad emission peak in the visible region, and a small shift to a lower wavelength was observed. A broad emission peak was also observed in the powder milled for 200 h, although there was a shift to a higher wavelength (peak wavelength at 602 nm). The chemically prepared PbTiO₃ showed a peak wavelength at about 600 nm when excited with 488.0 nm.[5,10] The starting powder showed no emission peak. The peaks observed in the starting powder relate to the characteristic Raman scattering of this material.
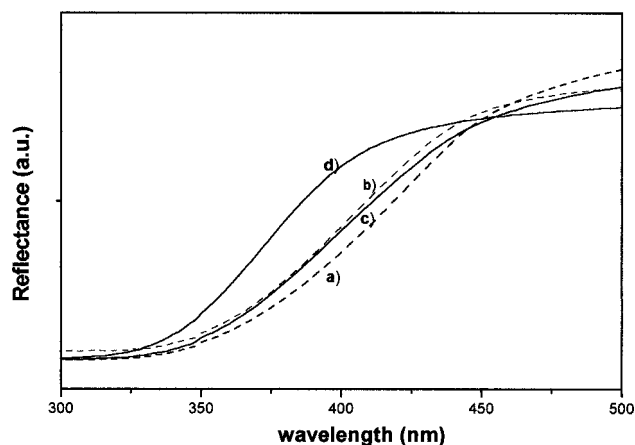
FIG. 4. Spectral dependence of the reflectance for the amorphized $PbTiO_3$ compound after different milling times [(b) after 3 h, (c) after 10 h, and (d) after 200 h] and for the ultrafine $PbTiO_3$ starting powder (a).

The PL reported in earlier articles[5,10] and observed in the chemically prepared amorphous $PbTiO_3$ was associated with a nonuniform band-gap structure with a tail of localized states and possible mobile edges. This photoluminescence in chemically prepared amorphous $PbTiO_3$ is believed to be associated with a radiative recombination between trapped electrons and trapped holes in tail and gap states. The PL peak position is mainly determined by the separation energy between those states. Specifically for this material, the spectral dependence of the reflectance measurement showed that the PL behavior was caused by the presence of the exponential optical edges and the absorption tail (a shift to a lower energy was observed).

In the case of nanostructured material prepared by mechanical milling, the spectral dependence of the reflectance showed a shift to a higher energy with increased milling time, as shown in Fig. 4. It is interesting to note that no red shift was present in the reflectance measurement or even any sign of exponential optical edges or the absorption tail, which is characteristic of amorphous semiconductors.[11]

An analysis of Figs. 3 and 4 demonstrates that the PL energy peak is lower than the band-gap energy. This finding suggests that the PL observed is not related to a direct electronic transition between the valence band to the conduction band. Hence, our preliminary results suggest that a radiative recombination between trapped electrons and trapped holes, which must be responsible for the PL, can occur in states located in an interfacial region between the crystalline PT and the amorphous PT formed by high-energy mechanical milling. This mechanism is believed to prevail when short milling times are used. In contrast, with long milling times, the fraction of amorphous material increases and, as a consequence, the PL is governed by the disordered material. For long milling times, the behavior of the PL is thought to be similar to that reported by Pizani *et al.*[5] and Leite *et al.*[10] for amorphous $PbTiO_3$ prepared by the sol–gel method.

To summarize, in this letter we have reported on a process to prepare nanostructured $PbTiO_3$ with PL emission in the visible range at room temperature. This method is based on the high-energy mechanical milling of ultrafine $PbTiO_3$ powder. Preliminary results suggest that high-energy mechanical milling may modify the particle structure, resulting in states located in an interfacial region between the crystalline PT and the amorphous PT. These localized states must be responsible for the PL that appears with short milling times. However, when long milling times are used, the amorphous layer that is formed causes the PL behavior. The findings reported on in this letter may give rise to an alternative method to process nanostructured wide-band-gap semiconductors with active optical properties, such as photoluminescence.

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