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Photoluminescence of disordered ABO_3 perovskites

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Intense photoluminescence in highly disordered (amorphous) $BaTiO_3$, $PbTiO_3$, and $SrTiO_3$ prepared by the polymeric precursor method was observed at room temperature. The emission band maxima from the three materials are in the visible region and depend on the exciting wavelength. The origin of the photoluminescence was not exactly identified. However, the line shape indicates that confinement effects are not probable. The experimental results indicate that it could be related to the disordered perovskite structure. © 2000 American Institute of Physics.
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ABO_3 (A and B are cations and O is the oxygen anion) type perovskites constitute one of the most important classes of ferroelectric materials and are used in several applications in electronic technology.^{1,2} Within this class of materials, $BaTiO_3$ (BT), $PbTiO_3$ (PT), and $SrTiO_3$ (ST), in their crystalline form, display a semiconductor behavior and have an energy band gap of about 3.0 eV. These materials are processed by solid state reaction or chemical synthesis, such as sol-gel. The advantages of the latter method are that the sintering temperature is normally much lower than that used in solid state reaction, allowing very pure mixed oxides to be obtained. Crystalline samples are obtained from a highly disordered state (amorphous) by thermal treatment.

ABO_3 amorphous materials, such as $Pb(Zr, Ti)O_3$ (PZT), BT, and ST, have recently attracted a good deal of attention due to their ferroelectric and electro-optical properties.³⁻⁵ Several studies have been reported on ferroelectric-like behavior in amorphous thin films prepared by physical or chemical methods. Despite the extensive studies of this class of amorphous materials, photoluminescence (PL) at room temperature has not yet been reported on. The study of PL in disordered or nanostructured materials has been a subject of interest since a report of PL in porous silicon. Photoluminescence in ABO_3 materials has so far been reported in only a few papers, which stated that a weak luminescence was observed only at cryogenic temperatures.^{6,7} This letter describes the characterization of intense photoluminescence observed at room temperature in amorphous BT, PT, and ST powder.

Amorphous BT, PT, and ST particles were processed by a sol-gel method, using the polymeric precursor method, which is based on the chelation of cations (metals) by citric acid, in a water solution. The citrate solution was mixed with ethylene glycol to promote polymerization through a polyesterification reaction. The reaction occurred after water had

been eliminated, at temperatures ranging from 90 to 120 °C. The polymeric precursors for BT, PT, and ST amorphous compound syntheses were calcinated at 300–400 °C for different lengths of time. These temperatures are sufficiently high to promote polymer pyrolysis, but not crystallization. An x-ray diffraction analysis showed that, after calcination at low temperatures, an amorphous phase is formed. Further details about the polymeric precursor synthesis of this compound can be found in Ref. 8.

The photoluminescence measurements were taken with a U1000 Jobin–Yvon double monochromator coupled to a cooled GaAs photomultiplier and a conventional photon counting system. The 457.9, 488.0, and 514.5 nm exciting wavelengths of an argon ion laser was used, with the maximum output power of the laser kept at 20 mW. A cylindrical lens was used to prevent the samples from overheating. The slit width used was 100 μm . All the measurements were taken at room temperature.

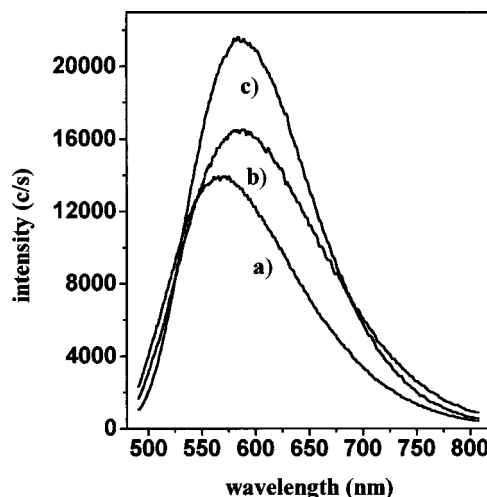


FIG. 1. Room temperature photoluminescence spectra of (a) BT, (b) PT, and (c) ST powder samples, excited with the 488 nm line of an argon ion laser.

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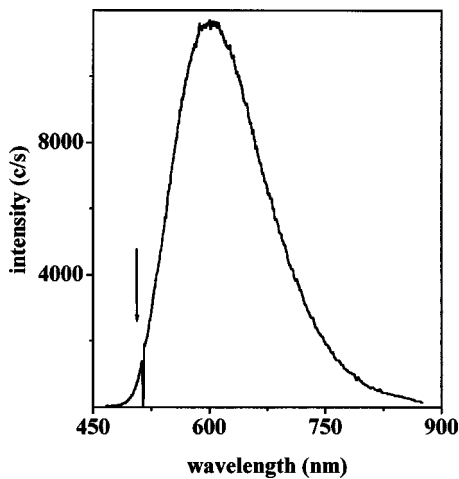


FIG. 2. PL spectrum of ST at room temperature showing Stokes and anti-Stokes emissions. The arrow indicates the exciting wavelength.

The photoluminescence spectra of the BT, PT, and ST samples were very similar in shape, presenting broad bands. Figure 1 displays the spectra of the three materials, excited with the 488.0 nm line. The materials' maximum peak positions were about 550 nm for BT and 580 nm for PT and ST. These results were corroborated by UV-Vis spectroscopy measurements showing differing optical band gap energy for the three amorphous materials. Figure 2 shows the Stokes and anti-Stokes spectrum of ST at room temperature, excited with the 488.0 nm line. Similar spectra were obtained for BT and PT. The line shape is typical of the multiphonon process, i.e., it has several relaxation channels indicative of a broad energy band gap. Although these are disordered materials, it is also a well known fact that the details of band structure in solids are mainly determined by the potential within the unit cell rather than by long range periodicity. Moreover, this line shape indicates that the confinement effect cannot be considered as the predominant mechanism of luminescence.

Figure 3 presents the spectral dependence of the optical absorbance of the crystalline and amorphous PT. These measurements were taken at room temperature in the total reflection mode, using Cary 5G equipment. In the case of crystal-

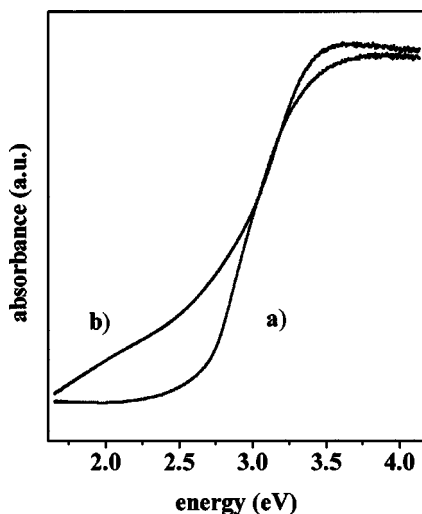


FIG. 3. UV-Vis absorption spectra of (a) crystalline and (b) disordered PT, at room temperature.

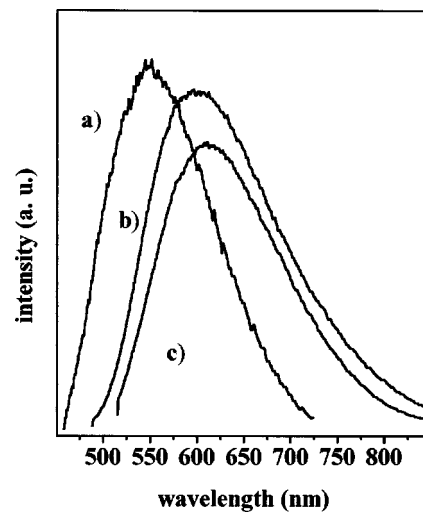


FIG. 4. PL spectra of PT as a function of exciting wavelength: (a) 458 nm, (b) 488 nm, and (c) 514 nm.

line PT, a direct band gap transition with a well defined gap energy was observed. For disordered PT, a shift to low energies was observed, associated with a nonuniform energy transition. This finding suggests strong interaction among photon-electron-phonon and is in agreement with the PL spectra shown in Fig. 2. It also indicates that quantum confinement is not the dominant mechanism in PL behavior, since a shift to high energies is expected in the spectral dependence of the optical absorbance when quantum confinement occurs.

The PL spectra of PT as a function of the exciting wavelength (457.9, 488.0, and 514.5 nm) are shown in Fig. 4. The Stokes shift is about 100 nm for the three wavelengths. The same behavior was observed in BT and ST samples.

Figure 5 shows the effect of carbon content in the PL of disordered PT material. The carbon content was measured by thermogravimetric analysis. After the calcination process at a low temperature, the material processed by the polymeric precursor method presents basically two phases, an inorganic and a carbon amorphous phase. Increasing the calcination time causes a decrease in the total carbon material content. If the PL behavior observed comes from the disordered inor-

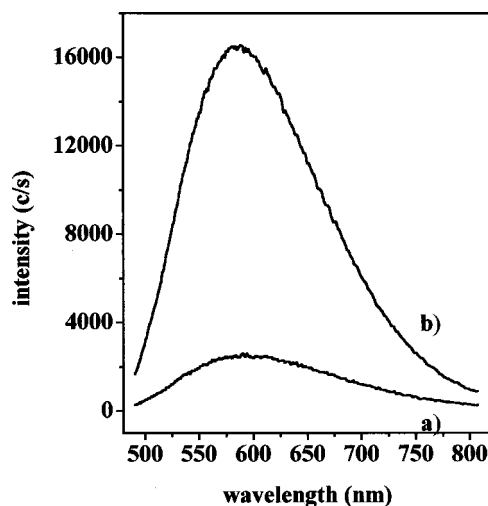


FIG. 5. PL spectra of PT for samples calcinated at 683 K during (a) 4 h and (b) 8 h.

ganic phase, more intense PL must occur for the material calcinated for a longer time. This behavior was observed in the PL spectrum shown in Fig. 5. After calcination at 673 K for 8 h, the PL spectrum was higher than the same material calcinated for 4 h. This finding is strongly indicative that the PL stems from the inorganic disordered phase. A similar behavior was observed for BT and ST samples. A slight increase in thermal treatment temperatures causes the sample to crystallize, and leads to the emergence of the Raman spectra typical of these materials and to the concomitant disappearance of the PL. This is a strong indication that the disordered phase is responsible for the PL.

Summarizing, intense photoluminescence at room temperature was observed in highly disordered PbTiO_3 , BaTiO_3 , and SrTiO_3 powder samples synthesized by the polymeric precursor method. The photoluminescence spectra of these materials are quite similar in shape, presenting broad bands in the visible region. The PL peak position was observed to depend on the exciting wavelength and on the nature of the cation present in the material. The photoluminescence of these ferroelectric materials is one more interesting property

for technological applications. Moreover, our preliminary results on photoluminescence of thin films of these materials on silicon substrate showed that they are also very promising materials for optoelectronic applications. Although the origin of the photoluminescence is not yet clear, it might be ascribed to the disordered perovskite structure. Further work will be required to clarify this point.

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