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Room temperature photoluminescence of amorphous $Ba_xSr_{1-x}TiO_3$ doped with chromium

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Abstract

ABO_3 amorphous materials, such as $BaTiO_3$ (BT), $SrTiO_3$ (ST), $PbTiO_3$ (PT), and $Ba_xSr_{1-x}TiO_3$ (BST) have recently attracted a good deal of attention due to their ferroelectric and electro-optical properties. Intense photoluminescence at room temperature was observed in amorphous titanate doped with chromium ($Ba_xSr_{1-x}Ti_{1-y}Cr_yO_3$) prepared by the polymeric precursor method. Results indicated that substantial luminescence at room temperature was achieved with the addition of small Cr contents to amorphous $Ba_xSr_{1-x}Ti_{1-y}Cr_yO_3$. Further addition of Cr or crystallization were deleterious to the intensity of the luminescent peak obtained for excitation using $\lambda = 488.0\,\text{nm}$.

Keywords: Amorphous $SrTiO_3$; Photoluminescence; Chromium

1. Introduction

The chemical solution method offers an opportunity to tailor-make the chemistry, structure and microstructure of materials to achieve specific optical and electrical properties. This kind of process has been used to prepare well-known compounds as well as new ones that cannot be produced otherwise. The development of materials with active optical properties, such as photoluminescence, electroluminescence, or non-linear optical properties, may lead to new optoelectronic devices with superior performance [1]. Although photoluminescence in crystalline titanates [2] has already been well established, this property has only been recently identified in amorphous titanate powders synthesized at low temperatures [3,4].

The development of nanostructured materials has been very active in the last years. Amorphous materials of the ABO_3 family (A and B are cations and O is oxygen), such as $BaTiO_3$, $PbTiO_3$ and $SrTiO_3$ have recently attracted a good deal of attention due to their ferroelectric and electro-optic properties [5,6]. In their crystalline form, ABO_3 compounds are typically wide-band gapped semiconductors. Much attention has also focused on crystalline $BaTiO_3$ and $SrTiO_3$. Particularly, when pure $SrTiO_3$ crystals are excited by radiation above their energy band gap, a broad luminescent band appears at low temperatures [7,8]. Several phenomena related to luminescence have also been reported for $BaTiO_3$ crystals, and the effects observed can be correlated to impurity centers, e.g., rare earth ions in doped $BaTiO_3$ compounds [9]. Among these materials, $Ba_xSr_{1-x}TiO_3$ (BST) crystalline thin films have been extensively investigated due to their high dielectric constant coupled with good thermal stability.

In addition, several studies have been carried out on the electrical behavior of both amorphous and crystalline BST thin films prepared by physical or chemical processes [10–12]. Pontes et al. [13] attributed intense visible photoluminescence in amorphous thin films obtained at low temperature to the disordered structure of $SrTiO_3$ and $BaTiO_3$ [13,14]. Titanate octahedra containing short Ti–O bonds also depicted efficient luminescence at room temperature [15,16]. Available

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experimental evidence can be correlated to a theoretical model based on oxygen vacancy defects [17,18]. The basis for the model is the loss of oxygen from the lattice to the gas phase with formation of a double ionized vacancy $V_{\ddot{o}}$, having two extra electrons attributed to the conduction band. In this model, holes are attributed to the O^- ion and electrons to the Ti^{3+} species.

Akhtar and co-workers [19] performed a theoretical study on $SrTiO_3$ defects. They studied undoped $SrTiO_3$ and mainly observed the presence of Schottky or Schottky-like defects. They also studied the effect of different dopants and the corresponding mechanisms. For instance, the substitution of Sr^{2+} in monovalent dopants need to be compensated by the formation of oxygen vacancies. Tetravalent dopants substitute either Sr^{2+}or Ti^{4+} according to the ionic radius. Higher valence dopants were not studied. Despite the recent advances on amorphous BST materials, photoluminescence at room temperature had not yet been reported. This paper discusses the intense photoluminescence observed at room temperature in amorphous BST doped with Cr and prepared by the polymeric precursor method [4].

2. Experimental

Nanometric particles of amorphous chromium-doped $BaSrTiO_3$ powders were prepared by the polymeric precursor method. The preparation is based on the chelation of metallic cations by citric acid in aqueous solution. The citrate solution was mixed with ethyleneglycol to promote polymerization by polyesterification reaction between 90°C and 120°C following the elimination of water. The polymeric precursor used in the synthesis of amorphous $Ba_xSr_{1-x}TiO_3$ doped with 2, 4, 6, 8 or 10 mol% of chromium was calcinated at 300°C for 1 h, for the pyrolisis of the obtained polyester, and 300°C for 40 or 80 h. These temperatures are sufficiently high to promote the pyrolisis of the polymer without crystallization. This method has the advantage of using common reagents not requiring special atmosphere [2,3]. Amorphous powders were characterized by thermogravimetric analysis (TG), X-ray diffraction (XRD) and photoluminescence measurements (PL). XRD patterns were obtained using Cu$K\alpha$ radiation and used to determine the formation of crystalline structures on the resulting powders.

Photoluminescence measurements were obtained using a U1000 Jobin-Yvon double monochromator coupled to a cooled GaAs photomultiplier and a conventional photon counting system. The 488.0 nm wavelength of an argon ion laser was used. The maximum output of the laser was set to 200 mW. All measurements were carried out at room temperature.

3. Results and discussion

The presence of residual carbon was estimated by thermogravimetric analyses. After calcining at low temperature, the material obtained by the polymeric precursor method consisted basically of two phases, i.e. amorphous $Ba_xSr_{1-x}TiO_3$ and a carbon bearing phase. Increasing the calcining time decreased the total amount of carbon present in the material. This was confirmed by thermogravimetric analyses (Figs. 1 and 2) which showed significant difference in weight loss upon calcining for 40 or 80 h at 300°C in flowing air. XRD patterns of $Ba_xSr_{1-x}TiO_3$ doped with 2–10% chromium calcined at low temperature (300°C/80 h) revealed that the addition of Cr did not alter the amorphous nature of the powder (Fig. 3). Crystallization started at 600°C as suggested by the thermogravimetric profile and confirmed by XRD. The amorphous state when obtained by a process that maintains chemical memory, such as organic precursor synthesis, transforms amorphous to crystalline phases with high crystallographic order [2,3,8,9].

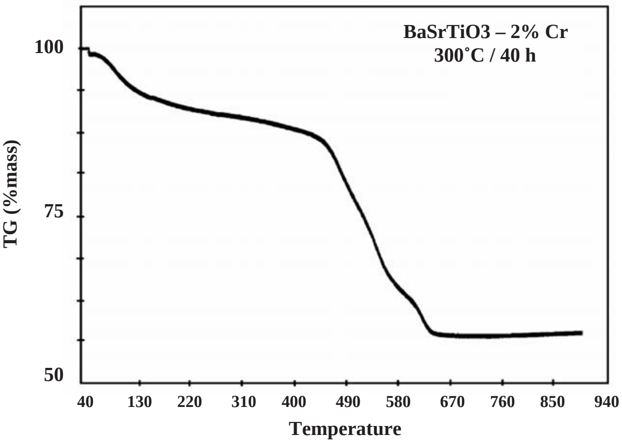


Fig. 1. TG pattern of $Ba_xSr_{1-x}TiO_3$ doped with 2% chromium obtained at 300°C for 40 h.

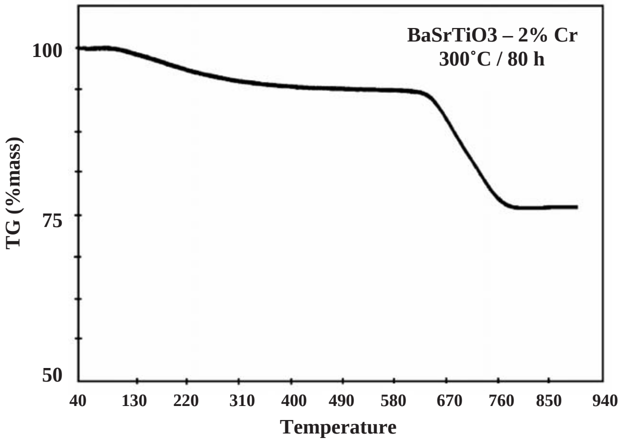


Fig. 2. TG pattern of $Ba_xSr_{1-x}TiO_3$ doped with 2% chromium obtained at 300°C for 80 h.

Photoluminescence at room temperature has been reported for crystalline, nanocrystalline and amorphous titanates. In nanomaterials, the effect has been attributed to the high concentration of superficial defects resulting in an amorphous-like surface [13,14]. In fully amorphous materials, such as Cr-doped BST calcined at low temperature, the coexistence of five- and six-fold oxygen–titanium bonds play a role in the property. It can be inferred from related studies that radioactive recombination of trapped electron–hole pairs in similar amorphous materials may have a role in determining the visible and intense photoluminescence observed at room temperature in highly disordered $Ba_xSr_{1-x}TiO_3$ synthesized by the polymeric precursor method [13]. Cr replaced Ti in the lattice, but its presence did not affect the organization of the structure of $Ba_xSr_{1-x}TiO_3$, as clearly indicated by the XRD patterns of BST doped with 2% or 10% Cr and calcined under different temperatures (Fig. 4). On the other hand, the mechanism of room temperature photoluminescence seems to be related to the concentration of non-bridging oxygen defects [3,7,8] in the disordered

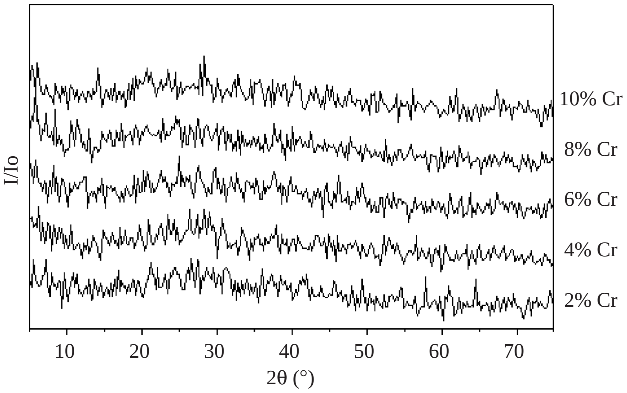
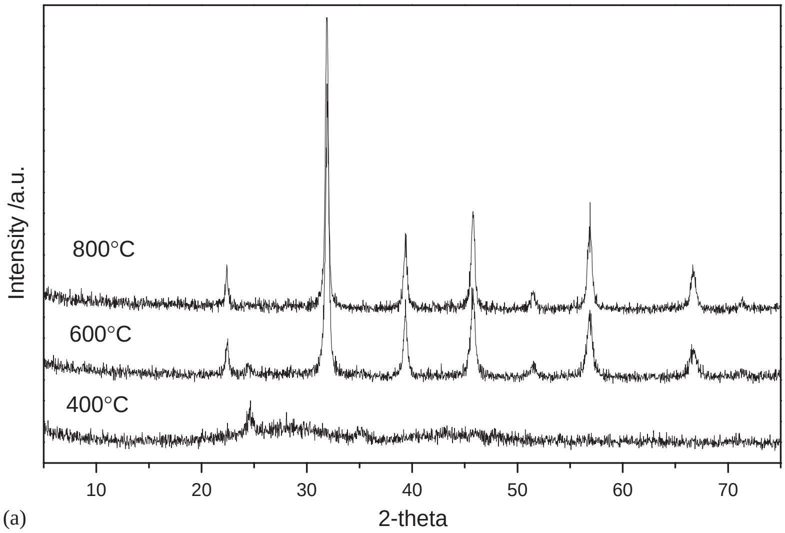


Fig. 3. XRD patterns of $Ba_xSr_{1-x}TiO_3$ doped with 2–10% Cr and calcinated at 300°C for 80 h.



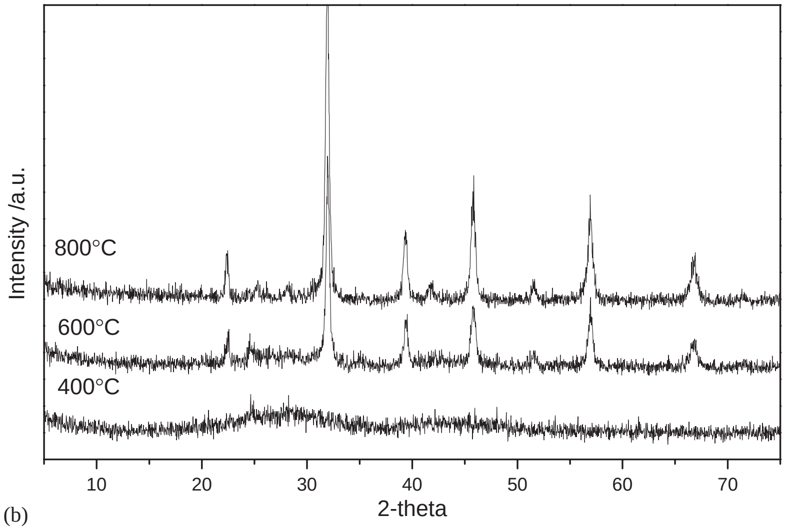


Fig. 4. XRD patterns of $Ba_xSr_{1-x}TiO_3$ doped with 2% or 10% Cr and calcinated at different temperatures.

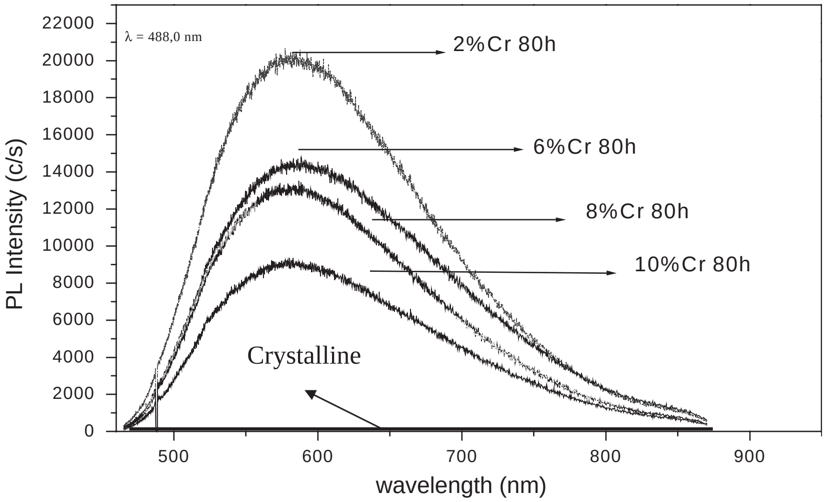


Fig. 5. Room temperature photoluminescence of $Ba_xSr_{1-x}TiO_3$ doped with 2%, 6%, 8% or 10% chromium at 300°C for 80 h.

structure of $Ba_xSr_{1-x}TiO_3$. Therefore, Cr contents significantly affected the photoluminescence intensity of the amorphous compound at room temperature (Fig. 5). The PL intensity steadily decreased as the Cr contents increased from 2% to 10%. The disordered structure of $BaSrTiO_3$ is caused by non-stoichiometric contents of SrO or BaO, the presence of vacancies, modifiers and site-to-site disorder in the *B* sub-lattice. Concurrently, according to ESR data on ABO_3 compounds including $BaTiO_3$ [20], PZT [21,22] and PLZT : Mn [23], charge compensation results in the appearance of Ti^{3+} in the *B* octahedral position. Cr ions act as impurities which occupy *B* sites, not only as Cr^{3+} but sometimes as Cr^{5+} in $PbTiO_3$ [24], $BaTiO_3$ [25,26] and PT [2,3,7]. Pure amorphous BaSrTiO3 with ABO_3 structure depicts luminescence due to ions at both *A* and *B* sites. In addition, the presence of color centers should be considered (including $V_{\ddot{o}}$, V''_{Sr}, or V''_{Ba} vacancies), donor–acceptor pairs and impurity (Cr) centers. These occupy either the substitutional site in $[AO_{12}]$ or $[BO_6]$ complexes and/or interstitial sites. In the case of Cr impurities in perovskite ($BaSrTiO_3$), one Cr ion replaces a Ti ion to form an octahedral CrO_6 complex, but the other ion replaces a Ti ion in a different octahedron, forming a CrO_5 complex plus an oxygen vacancy, $V_{\ddot{o}}$. If these two different structures coexist in the amorphous material, the charge corresponding to two holes is compensated by one oxygen vacancy. If Cr^{3+} ions substitute the Ti^{4+} site, the presence of the $[CrO_6]$ and $[CrO_5V_{\ddot{o}}]$ complexes will stabilize the defect by charge compensation, resulting in the decrease of the luminescence intensity with increasing Cr concentration. As the material begins to organize in its crystalline form, the intensity of photoluminescence decreases to virtually zero at room temperature (Fig. 5).

4. Conclusions

Room temperature luminescence was observed in amorphous $Ba_xSr_{1-x}TiO_3$ doped with chromium and synthesized using the polymeric precursor approach. Addition of 2% Cr and calcining at 300°C for 80 h yielded maximum luminescence for this compound. Higher contents of Cr did not affect the amorphous nature of the material but steadily decreased the intensity of the luminescent peak for excitation at $\lambda = 488.0$ nm. No luminescence was observed in crystalline Cr-doped BST.

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