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Violet-blue photoluminescence was produced at room temperature in a structurally disordered SrZrO₃ perovskite structure with a 350.7 nm excitation line. The intensity of this emission was higher than that of any other perovskites previously studied. The authors discuss the role of structural order-disorder that favors the self-trapping of electrons and charge transference, as well as a model to elucidate the mechanism that triggers photoluminescence. In this model the wide band model, the most important events occur before excitation. © *2007 American Institute of Physics.*
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In recent years, perovskite materials have been the object of exhaustive research due to their potential technological applications, which include flat-screen full-color displays and compact laser devices operating in the blue region to develop a new generation of digital video disk recorders.[1,2]

The broad luminescent band usually observed at low temperatures in perovskite-type crystals is associated with the presence of imperfections or defects.[3] Based on advanced studies of the electronic transitions that display photoluminescence (PL) emission, Kan *et al.*[4] concluded that oxygen deficiency in Ar⁺-irradiated SrTiO₃ is the unique cause for blue light PL emission at room temperature. However, the literature includes several papers explaining the favorable conditions for PL emission in materials presenting a degree of order-disorder.[5–7] The authors attributed the radiative decay process to distorted octahedra,[5] self-trapped excitons, oxygen vacancies, surface states,[6] and a charge transfer via intrinsic defects inside an oxygen octahedron.[7] As can be seen, there is no general consensus in the literature to explain *why* and *how* radiative decay takes place in perovskitelike structures with a certain degree of disorder. Our group demonstrated that a series of structurally disordered titanates (*A*TiO₃, where *A*=Ca, Sr, and Ba) displays intense photoluminescence at room temperature when excited by a 488 nm laser excitation line,[8–10] and that more intense PL emission is obtained with a certain structural order-disorder in the material.

Intense violet-blue PL emission was recently reported in SrZrO₃ (SZ) nanocrystals and this emission was attributed to the existence of defect levels.[11] However, PL properties in disordered SZ at room temperature have not yet been reported.

In this letter, we report violet-blue emission by structurally disordered SZ and discuss the conditions favorable to obtaining highly intense broad violet-blue PL. In addition, we discuss the role of structural order-disorder that favors the self-trapping of electrons and charge transfer in the SZ lattice, which give rise to the emission process.

Ordered and disordered SZ powders were prepared by the polymeric precursor method.[12] The polymeric resin was pyrolytically treated at 350 °C for 2 h and produced powders with organic residue resulting from the method employed. The powders were heat treated at 350, 375, 400, 425, 450, 475, 500, 660, and 1250 °C for 2 h in an oxygen atmosphere. The SZ powders were then characterized by x-ray diffraction and PL spectroscopy. The powder phase was analyzed by x-ray powder diffraction, using a Bragg-Brentano diffractometer (Rigaku 2000) and Cu *Kα* radiation. The PL was measured with a Thermal Jarrel-Ash Monospec 27 monochromator and a Hamamatsu R446 photomultiplier. The 350.7 nm exciting wavelength of a krypton ion laser (Coherent Innova) was used, with the laser's nominal output power kept at 200 mW. All the measurements were taken at room temperature.

Figure 1 shows x-ray diffraction patterns of SZ powders annealed at 350, 375, 400, 425, 500, 660, and 1250 °C. The presence of diffraction peaks can be used to evaluate long-range structural order. Powders annealed at 660 and 1250 °C showed diffraction peaks, indicating the long-range order of these materials. Moreover, because they comprised a single phase, they were completely indexed based on orthorhombic ICDD (*Pbnm*).[13] SZ powders annealed at temperatures as
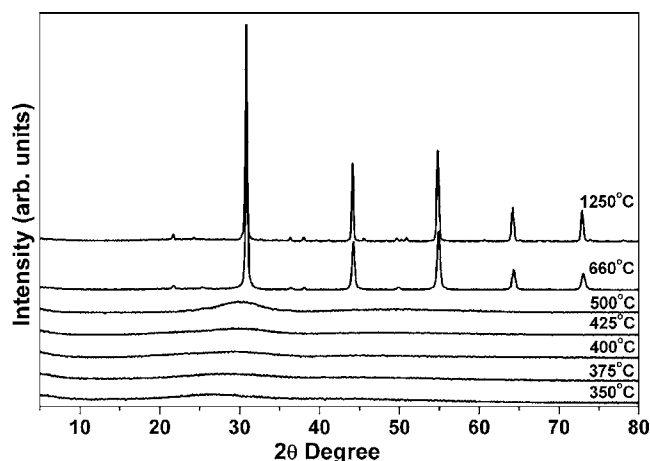
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FIG. 1. (a) X-ray powder diffraction patterns of SZ powders heat treated at 350, 375, 400, 425, 500, 660, and 1250 °C.
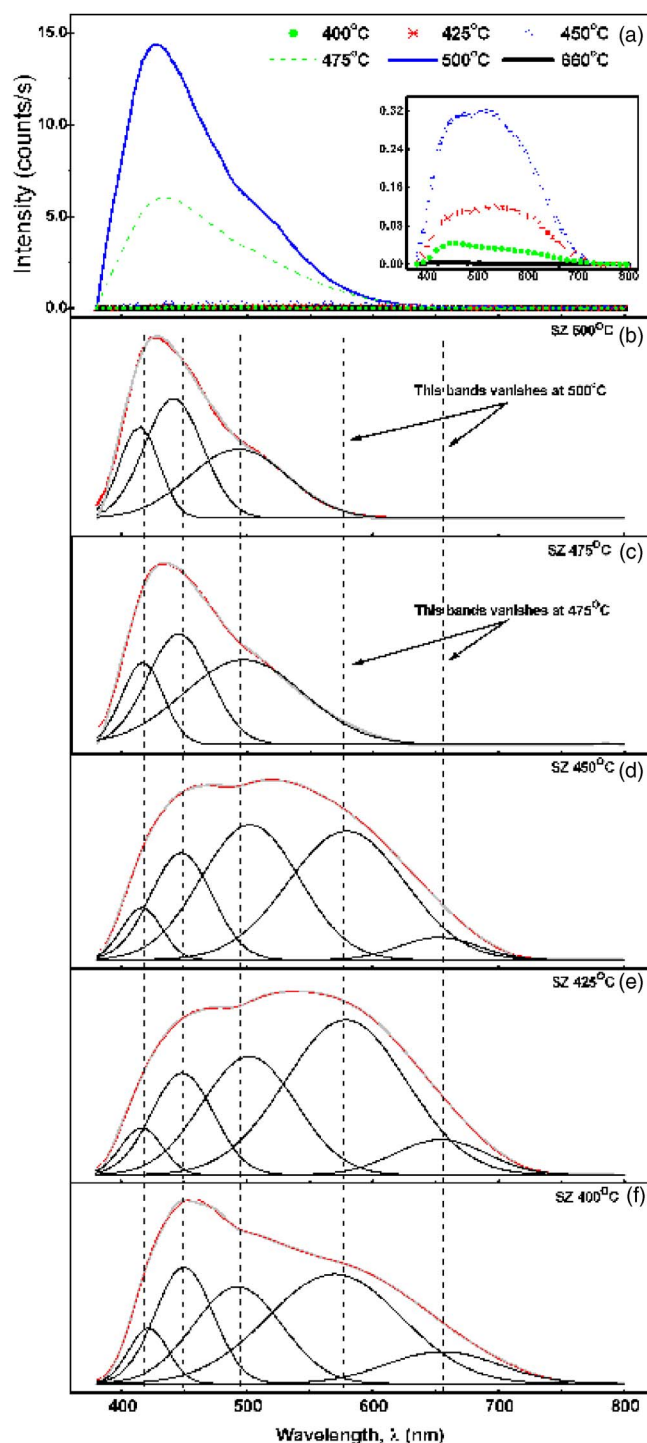

FIG. 2. (Color online) (a) PL spectra for SZ annealed at 400, 425, 450, 475, 500, and 660 °C. Inset: PL spectra of samples annealed at 400, 425, 450, and 660 °C [(b)–(f)] Deconvolution PICKFIT for the samples annealed at 400, 425, 450, 475, and 500 °C, respectively.

low as 660 °C have not yet reached a complete structural order.

Figure 2(a) depicts PL spectra recorded at room temperature for the SZ powders heat treated at 400, 425, 450, 475, 500, and 660 °C. The inset in Fig. 2(a) shows the samples annealed at 400, 425, 450, and 660 °C in greater detail. The profile of the emission band is typical of a multiphonon process, i.e., a system in which relaxation occurs by several paths, involving the participation of numerous states within the band gap of the material. This behavior is associated with the structural disorder of SZ and indicates the presence of additional electronic levels in the forbidden band gap of the material.

The general aspect of the spectra is a broad band covering a large part of the visible spectra from ∼370 to 850 nm. As can be seen, the structurally disordered powder annealed at 400 °C displayed low PL emission, and after annealing at 660 °C, the SZ powder was structurally ordered and PL emission had disappeared. Therefore, the interesting PL properties of structurally ordered-disordered SZ powders occur within the range of 400–660 °C. The intensity of the violet-blue light luminescence appeared after annealing at 400 °C and increased gradually as the annealing temperature rose. The bands were broad and intense, particularly in the disordered powder annealed at 500 °C and centered at 430 nm (2.9 eV). This violet-blue light emission was so intense that it was visible to the naked eye.

To better understand the properties of PL and its dependence on the structural order-disorder of the lattice, the PL curves were analyzed by PEAKFIT (Ref. 14) deconvolution. Based on the Gaussian line broadening mechanism for luminescence processes, the fine features in the PL spectra of samples annealed at different temperatures were deconvoluted, as shown in Figs. 2(b)–2(f).

We believe that the PL curves shown in Fig. 2 represent five PL components, herein named components violet (maximum below 418 nm), blue (maximum below 448 nm), green (maximum below 493 nm), yellow (maximum below 577 nm), and red (maximum below 657 nm), in allusion to the regions where the component's maxima appear.

As this figure indicates, increasing the annealing temperature causes the structure of SZ powders to become more ordered, favoring higher energy violet-blue light emission (smaller wavelength).

Each color represents a different type of electronic transition and is linked to a specific structural arrangement. Zirconium, which is the former lattice, ideally tends to bond with six oxygen atoms, but before reaching this ideal configuration, there are various coordination numbers for the Zr atom in the structure. Before crystallization occurs, the structure consists of a mixture of ZrO_x clusters (x=mostly 5 and 6) intercalated by Sr atoms. The higher the calcining temperature, the more frequent the ZrO_6 conformation and the more ordered the structure. The yellow and red peaks de-
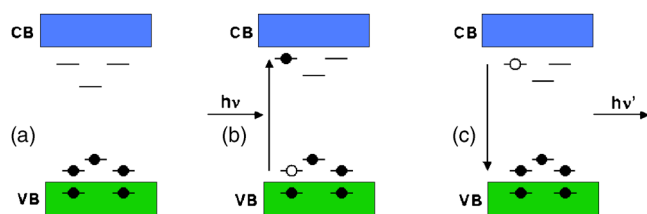
FIG. 3. (Color online) Wide band model: (a) before excitation, (b) excitation (formation of STE), and (c) after excitation (recombination of e' and $h^{\bullet}$.

crease and the violet-blue peaks increase with heat treatment, since yellow-red emission is linked to the disordered structure and violet-blue to the ordered structure.

Experimental results obtained by x-ray absorption near edge structure confirmed the coexistence of two types of Ti coordination in the structurally ordered-disordered perovskite titanate compounds, namely, fivefold oxygen-Ti coordination (TiO_5 square base pyramid) and sixfold oxygen-Ti coordination (TiO_6 octahedron).[15] First principle calculations revealed that this disordered structure leads to local polarization and a charge gradient in the structure.[9] We believe that the same mechanism takes place in structurally disordered SZ powders.

Many valid hypotheses put forward in the literature[16,17] explain all the possible mechanisms that occur during the process of photon excitation and decay. Using time-resolved spectroscopy, Leonelli and Brebner proposed a model to describe the luminescence process, whereby electrons form small polarons and holes interact with these polarons to produce self-trapped excitons (STEs), and the recombination of STEs results in visible emission either immediately before or after being trapped for a certain time by impurities and defect.[16] More recently, several PL phenomena at low temperature have been reported for the perovskite-type structure and the effects observed have been linked to the recombination of electrons and hole polarons, forming a charge transfer vibronic exciton.[17]

Because band gap energies are much higher than the excitation energy (3.54 eV) that is used for collecting PL spectra, the PL-triggering mechanism is not a band-to-band process. These observations confirm the fact that PL is directly associated with the localized states existing in the band gap and that the degree of order-disorder alters these localized states. These electronic states give rise to PL spectra of different colors and are linked to different electronic transitions. First principle quantum mechanical calculations have shown that the break in lattice symmetry due to structural disorder is responsible for the presence of electronic states in the band gap.[10] In our model—the wide band model illustrated in Fig. 3—the most important events occur before excitation, i.e., before the photon arrives. The short- and intermediate-range structural defects generate localized states in the band gap and inhomogeneous charge distribution in the cell, thus allowing for the trapping of electrons. The localized levels are energetically distributed so that various energies are able to excite the trapped electrons.

After excitation of the photon, the recombination and decay process follows the many valid hypotheses presented in the literature.[16,17]

In summary, $SrZrO_3$ powders were synthesized by a low-cost polymeric precursor method. The calcining temperatures were progressively increased until complete crystallization of the phase, which occurred at 660 °C. Strong violet-blue light PL emission was achieved at room temperature after exciting a noncrystalline SZ sample with the 350.7 nm excitation line of a krypton ion laser. The decrease in gap energy due to the localized levels in the band gap, together with charge discontinuities induced by local disorder, favored the trapping of electrons and holes and led to the PL emission. The electronic states were strongly related with the structural order-disorder in the lattice.

[1] R. V. Shende, D. S. Krueger, G. A. Rosetti, Jr., and S. J. Lombardo, J. Am. Ceram. Soc. **4**, 1648 (2001).
[2] B. J. Kennedy and C. J. Howard, Phys. Rev. B **59**, 4023 (1999).
[3] W. F. Zhang, Z. Yin, M. S. Zhang, Z. L. Du, and C. W. Chen, J. Phys.: Condens. Matter **11**, 5655 (1999).
[4] D. Kan, T. Terashima, R. Kanda, A. Masuno, K. Tanaka, S. Chu, H. Kan, A. Ishizumi, Y. Kanemitsu, Y. Shimakawa, and M. Takano, Nat. Mater. **4**, 816 (2005).
[5] W. F. Zhang, J. W. Tang, and J. H. Ye, Chem. Phys. Lett. **418**, 174 (2006).
[6] F. Chen, H. W. Liu, K. F. Wang, H. Yu, S. Dong, X. Y. Chen, X. P. Jiang, Z. F. Ren, and J. M. Liu, J. Phys.: Condens. Matter **17**, L467 (2005).
[7] M. S. Zhang, J. Yu, J. H. Chu, Q. Chen, and W. C. Chen, J. Mater. Process. Technol. **137**, 78 (2003).
[8] P. S. Pizani, H. C. Basso, F. Lanciotti, T. M. Boschi, F. M. Pontes, E. Longo, and E. R. Leite, Appl. Phys. Lett. **81**, 253 (2002).
[9] E. Orhan, J. A. Varela, A. Zenatti, M. F. Gurgel, F. M. Pontes, E. R. Leite, E. Longo, P. S. Pizani, A. Beltrán, and J. Andrés, Phys. Rev. B **71**, 085113 (2005).
[10] E. Longo, E. Orhan, F. M. Pontes, C. D. Pinheiro, E. R. Leite, J. A. Varela, P. S. Pizani, T. M. Boschi, F. Lanciotti, Jr., A. Beltrán, and J. Andrés, Phys. Rev. B **69**, 125115 (2004).
[11] A. Zhang, M. Lu, S. Wang, G. Zhou, S. Wang, and Y. Zhou, J. Alloys Compd. (2006) (in press).
[12] M. Kakihana and M. Yoshimura, Bull. Chem. Soc. Jpn. **72**, 1427 (1990).
[13] ICCD Card No. 42-423.
[14] T. Ding, W. T. Zheng, H. W. Tian, J. F. Zang, Z. D. Zhao, S. S. Yu, X. T. Li, F. L. Meng, Y. M. Wang, and X. G. Kong, Solid State Commun. **232**, 815 (2004).
[15] F. M. Pontes, C. D. Pinheiro, E. Longo, E. R. Leite, S. R. de Lazaro, J. A. Varela, P. S. Pizani, T. M. Boschi, and F. Lanciotti, Mater. Chem. Phys. **78**, 227 (2003).
[16] R. Leonelliand J. L. Brebner, Solid State Commun. **54**, 505 (1985).
[17] R. I. Eglitis, E. A. Kotomim, and G. Bostel, Eur. Phys. J. B **27**, 483 (2002).