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Photoluminescent behavior of SrBi$_2$Nb$_2$O$_9$ powders explained by means of β-Bi$_2$O$_3$ phase

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Photoluminescence (PL) behavior of SrBi$_2$Nb$_2$O$_9$ (SBN) powders was explained by means of β-Bi$_2$O$_3$ phase on the SBN lattice. Oxygen vacancies and recombination of electrons holes in the valence band lead to the formation of $[\text{NbO}_5 \cdot V_\text{O}^x]$, $[\text{NbO}_5 \cdot V_\text{O}^\bullet]$ and $[\text{NbO}_5 \cdot V_\text{O}^{\bullet\bullet}]$ complex clusters which are the main reason for the PL at room temperature. X-ray diffraction and Fourier transform Raman spectroscopy were used as tools to investigate the structural changes in SBN lattice allowing to correlate $[\text{NbO}_5 \cdot V_\text{O}^\bullet]/[\text{NbO}_6]'$ ratio with the evolution of the visible PL emission in the SBN powders. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2753114]

SrBi$_2$Nb$_2$O$_9$ (SBN) is a member of the Aurivillius family of Bi-layered compounds first described in 1949.[1] At temperatures below the ferroelectric Curie temperature (T_C), SBN crystallizes in the polar orthorhombic space group $A2_1am$,[2] according to Ref. 3. On passing through T_C, both phases appear to transform directly into a tetragonal paraelectric phase, space group $I4/mmm$.[4] In general, the Aurivillius (perovskite) phase is represented by $(\text{Bi}_2\text{O}_2)^{2+}(A_{m-1}B_m\text{O}_{3m+1})^{2-}$, where A is a divalent ion such as Sr^{2+}, Ba^{2+}, and Ca^{2+}, B is a metal of valence 5+, usually, Nb^{5+} or Ta^{5+}, and m is the number of the perovskite unit cells between Bi$_2$O$_2$ layers.[5–9] SBN belongs to the perovskite orthorhombic structure (ferroelectric phase) at room temperature, with a high T_C of approximately 440 °C.[10] Among Bi-layered perovskite oxides, SBN is a preferred choice due to its lower crystallization temperature than that of SrBi$_2$Ta$_2$O$_9$.[11] Miura[12] and Yang *et al.*[13] showed that the SBN phase was crystallized via a metastable fluoritelike phase in a cubic structure. In this system, stoichiometric deviations can occur, leading to intermediary pyrochlore and fluorite phases.[14] However, to the best of our knowledge, photoluminescence (PL) properties in SBN powders have not been reported so far. In this letter, we investigate the photoluminescence properties at room temperature as a function of the degree of structural order-disorder in the SBN lattice.

SBN resin was prepared by the polymeric precursor method, as reported in detail by Zanetti *et al.*[15] The polymeric resin was then placed in a furnace and heated to 350 °C for 4 h, causing it to pulverize into powder. The powders were heat treated at 350, 400, 450, 500, 550, 600, 650, and 700 °C for 2 h in oxygen atmosphere at a heating rate of 5 °C min^{-1}. The SBN powders were also characterized by means of x-ray diffraction (XRD), Fourier transform Raman spectroscopy (FT-Raman), and PL measurements.

The diffraction patterns of the crystalline powders were recorded in a Rigaku DMax 2500PC diffractometer. The

power tube used was 6000 W in a 2θ interval from 10° to 75°, using Cu $K\alpha$ with graphite monochromator. FT-Raman spectra were recorded on a (Bruker RFS 100/S) spectrometer, excited by a Nd doped yitrium aluminum garnet laser at 1064 nm with a spectral resolution of 4 cm^{-1}. Photoluminescence spectra were produced in 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 nominal output power kept at 200 mW. All the measurements were taken at room temperature.

Figure 1 shows the XRD patterns of SBN powders heat treated from 350 up to 700 °C for 2 h in oxygen atmosphere.

The powders heat treated from 350 to 400 °C contain only the bismuth oxide (Bi$_2$O$_3$) phase. According to Shuk
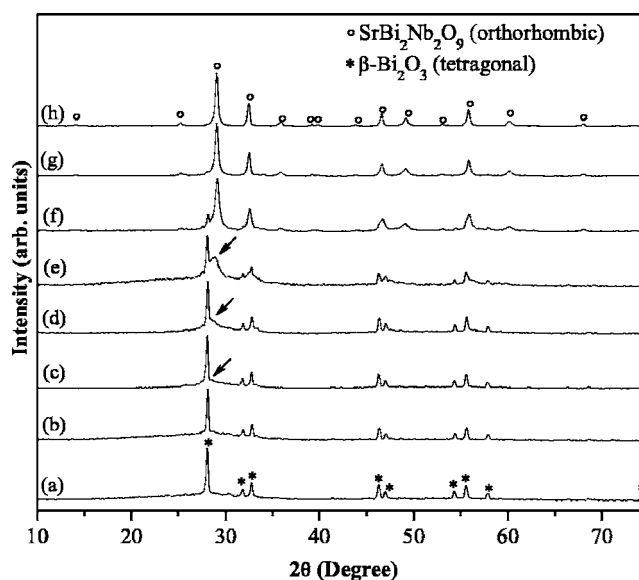

FIG. 1. XRD patterns of SBN powders heat treated at (a) 350 °C, (b) 400 °C, (c) 450 °C, (d) 500 °C, (e) 550 °C, (f) 600 °C, (g) 650 °C, and (h) 700 °C for 2 h in oxygen atmosphere. The arrow indicates the appearance of SBN phase.

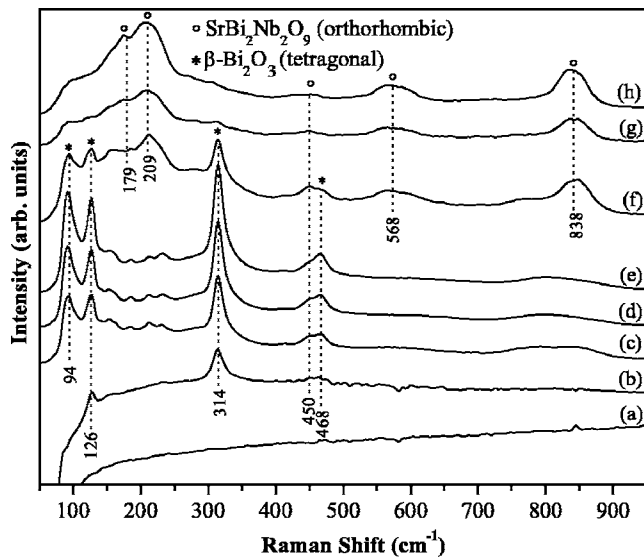a)Electronic mail: laeciosc@bol.com.br

FIG. 2. Room temperature depolarized Raman spectra of SBN powders heat treated at (a) 350 °C, (b) 400 °C, (c) 450 °C, (d) 500 °C, (e) 550 °C, (f) 600 °C, (g) 650 °C, and (h) 700 °C for 2 h in oxygen atmosphere.
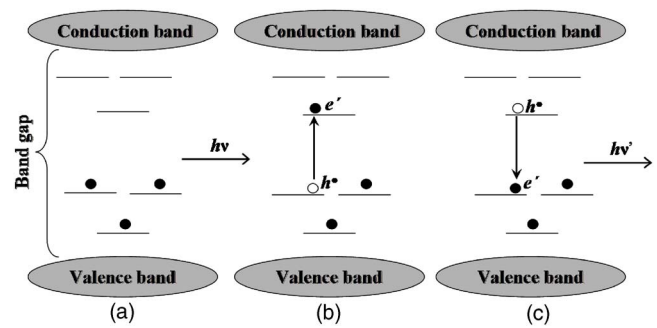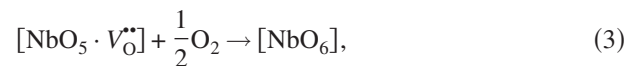

FIG. 3. Wide band model: (a) before excitation, (b) excitation (formation of self-trapped excitons), and (c) after excitation [recombination of electron (e') and hole ($h^{\bullet}$)].

et al.,[16] four main phases were evidenced for Bi_2O_3 system: α, β, γ, and δ. In this work, we have a tetragonal structure, β-Bi_2O_3 with space group $P\bar{4}2_1m$, according to Ref. 17 [see Figs. 1(a) and 1(b)]. On the other hand, the powders heat treated from 450 to 600 °C presented a mixture of the β-Bi_2O_3 phase (tetragonal) and SBN phase (orthorhombic) [Figs. 1(c)–1(f)]. At 550 °C [see Fig. 1(e)], peaks of β-Bi_2O_3 phase began to disappear and the structural transition from tetragonal to orthorhombic structure took place. Thus, at 650 °C [see Fig. 1(g)] the crystallization of SBN phase occurs that is improved with increasing annealing temperature. At 700 °C, all the XRD patterns correspond to the orthorhombic phase, based on Ref. 3.

At 700 °C, all the XRD patterns correspond to the orthorhombic phase, based on Ref. 3. These findings suggest that the crystallization of SBN starts from an intermediate tetragonal phase β-Bi_2O_3 to orthorhombic phase SBN [see Figs. 1(e)–1(h)]. The peaks relating to β-Bi_2O_3 phase disappear with the consequent crystallization of the SBN. Asai *et al.*[18] reported the appearance of a fluorite intermediary phase in SBN nanopowders obtained by an aqueous solution method based on water-soluble compounds, Sr-EDTA, Bi-EDTA, and Nb-citrate. Their results are in agreement with the present work.

Figure 2 shows the Raman spectra in the 50–950 cm^{-1} range of the SBN powders heat treated at different temperatures.

The Raman-active phonon mode for SBN powder heat-treated at 350 °C for 2 h was not detected due to the sample's dark coloration [see Fig. 2(a)]. In Figs. 2(b)–2(f), the phonon modes at −94, 126, 314, and 468 cm^{-1} were attributed to the intermediary β-Bi_2O_3 phase with tetragonal structure, which crystallized before the SBN orthorhombic phase. Rising temperatures led to an increase of orthorhombic vibrational modes [Figs. 2(f)–2(h)] and resulted in a reduction of the tetragonal peaks. The phonon modes at $\sim$450 cm^{-1} evidenced the coexistence of both phase [see Fig. 2(c)]. The modes located at $\sim$179, 209, 450, 573, and 838 cm^{-1} are related to orthorhombic phase and are in agreement with those reported by Nelis *et al.*[19] and Kojima *et al.*[20] The peak

located at 838 cm^{-1} [Figs. 2(f)–2(h)] can be attributed to a symmetric stretching of the octahedral NbO_6.[20,21] The presence of NbO_6 octahedra starting from 600 °C [see Figs. 2(f)–2(h)], is in agreement with the XRD patterns [Figs. 1(f)–1(h)], which indicate predominance of the orthorhombic phase. This behavior may be related to the phase transition from tetragonal to orthorhombic phase. The main difference in the Raman modes was caused by local inhomogeneities in the distribution of both phases. As the temperature was increased, the peaks corresponding to the tetragonal phase disappeared [Figs. 2(g) and 2(h)].

A proposed model for wide band PL property[22] is illustrated in Fig. 3. The most important events occur without excitation, i.e., before the photons arrive.

The oxygen complex clusters generate localized states in the band gap and inhomogeneous charge distribution in the cell, thus allowing for electron trapping. The localized levels are distributed energetically, so that various energies are able to excite the trapped electrons. Before donor excitation, a hole in the acceptor state and an electron in the donor state are created. This model suggests that the increase of temperature reduces the disorder promoted by intermediate tetragonal phase in the powders, creating electron-captured oxygen vacancies, according to equations

$$[NbO_5 \cdot V_O^x] + [NbO_6]^x \rightarrow [NbO_5 \cdot V_O^{\bullet}] + [NbO_6]', \quad (1)$$

$$[NbO_5 \cdot V_O^{\bullet}] + [NbO_6]^x \rightarrow [NbO_5 \cdot V_O^{\bullet\bullet}] + [NbO_6]', \quad (2)$$

$$[NbO_5 \cdot V_O^{\bullet\bullet}] + \frac{1}{2}O_2 \rightarrow [NbO_6], \quad (3)$$

where $[NbO_6]'$ is donor, $[NbO_5 \cdot V_O^{\bullet}]$ is donor-acceptor, and $[NbO_5 \cdot V_O^{\bullet\bullet}]$ is acceptor.

Therefore, most of the oxygen vacancies are vacancy complexes in the intermediate structure. In this structure, $[NbO_5 \cdot V_O^x]$ complex cluster is a donor candidate and $[NbO_6]^x$ an acceptor candidate. We speculated that these oxygen complex vacancies induce new energy in the band gap and can be attributed to the niobium-oxygen complex vacancy centers.

Figure 4 presents the PL spectra recorded at room temperature for the SBN powders heat treated at different temperatures for 2 h in oxygen atmosphere.

PL emission is associated with defects promoted by intermediate phase in the SBN lattice creating oxygen vacancies in the band gap. We attributed the structural disorder in the lattice to oxygen vacancies V_O^x, $V_O^{\bullet}$, and $V_O^{\bullet\bullet}$ in the $[NbO_6]$
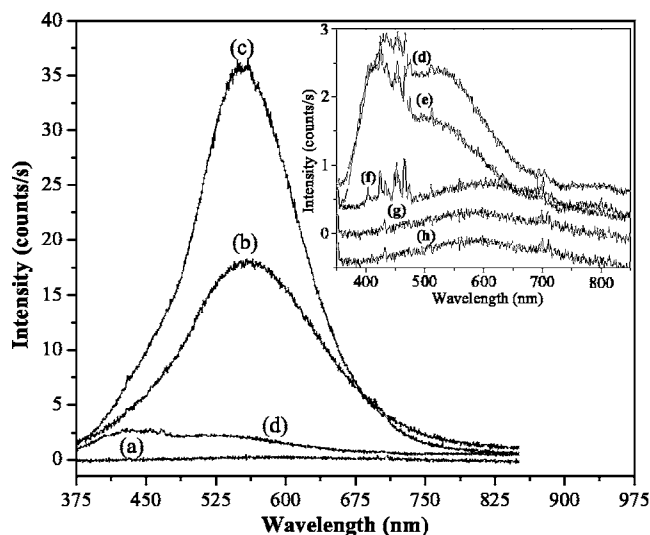
FIG. 4. PL spectra of SBN powders heat treated at (a) 350 °C, (b) 400 °C, and (c) 450 °C. The inset shows PL spectra of SBN powders heat treated at (d) 500 °C, (e) 550 °C, (f) 600 °C, (g) 650 °C, and (h) 700 °C for 2 h in oxygen atmosphere, and excited with the 350.7 nm line of a krypton ion laser.

clusters associated with the intermediate β-Bi_2O_3 phase. According to Blasse,[23] NbO_6 octahedron is the luminescent center in the perovskitelike niobates. It is well known that electrons determine the transport properties, e.g., electrical conductivity, but no role-related phenomena were observed. This indicates that holes are almost trapped around defects.[24] According to the hypothesis proposed by Korzhik *et al.*,[25] there are vacant localized states associated with defects such as oxygen vacancies in the band gap above the valence band and below the conduction band. Increasing the temperature reduces these vacancies, in which an electron from the conduction band loses its energy and reoccupies the energy levels of electrons (e')/hole$(h^\bullet)$ in the valence band.

PL emission presents low intensity due to the presence of β-Bi_2O_3 (tetragonal phase) and the large amount of defects caused by disorder in the SBN lattice [see Fig. 4(a)]. When the temperature increased, the degree of structural order-disorder caused by the oxygen vacancies in complex clusters in the SBN lattice enhanced the intensity of the PL [see Fig. 4(b)]. The presence of the centers of $[NbO_6]'$ and $[NbO_5 \cdot V_O^\bullet]$ complex clusters stabilizes the defects via charge compensation. Therefore, the center is considered to be associated with oxygen, strontium, and bismuth ions found in this material. A broad intense luminescence band with a maximum PL at about 553 nm in the visible region (green) was observed. Thus, the charge transference in the $([NbO_5 \cdot V_O^\bullet]/[NbO_6]')$ complex clusters may be responsible for the PL behavior resulting simultaneous from the structural order-disorder in the SBN lattice [see Figs. 4(c)–4(e)]. However, the increase of $[NbO_6]'$ complex clusters affects the structural order in the system, reducing the PL intensity [Figs. 4(f)–4(h)]. Besides, in Fig. 4(h), the disappearance of PL was caused mostly by the organization of the system due to $[NbO_6]$ clusters and the negligible fraction of defects and structural disorder. Yang *et al.*[26] suggest that the photoluminescence process may involve intermediate defect states at the crystallite boundaries. The main mechanism involved in the photoluminescence behavior was the Nb^{4+}–O^- exciton species in the NbO_6 octahedron. Alternatively, we related the PL emission in the SBN lattice with its structural evolution, i.e., in terms of structural order-disorder caused by phase transformation.

In short, XRD and Raman techniques were used to investigate the structural formation of orthorhombic phase SBN via tetragonal phase β-Bi_2O_3. Intense PL behavior at room temperature (around 553 nm), produced by structural order-disorder in the SBN lattice, was controlled by self-trapping of electrons and charge transference in complex clusters. Therefore, oxygen vacancies were found to play an important role in PL emission via a recombination of electrons in oxygen vacancies with photoexcited hole in the valence band.

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