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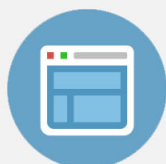
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Room-temperature photoluminescence in structurally disordered SrWO₄

M. Anicete-Santos,^{a)} F. C. Picon, M. T. Escote, and E. R. Leite

Departamento de Química, Universidade Federal de São Carlos, C.P. 676, 13565-905 São Carlos, São Paulo, Brazil

P. S. Pizani

Departamento de Física, Universidade Federal de São Carlos, C.P. 676, 13565-905 São Carlos, São Paulo, Brazil

J. A. Varela and E. Longo

Instituto de Química, Universidade Estadual Paulista, C.P. 355, 14801-907 Araraquara, São Paulo, Brazil

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Intense and broad visible photoluminescent (PL) band in structurally disordered SrWO₄ compounds was observed at room temperature. The polycrystalline scheelite strontium tungstate (SrWO₄) samples prepared by the polymeric precursor method at different temperatures of annealing were structurally characterized by x-ray diffraction and Fourier transform Raman spectroscopy measurements. Quantum-mechanical calculations showed that the local disorder in the cluster of the network modifiers Sr has a very important role in the charge transfer. The experimental and theoretical results are in good agreement, indicating that the generation of the intense visible PL band can be related to short-range order-disorder degree in the scheelite structure. © 2006 American Institute of Physics. [DOI: 10.1063/1.2207491]

There is an increasing demand for light-emitting devices in displays and communication. In many optoelectronic devices, structurally disordered semiconductors can replace single crystal semiconductors, particularly when cost is an important factor.

Numerous investigations on the photoluminescent property of scheelite tungstate crystals have been carried out for several decades.^{1–5} However, there are still issues in debate, as for example the origin of color centers to photoluminescent (PL) emission band, mainly the green one. Blasse and Grabmaier,³ Groeninckx and Blasse,⁴ and Annenkov *et al.*¹ attributed the green emission as originating from (WO₃+F) center in nondoped PbWO₄. On the other hand, Shi *et al.*⁵ suggest the (WO₄+O_i) center as being the green luminescence center.

In particular, the strontium tungstate (SrWO₄) (SWO) crystal is a perspective material for application as Raman converters, lasers, and amplifiers.⁶ Despite the studies of PL in disordered perovskitelike titanates^{7,8} being a subject of interest since a report of PL in porous silicon,⁹ the intense PL property at room temperature is not usually reported in the structurally disordered scheelite tungstates.

This letter characterizes the type of structural disorder (short-range order-disorder) in disordered SrWO₄ lattice that favors the intense and broad visible PL band at room temperature, and the important role of the network modifiers Sr locally disordered for charge transference. The SWO polycrystalline samples were prepared by the polymeric precursor method.^{10,11} The photoluminescent property is investigated in terms of experimental results and *ab initio* periodic quantum-mechanical calculations. The aim of our synergetic strategy between experimental and theoretical results is not to explain all the possible PL mechanisms that occur during the photon excitation and decay processes, as many valid hypotheses already present in the literature, but to discuss the

favorable conditions to generate intense PL emission in disordered SWO powders.

The SrWO₄ polycrystals were annealed at different temperatures and characterized by x-ray diffraction, Fourier transform (FT) Raman, PL, and UV-vis spectroscopy. Photoluminescence was measured using a U1000 Jobin-Yvon double monochromator coupled to a cooled GaAs photomultiplier, a conventional photon-counting system, and argon-ion laser ($\lambda=488.0$ nm). FT Raman spectra were recorded by means of a Bruker RFS100 instrument and the UV-vis measures used a Cary 5G spectrophotometer. All the measurements were performed at room temperature.

Periodic *ab initio* quantum-mechanical calculations based on density functional theory (DFT) with the B3LYP hybrid functional have been performed by CRYSTAL98 computer code.¹² The basis sets used for W, (HAYWSC-31G) Sr, and (6-31G*) O atomic centers are described in Ref. 12. The program OPTIM (Ref. 13) was used to optimize the cell parameters and oxygen fractional atomic positions.

The scheelite SWO crystallizes in a tetragonal structure (space group $I4_1/a$, C_{4h} symmetry). For computational simplification, the CRYSTAL98 code works in the primitive unit cell rather than in the conventional one. We performed three different periodic models. A primitive cell was used as a periodic model to represent the crystalline SWO (SWO-*c*), see Fig. 1(a). A second model was created displacing W2 0.2 Å in the direction opposite to oxygen atom O1, this periodic model is labeled as SWO-*w*, see Fig. 1(b). Starting from the previous SWO-*c* model the W2 and Sr2 atoms were displaced 0.2 and 0.3 Å in the direction opposite to the O1 and O2 oxygens, respectively, this third periodic model is labeled as SWO-*sw*, Fig. 1(c).

Many displacement tests were executed. The results of these displacements are similar to that seen in Table I. Although, these results are quantitatively different they do not change the focus of the proposed models in this work.

^{a)}Electronic mail: marcos@liec.ufscar.br

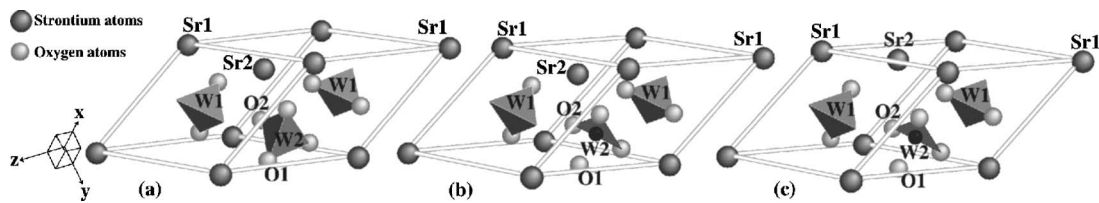


FIG. 1. (a) SWO-c, (b) SWO-w, and (c) SWO-sw primitive unit cell periodic models of the SrWO_4 structure.

Figure 2(a) shows the x-ray diffraction patterns of SrWO_4 samples heat treated at 500, 600, and 700 °C for 2 h in air. The crystallization process of the structurally disordered SWO is already very advanced starting from the annealing temperature of 500 to 700 °C. All diffraction pattern peaks are ascribed to the scheelite tetragonal structure (space group $I4_1/a$, C_{4h}^6 symmetry), suggesting a direct crystallization from the disordered phase by thermal treatment. Rietveld analysis of these data revealed that, as the temperature increases, the structural parameters evolve to the scheelite structure described in literature.¹⁴ In particular, the lattice parameters and the Sr–W bond lengths for sample heat treated at 700 °C are closer to those values described in this work, which indicated higher degree of crystallinity.

In Fig. 2(b), the sample treated at 700 °C presents several peaks referring to the Raman-active internal modes of the WO_4 tetrahedra: stretching $\nu_1(A_g)$, $\nu_3(B_g)$, and $\nu_3(E_g)$; bending $\nu_2(A_g)$, $\nu_2(B_g)$, $\nu_4(B_g)$, and $\nu_4(E_g)$. The external modes ν_{ext} correspond to motion of the Sr cation and the rigid molecular WO_4 unit.¹⁵ The compound treated at 600 °C only presents some large peaks of the $\nu_1(A_g)$ and $\nu_2(A_g+B_g)$ internal modes and does not present the external modes ν_{ext} , indicating that the Sr atoms are more short-range disordered than atoms of the WO_4 tetrahedra. The sample treated at 500 °C does not present any Raman-active phonon mode. Such results seem to be in agreement with the lower degree of crystallinity observed for the x-ray patterns of samples heat treated at 500 and 600 °C.

The experimental gap energies were obtained starting from the absorbance spectral dependence data (Fig. 3) by means of the Wood and Tauc method. The gap energies of the SWO sample treated at 700 and 600 °C are 4.7 and 4.5 eV, respectively. The theoretical gap energies of the SWO-c, SWO-w, and SWO-sw periodic models are 6.19, 5.40, and 5.37 eV, respectively (see Table I). The absorbance of curve (b) demonstrates a smoother slope than curve (a) in Fig. 3. This behavior indicates that the localized states density in the band gap of the powder treated at 600 °C is greater than of the compound treated at 700 °C.

Figure 4 shows that the SWO sample treated at 500 °C does not present photoluminescent property, while the sample treated at 600 °C presented the widest and most in-

tense visible PL emission. This broad band is typical of a multiphonon process, i.e., a system in which relaxation occurs by various paths, involving the participation of numerous states. To the highly ordered powder, treated at 700 °C, the PL emission decreases dramatically.

Table I illustrates charges of each individual cluster for the three periodic models proposed and their respective gap energies. The charge differences among the clusters of the model SWO-sw are larger than of the model SWO-w.

The quantum-mechanical calculations show, in disordered SWO lattice, locally disordered W atoms in the WO_4 clusters that generate localized states in the band gap and consequently decrease the gap energies, see Table I. As gap energy decreases, the structural disorder increases. This can favor PL emission with an excitation energy smaller than the crystalline gap energy. But only this effect is insufficient to generate intense visible PL at room temperature, as can be seen in the more disordered sample (treated at 500 °C) which does not present intense visible PL property.

Furthermore, these calculations also show that the network modifiers Sr locally disordered in its clusters cause great charge differences among the clusters. Great charge differences among the clusters favor more charge transferences among them, when there is photon excitation. Charge transference is fundamental for the PL effect.

The aforementioned experimental and quantum-mechanical calculation results strongly indicate that the presence of simultaneous order and disorder (order-disorder) in the SWO structure, mainly at short range, is favorable to generate intense and visible PL emission at room temperature.

As the experimental gap energies, by absorption measurements, are much higher than the excitation energy that is used for collecting the PL spectra (2.54 eV; 488 nm), such observation confirms the fact that Montoncello *et al.*¹⁶ indeed pointed out that PL often highlights features that absorption measurements would rarely define, as the properties of the energy levels lying within the band gap of a material.

Summarizing, the intense studies of PL property in non-doped scheelite tungstate crystals are focused on defects related to the tetrahedra WO_4 . These tetrahedra associated with such defects are broadly considered as visible color centers,

TABLE I. Gap energies and charge variations for each individual cluster of the SWO periodic models before and after the deformations.

Charges of the SWO-c clusters e	Charge of the SWO-w clusters e	Charge of the SWO-sw clusters e	Charge gains δ_q of the SWO-w clusters e	Charge gains δ_{sw} of the SWO-sw clusters e
Sr1O ₈ : -1.68	Sr1O ₈ : -1.89	Sr1O ₈ : -2.32	Sr1O ₈ : -0.21	Sr1O ₈ : -0.64
Sr2O ₈ : -1.68	Sr2O ₈ : -1.89	Sr2O ₈ : -1.05	Sr2O ₈ : -0.21	Sr2O ₈ : +0.63
W1O ₄ : 1.68	W1O ₄ : 1.67	W1O ₄ : 1.46	W1O ₄ : -0.01	W1O ₄ : -0.22
W2O ₄ : 1.68	W2O ₃ : 2.11	W2O ₃ : 1.91	W2O ₃ : +0.43	W2O ₃ : +0.23

Gap energy = 6.19 eV

Gap energy = 5.40 eV

Gap energy = 5.37 eV

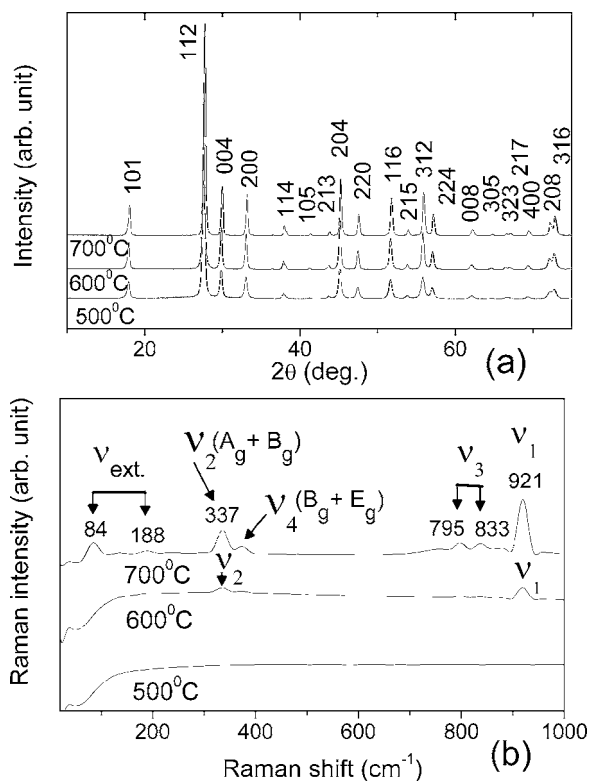


FIG. 2. (a) X-ray diffraction patterns and (b) FT Raman spectra recorded at room temperature for the SrWO₄ samples heat treated at 500, 600, and 700 °C for 2 h in air atmosphere.

mainly green color centers. Part of our result is similar to studies realized on nondoped crystalline tungstates, the local disorder (a defect type) in the WO₄ tetrahedra is important for the PL emission, due to localized states in the band gap. But unlike studies in tungstate crystals, we have also investigated the short-range order-disorder in the clusters of the network modifiers Sr to the disordered SWO. Such order-

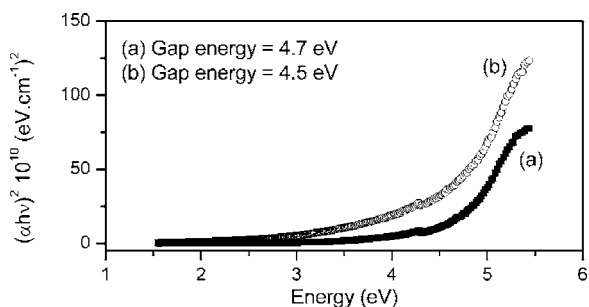


FIG. 3. Spectral dependence of the absorbance for the SrWO₄ samples heat treated at (a) 700 and (b) 600 °C.

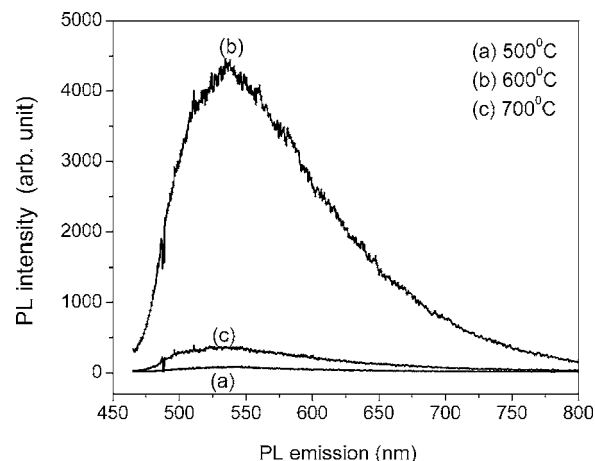


FIG. 4. Room-temperature photoluminescence spectra of the SrWO₄ samples heat treated at 500, 600, and 700 °C.

disorder promotes great charge density differences in the lattice among clusters, favoring more charge transfer among them, when there is photon excitation. This greater charge transfer among the clusters can generate the intense and broad visible PL property at room temperature.

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