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Structural and optical properties of SrWO₄ powders prepared by the microwavehydrothermal and polymeric precursor methods

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Abstract - SrWO₄ powders were prepared by the microwave-hydrothermal and polymeric precursor methods. These powders were analyzed by X-ray diffraction (XRD), ultraviolet-visible (UV-vis) absorption spectroscopy and photoluminescence (PL) measurements. XRD patterns showed that these compounds crystallize in a scheelite-type tetragonal structure. The different optical band gap values estimated from the UV-vis spectra suggested the existence of intermediary energy levels within the band gap. When exited with 350 nm wavelengths, these materials exhibited green PL emissions at room temperature.

In the last years, the strontium tungstate (SrWO₄) has attracted considerable attention of several technological fields because of its blue or green luminescence emissions at room temperature, which are attractive characteristics for the development of new electrooptics devices [1]. In principle, different synthetic routes have been employed to obtain this material, mainly including: spray pyrolysis [1], pulsed laser deposition [2], and Czochralski growth [3]. However, these methods require expensive and sophisticated equipments, high heat treatment temperatures, long processing times, expensive precursors and high consumption of electric energy. Thus, the microwave-hydrothermal (MH) as well as the polymeric precursor (PP) methods can be a good alternative in order to minimize these drawbacks.

Therefore, in this work, SrWO₄ powders were prepared by both MH and PP methods. In the MH treatment, tungstic acid (99% purity, Aldrich), strontium acetate (99.5% purity, Aldrich) and 0.1 g of polyethylene glycol (Mw 200) (99.9% purity, Aldrich) were dissolved in deionized water at room temperature under constant stirring. After co-precipitation reaction, this solution was transferred into a Teflon autoclave, which was sealed and placed inside the MH system (2.45 GHz, maximum power of 800 W). Each MH processing was performed at 140 °C for different times (0.5 h, 1 h, 2 h, 5 h). After MH processing, the autoclave was naturally cooled to room temperature. The resulting solution was washed with deionized water several times to neutralize the solution pH (≈7). Finally, the white precipitates were collected and dried in a conventional furnace at 50 °C for some hours. In the PP method, a tungsten citrate was prepared with citric acid/metal molar ratio fixed at 6:1. In the sequence, a stoichiometric quantity of strontium acetate (99,5% purity, Aldrich) was dissolved into this citrate solution. After solution homogenization, ethylene glycol (99.5% J.T. Baker) was added into the solution heated at 110 °C in order to promote the citrate polymerization. The citric acid/ethylene glycol mass ratio was fixed at 60/40 wt%. The resulting solution was heated at 120 °C under constant stirring to eliminate water, consequently forming a polymeric resin. This polymeric resin was then placed in a conventional furnace and heat treated at 300 °C for 2 h to promote the organic compound decomposition arising from citric acid and ethylene glycol. The obtained precursor powders were heat treated from 500 °C to 700 °C for 2 h under air atmosphere, using a heating rate of 10 °C/min.

The X-ray diffraction patterns showed that the SrWO₄ powders obtained by both methods present a scheelite-type tetragonal structure with space group $I4_1/a$. In addition, the diffraction peaks showed that all powders formed under MH conditions (140 °C for different times) are well-crystallized at long-range, while that those obtained by the PP method exhibited a high degree of structural organization after heat treatment performed at 600 °C for 2h. UV-vis absorption spectra indicated that the variations on the E_{gap} values can be associated with the contribution of different intermediary energy levels within the band gap. The origin of these energy levels for the powders obtained by the MH method was related with the distortions on the [WO₄] tetrahedrons by the microwave radiation. On the other hand, in the PP method, it was attributed to the existence of structural order-disorder into the SrWO₄ lattice due to a symmetry break between the Sr-O and W-O bonds (oxygen vacancies). Probably, the structural organization changes were responsible for a reorganization of these intermediary energy levels within the band gap, resulting in variations on the PL intensities of these materials.

References:

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