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# Photoluminescent property of mechanically milled $BaWO_4$ powder

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## Abstract

Crystalline $BaWO_4$ (BWO) powder obtained by the polymeric precursor method was structurally disordered by means of high-energy mechanical milling. For the first time a strong and broad photoluminescence (PL) has been measured at room temperature for mechanically milled BWO powder and interpreted by ground-state quantum mechanical calculations in the density functional theory framework. Two periodic models have been studied; one representing the crystalline form and the other one representing the disordered BWO powder. These models allowed the calculation of electronic properties, which are consistent with the experimental results, showing that structural disorder in the lattice is an important condition to generate an intense and broad PL band.

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## 1. Introduction

The development of new materials with optical properties such as electroluminescence and photoluminescence (PL) may lead to new optoelectronic devices with high performance [1]. Structurally disordered semiconductors can replace crystalline semiconductors, particularly when cost is an important factor.

Although numerous investigations have been performed on the photoluminescent property of scheelite tungstate single crystals, there are still issues in debate regarding the origin of the green PL emission band. Blasse et al. [2] and Korzhik et al. [3–6] concluded that the green emission originates from ($WO_3+F$) center in $PbWO_4$ single crystals. On the other hand, several authors attributed the photoluminescent green component to defect centers with interstitial oxygen: Shi et al. [7–9] suggested the ($WO_4+O_i$) center (where $O_i$ is an interstitial oxygen) as green luminescence center while Huang et al. [10] concluded that the interstitial oxygen $O_i$ enhances the green luminescence.

Barium and strontium tungstate crystals are prospective materials for application of Raman converters, lasers and amplifiers [11–16]. In particular, barium tungstate $BaWO_4$ (BWO) crystals have been considered as unique crystals for a wide variety of pump pulse duration that extend from nanoseconds to picoseconds [17].

Ever since Canham [18] first observed visible PL at room temperature in porous silicon, the study of PL in disordered materials has focused on development of new luminescent materials, owing to their potential technological applications. PL in titanate [19] and tungstate [2–9] single crystals is already well known, but recent works show that titanate [20–28] and tungstate [29,30] compounds with structural disorder present broad and intense PL at room temperature.

In the present paper, the PL of disordered BWO is investigated for the first time. We combined laboratory

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experiments and theoretical calculations into a synergystic strategy to understand the PL origin in BWO. The powders were prepared by the polymeric precursor method and the structurally disordered BWO presented broad and intense PL at room temperature. Periodic models representing the crystalline and disordered BWO structures were used to investigate their electronic structures and to offer interpretation in theoretical terms of the conditions needed for PL to occur at room temperature. The purpose of our strategy between experimental and ground-state theoretical results is not to explain the mechanisms occurring after the excitation by the laser light, but to discuss the favorable conditions existing in disordered BWO powders for generating intense PL emission. The method we use for the calculation, density functional theory (DFT) is by the way a ground-state method; it is not designed to describe excited states. But we aim at demonstrating that the disorder existing in the powder after mechanical milling creates ad hoc perturbations on the band gap and on the charge distribution for enhancing wide-band PL emission.

## 2. Experimental

The BWO powders studied in the present work were synthesized following a soft chemical method, the so-called polymeric precursor method [31]. This process offers advantages over other synthesis techniques such as low cost, good compositional homogeneity, high purity and low processing temperatures. The synthesis involved dissolution of citric acid ($C_6H_8O_7$) in water and subsequent addition of tungstic acid ($H_2WO_4$). The tungsten citrate formed was then stirred and heated up to 60 °C and barium carbonate ($BaCO_3$) was added. Ammonium hydroxide was used to adjust the pH of the solution to 7–8 and to prevent precipitation of barium citrate that is favored in an acid solution. After homogenization of the solution, ethylene glycol ($C_2H_6O_2$) was added in 60:40 proportions (in mass) of citric acid/ethylene glycol to promote citrate polymerization by polyesterification reaction. With continuous heating from 60–90 °C, the solution became more viscous and homogeneous, resulting in a polymeric resin, in which the Ba ions were evenly distributed. The polymeric resin was heat treated at 200 °C during 60 min to pyrolyse the organic material. The obtained polymeric precursor was deagglomerated and heat treated at 300 °C for 2 h to remove most of the organic matter. The obtained powder was then calcined at 700 °C for 4 h. The crystalline BWO powders were then mechanically milled in a high-energy attrition mill for 4, 8 and 16 h. X-ray diffraction (XRD) measurements were used to investigate the attrition-induced disorder process in the BWO powders. The diffraction patterns were recorded on a Siemens D5000 machine in a $\theta$–$2\theta$ configuration, using a graphite monochromator. The crystallite sizes were estimated by Scherrer's equation. To measure the PL property, we used a U1000 Jobin–Yvon double monochromator coupled to a cooled GaAs photomultiplier and a conventional photon-counting system. The 488.0 nm exciting wavelength of an argon-ion laser was used, with the laser's maximum output power kept within 200 mW. All the measurements were taken at room temperature.

## 3. Computational methods

Calculations were carried out with the CRYSTAL98 package [32], within the framework of the density functional theory [33]. The gradient-corrected correlation functional by Lee, Yang and Parr was used, combined with the Becke3 exchange functional, B3LYP [34,35], that was demonstrated by Muscat et al. [36] to be suitable to calculate structural parameters and accurate band structures for a wide variety of solids.

The basis sets used to describe O (6-31G*) and Ba (HAYWSC-31 G) atomic centers can be found at reference [37] and for W in the paper by Cora et al. [38]. The *k* points sampling was chosen to be 40 points within the irreducible part of the Brillouin zone. The OPTIM program [39] was used to optimize the cell parameters and atomic positions. OPTIM is a general optimization tool that minimizes a function, which in this case is the CRYSTAL98-computed total energy. The initial values of cell parameters and atomic positions were taken from experimental data [40,41].

The XCrysDen [42] program was used as a graphical tool to design the density of states and the band structure diagrams.

## 4. Crystal structure and periodic models

The scheelite BWO crystallizes in a tetragonal structure (space group $I4_1/a$, $C_{4h}^6$ symmetry). Tungsten atoms are surrounded by four oxygen atoms in a tetrahedral configuration and barium atoms are surrounded by eight oxygens in a pseudo-cubic configuration. The $a$ and $c$ experimental cell parameters are 5.6148(5) and 12.721(1) Å, respectively [40]. The optimized values of the cell parameters and oxygen fractional atomic positions [41] are presented in Table 1. The Ba and W fractional atomic positions are $(0, \frac{1}{4}, \frac{5}{8})$ and $(0, \frac{1}{4}, \frac{1}{8})$, respectively.

For computational simplification, the CRYSTAL98 code works in the primitive unit cell rather than in the conventional one. In this case, the primitive cell refined parameters are $a = b = c = 7.41309$ Å, $\alpha = \beta = 135.9230°$ and $\gamma = 64.0994°$. We have used a $1 \times 1 \times 2$ supercell of the primitive cell as a periodic model to represent the crystalline BWO. It results in 24 atoms in the supercell, see Fig. 1(a). This first supercell model will be called BWO-c in the following for BWO crystalline.

Our objective is to compare the ground-state electronic structure of BWO-c model with the ground-state electronic structure of a simple disordered model (BWO-d) used to make contact with the structurally disordered powder. We know from earlier studies on titanate compounds that during the crystallization process, the lattice-forming