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
experiments and theoretical calculations into a synergistic 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\textsubscript{6}H\textsubscript{8}O\textsubscript{7}) in water and subsequent addition of tungstic acid (H\textsubscript{2}WO\textsubscript{4}). The tungsten citrate formed was then stirred and heated up to 60 °C and barium carbonate (BaCO\textsubscript{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\textsubscript{2}H\textsubscript{4}O\textsubscript{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 θ–2θ 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 XCrystRen [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 I\textsubscript{4}1/a, C\textsubscript{4h}\textsubscript{1} 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 crystal parameters are 5.6148(5) and 12.7211(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, 1/2, 0) and (0, 1/2, 1/2), 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, \(\alpha = \beta = 135.9230^\circ\) and \(\gamma = 64.0994^\circ\). 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
clusters are the first to be built, as TiO$_6$ and TiO$_5$ clusters [21,22], by opposition to the lattice-modifying clusters (AO$_{12}$ in ABO$_3$ perovskites). From this information and mostly from Refs. [2–6] that presume the existence of WO$_3$ (or distorted WO$_4$) and WO$_4$ clusters, we assume that before complete crystallization of the powder, i.e. before the heat treatment reached 700 °C, the structure is composed of a random mixture of WO$_4$ and WO$_3$ clusters separated by the Ba ions. During mechanical milling, we assume that the disordered powder also contains a mixture of WO$_4$ and WO$_3$ clusters.

Starting from the previous BWO-c model, the W2 and W4 atoms were displaced by 0.1, 0.2, 0.3, 0.4 and 0.5 Å in the direction opposite to the starred oxygen atoms of Fig. 1(b) in order to weaken the W2–O* and W4–O* bonds, thus obtaining the previously described WO$_3$ clusters. Among these models, we chose the 0.5 Å displaced value for leading to the most striking results although the tendency is the same for all deformation distances (see Table 2), the band gap energy decreases. This new periodic model will be called BWO-d. The W2 and W4 atoms are now surrounded by three oxygen atoms with trigonal coordination.

Our proposal regarding the use of this BWO-d model is to offer a simple scheme allowing to understand the effects of structural deformation without completely suppressing the geometry of the cell that is useful for reducing the calculation costs. Using the same kind of distorted model we successfully explained the PL of various perovskite titanates [23,27,43,44].

5. Results and discussion

Fig. 2 exhibits PL spectra of BWO powders milled for 0, 4, 8 and 16 h, measured at room temperature. For the starting powder (0 h milling), i.e., for the crystalline BWO phase, the PL emission is not observed, only the Raman modes are visible. Broad and intense bands of PL in the visible region appear when the powder is submitted to a milling process during 4, 8 and 16 h. The PL behavior of the BWO material is thus sensitive to the milling history. The PL intensity increases with the increase of milling time and presumable with increase of structural disorder of the material.

The X-ray patterns of the BWO powders milled for different lengths of time at room temperature are shown in Fig. 3. The diffraction peaks become broader indicating increase of structural disorder in the lattice. Attrition-induced disorder already occurs for short length of milling time already observed for the powder milled for 4 h. The crystallite size of the BWO grains was estimated from the full-width at half-maximum (FWHM) of the more intense diffraction peaks by means of the Scherrer equation. It was observed that the size of crystallite decreases with the increase of milling time (see Fig. 4). The crystallite size for the powder milled for 16 h is about 20 nm.

In Fig. 5, the spectral dependence of the absorbance for three BWO samples is presented. The crystalline powder presents one well-defined absorption front while the structurally disordered powders exhibit typically a continuous smooth absorption increase as a function of the wavelength (see inset), suggesting the presence of localized states inside the band gap. The optical gaps obtained by extrapolation of the linear curve regions according to the
Wood and Tauc method [45] are 5.76 eV for the crystalline powder, and, respectively, 5.61 and 5.23 eV for the powders milled during 4 and 16 h. The absorbance measurements, associated with the PL characterization of disordered BWO powders suggest a nonuniform band gap structure with a tail of localized states. Before any further analysis, let us discuss the PL results in the light of the energy-gap variation. The band gap values for the BWO powders range from 5.76 to 5.23 eV. The photon energy for a 488 nm (2.54 eV) laser excitation line is too low to cause a direct transition. The PL phenomena observed here is therefore not due to a valence to conduction band transition mechanism but more probably to transitions involving the localized states.

As explained by Blasse and Grabmaier [46], the PL arises from a radiative return to the ground state, a phenomenon that is in concurrence with the nonradiative return to the ground state where the energy of the excited states is used to excite the vibrations of the host lattice. The radiative emission process occurs more easily if it exists in the structure-trapped holes or trapped electrons. In order to understand the electronic structure of the mechanically milled BWO powders, an interpretation in terms of ground-state density of states (DOS) was performed in a simple model (BWO-d) aiming at rationalizing the relations between PL and structural disorder.

The calculated total, atom- and atomic orbital-projected DOS of the BWO-c and BWO-d models are shown in
The energy window ranges from $-6$ to $11$ eV. The zero of energy is taken at the top of the last occupied level (Fermi level). For BWO-c model, the upper valence band (VB) is mainly made of the O (2p) states and equivalently distributed at each oxygen. The projections on the oxygen and tungsten atoms reveal that the upper VB states are mostly nonligand states in relation to the W–O bonds. The strong covalent hybridization between the 2p O and 5d W levels is clearly visible both in the conduction band and in the lower valence band. This plot does not include the atom- or the atomic orbital-projected DOS contributions of the Ba atoms, since these were found to be negligible in this energy range.

In Fig. 6 (bottom) the BWO-d model, the upper VB is also predominately made of the O (2p) states, but the states above 0 eV (localized states) are mostly of 2p $O^*$ nonbonding characters, the two oxygen atoms that lose connection with W2 and W4 tungsten atoms (see Fig. 1(b)). The lower conduction band (CB) is also made of the 5d W states in both cases. Localized states were created below the CB of the BWO-d model due to the 5dz$^2$ orbital of the displaced tungsten atoms, W2 and W4. The covalent interaction between oxygen and tungsten is also visible.

The aforementioned experimental and theoretical results strongly indicate that PL is related to the structural disorder in the lattice. The X-ray diffraction showed a progressive structural disorganization of the powders milled for different times. The PL intensity increases when the powder is submitted to mechanical milling and its optical gap value decreases. This disorder caused in the system is a favorable condition to generate intense and broad PL band. The disorder in the lattice induces the presence of localized states of 2p ($O^*$) and 5dz$^2$ (W2 and W4) characters in the band gap of the disordered model, as shown both by the calculations and by the reflectance spectra of Fig. 5 (inset).

6. Conclusions

BWO powders were successfully prepared following a low-cost soft chemical so-called polymeric precursor method and visible PL band at room temperature was evidenced for the mechanically milled BWO samples.

XRD results show that when the BWO powder is submitted to mechanical milling it becomes structurally disordered and this disorder increases with the increase of milling time.

For the crystalline powder no PL is observed. On other hand, the disordered powders present intense and broad PL band. It can be observed that the PL intensity increases with increase of the milling time.

An analysis of the calculated atom- and atomic orbital-projected DOS of the periodic models, obtained by first principles calculations, reveals that the character of dominant localized states of the disordered BWO are the 2p orbitals of the oxygen atoms in the distorted tungsten tetrahedra.

These observations confirm the fact that the PL property is directly related to the structural disorder in the BWO lattice and to the localized states in the band gap. The localized states are those that can favor the easy trapping of electrons and holes during the excitations process and the electron-hole recombination leads to the PL emission.

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