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Rapid Communication

Effect of different surfactants on the shape, growth and photoluminescence behavior of $MnWO_4$ crystals synthesized by the microwave-hydrothermal method

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ABSTRACT

In this communication, we report the effect of different surfactants [cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS) and sodium bis(2-ethylhexyl)sulfosuccinate (AOT)] on the shape, growth and photoluminescence (PL) behavior of manganese tungstate ($MnWO_4$) crystals synthesized by the microwave-hydrothermal (MH) method at 413 K for 45 min. These crystals were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), ultraviolet–visible (UV–vis) absorption spectroscopy and PL measurements. XRD patterns proved that these crystals have a monoclinic structure. FE-SEM images showed that $MnWO_4$ crystals exhibit different shapes and growth mechanisms depending on the surfactant employed. The CTAB cationic surfactant promotes the hindrance of small nuclei that leads to the formation of flake-like nanocrystals, while SDS and AOT anionic surfactants promote a growth of crystals to plate-like and leaf-like crystals due to considerable size effect of counter-ions (RSO_4^- and RSO_2O^-) and an increase in Na^+ ion remnants. UV–vis absorption spectroscopy revealed different optical band gap values due to modifications in the shape, surface and crystal size. Finally, the effect of surfactants on the crystal shapes and average crystal size distribution causing changes in the PL behavior of $MnWO_4$ crystals was explained.

1. Introduction

In recent years, research in the materials science area related to inorganic compounds has been widely explored due to its functional properties (optical, magnetic, environmental ambience, electrical and sensor) caused by a size reduction [1] which is possible using capping agents, templates and/or surfactants in the chemical solution [2]. The use of surfactants in the chemical synthesis of nanomaterials has been employed to obtain new shapes and different sizes, which promotes the formation of materials with a large number of electronic properties [3–5]. Manganese tungstate ($MnWO_4$) has a wolframite-type monocline structure, where the manganese and tungsten atoms are surrounded by six oxygens which form distorted octahedrons [MnO_6]/[WO_6] clusters [6]. $MnWO_4$ crystals have been extensively explored because nanocrystals present a great number of properties, such as magnetic [7,8], multiferroic [9,10], photocatalysis [11], photoluminescence (PL) [12–14] and as a humidity sensor [15]. Several synthesis methods (aqueous and solvothermal reactions) have been employed in the preparation of $MnWO_4$ crystals. However, these methods exhibit some disadvantages due to long processing times and the use of high temperatures [16,17]. The microwave-hydrothermal (MH) method has proven to be quite efficient in the synthesis of tungstates crystals because it is possible to produce crystalline materials in shorter time and at lower temperatures [18].

Therefore, in this communication, we report the effect of different surfactants, such as [cetyltrimethylammonium bromide (CTAB)], sodium dodecyl sulfate (SDS), and dioctyl sodium sulfosuccinate (AOT) on the shape, growth and photoluminescence behavior of $MnWO_4$ crystals synthesized by MH method at 413 K for 45 min.

2. Experimental details

In a beaker with 100 mL of solution, 0.08 mol of the different surfactants [AOT, SDS, CTAB] were dissolved. Then 1×10^{-3} mol of a dissolved tungstate sodium dihydrate solution [($Na_2WO_4 \cdot 2H_2O$), 99% purity, Aldrich] was added along with 1×10^{-3} mol of manganese acetate [$Mn(CH_3COO)_2$, 99% purity, Aldrich]; this mixture was stirred for 10 min. In the sequence, this suspension was transferred into a Teflon autoclave which was sealed and placed inside a domestic MH system and processed at

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