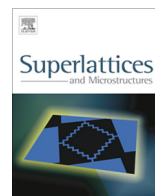




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Letter to the Editor

Structural and optical properties of ZnS/MgNb<sub>2</sub>O<sub>6</sub> heterostructuresL.P.S. Santos<sup>a,\*</sup>, L.S. Cavalcante<sup>b</sup>, M.T. Fabbro<sup>c,d</sup>, H. Beltrán Mir<sup>c</sup>,  
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## ABSTRACT

In this letter, we report a simple and efficient synthetic procedure where the first step is a coprecipitation/calcination method used to obtain magnesium niobate MgNb<sub>2</sub>O<sub>6</sub>(MN) nanocrystals and in the second stage a microwave assisted hydrothermal method (MAH) is employed to synthesize zinc sulfide (ZnS) nanocrystals and ZnS/MN heterostructures. These heterostructures were characterized by X-ray diffraction (XRD), micro-Raman (MR) spectroscopy, field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), high-resolution TEM (HR-TEM), selected area electron diffraction (SAED), energy dispersive X-ray spectrometry (EDX). XRD patterns and MR spectra indicate that MN and ZnS nanocrystals have an orthorhombic and cubic structure, respectively. FE-SEM, TEM and HR-TEM images proved the presence of aggregated MN nanocrystals, ZnS nanocrystals and the presence of ZnS nanocrystals on the surface of MN nanocrystals. Their optical properties were investigated by ultraviolet–visible spectroscopy (UV–vis) and photoluminescence (PL) measurements at room temperature. ZnS/MN heterostructures show a decrease in the values for the optical band gap with respect

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to both components. The presence of the ZnS nanocrystals in this heterostructure promotes a high intense PL emission.

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## 1. Introduction

Ceramic samples based on binary niobates with general formula  $[(M)Nb_2O_6]$  (where:  $M = Ca^{2+}$ ,  $Mg^{2+}$ , or a transition metal) exhibit a crystalline columbite-type orthorhombic structure at room temperature [1,2]. There is a growing interest in this material because this ceramic oxide presents an interesting electronic structure [3,4]. In particular, magnesium niobate  $MgNb_2O_6$  (MN) nanoparticles show excellent dielectric and optical properties [5–8]. It has been widely used as a precursor in the synthesis of  $Pb(Mg_{1/3}Nb_{2/3})O_3$  (PMN) (single-phase) and PMN– $PbTiO_3$  (PT) solid solutions. The synthesis of zinc sulfide (ZnS) nanoparticles has been the focus of recent scientific research due to their important nonlinear optical properties, luminescence, and other important physical and chemical properties [9,10].

The ability to synthesize semiconductor/semiconductor heterostructures with enhanced luminescence and conductive properties is a challenging problem [11,12]. The photoluminescence behavior of nanostructured materials depends not only on the structure but also is controlled by surface chemical bonding and optical transitions in the region of the surface/interface [13–15]. MN is a luminescent material with energy gap of 3.6 eV, while ZnS can presents a zinc-blende and/or wurtzite phases, with energy gaps of 3.7 eV and 3.8 eV, respectively.

Fig. 1(a) and (b) shows a schematic representation of the  $MgNb_2O_6$  and ZnS crystals ( $1 \times 1 \times 1$ ) unit cells with their respective clusters.

Fig. 1(a) illustrates a unit cell for MN crystals with a columbite-type orthorhombic structure, a space group of (*Pbcn*) and point-group symmetry ( $D_{2h}$ ). In this unit cell, magnesium atoms (Mg) and niobium (Nb) atoms are coordinated to six oxygen (O) atoms which form distorted octahedral  $[MgO_6]/[NbO_6]$  clusters [16]. These octahedra are formed by 6-vertices, 6-faces and 12-edges. In addition, the MN crystals are characterized by an ionic character between the Mg–O bonds, while the Ti–O bonds present a covalent nature. Fig. 1(b) shows a unit cell for ZnS crystals with a sphalerite-type cubic structure, space group (*F-43 m*) and point-group symmetry ( $T_d$ ). In this unit cell, the zinc (Zn) atoms are coordinated to four oxygen atoms forming the polyhedra with a tetrahedral configuration related to  $[ZnS_4]$  clusters [17]. These tetrahedra are formed by the 4 vertices, 4 faces and 6 edges.

In this research, MN nanocrystals were obtained by a coprecipitation/calcination method and in the second stage a microwave assisted hydrothermal method was employed to synthesize zinc sulfide (ZnS) nanocrystals and ZnS/MN heterostructures in the order to investigate the optical and structural properties of these novel heterostructures. Based on the experimental results, a plausible mechanism for a relationship between optical properties and order–disorder effects is proposed.

## 2. Experimental details

### 2.1. Synthesis of $MgNb_2O_6$ nanocrystals

$MgNb_2O_6$  nanocrystals were synthesized by the coprecipitation/calcination method. First, a stoichiometric amount of niobium chloride ( $NbCl_5$ , 99.9%, Aldrich) was dissolved in deionized water and stirred at 40 °C until total solution was obtained, with a  $NbCl_5:H_2O$  molar ratio was 1:1. The above solution was mixed with another solution containing magnesium acetate (99%, Vetec,  $Mg(OAc)_2:H_2O$  molar ratio 1:1) to obtain a final solution with a Mg:Nb molar ratio of 1:2. Ammonium hydroxide ( $NH_4OH$ , 30%, Synth) was slowly added to the above solution dropwise and this solution was stirred at 70 °C until a gel was formed. The gel was dried at 60 °C for 12 h in an oven. The resulting white and dry powder was then ground with an agate pestle. This powder was calcined between 700 °C and 1000 °C for 1 h in an electric furnace for crystallization of MN nanocrystals.

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