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Optical, morphological and structural characterization of Er^{3+}-Bi^{3+} co-doped PbS nanocrystals grown by chemical bath

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ABSTRACT

PbS nanocrystals co-doped simultaneously in $Er^{3+}$and Bi^{3+} solutions were grown and the modification of morphological, structural and some optical properties was investigated. The thicknesses of the undoped and doped PbS films were in the ~560–400 nm range. The morphological changes of the nanocrystals were analyzed using Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) techniques. Fourier transform infrared spectroscopy ((FT-IR)) spectra showed a broad absorption band located at ~3500 cm^{-1} attributed to stretching of the –OH groups and a sharp band at ~1384 cm^{-1} owing to stretching vibrations mode of CO_3^{2-} ions. X-ray diffraction displayed a cubic phase in all films and grain size (GS) of the undoped and doped samples were ~33 and ~21–17 nm, respectively. The films showed stress, a typical behavior of doped nanocrystals displaying residual strain. The absorbance spectra of PbS film exhibited four absorption bands located at ~251 nm (~4.9 eV), ~610 nm (~2.0 eV), ~668 nm (~1.8 eV) and ~830 nm (~1.4 eV) due to strong confinement effect and ~446 nm (~2.7 eV), ~478 nm (~2.5 eV) corresponding to $^4F_{7/2}\rightarrow{}^4I_{5/2}$, $^4F_{3/2}\rightarrow{}^4I_{15/2}$ ($f\rightarrow f$) transitions of Er^{3+} ions. Sharp bands were found at ~287 nm (~4.3 eV) and 366 nm (~3.38 eV), corresponding to transitions of Bi^{3+}ions. The band gap energy of films showed a shift in the ~0.9–1.2 eV range. Raman spectra showed two bands located at ~450 cm^{-1} due to the first overtone of the longitudinal optical (LO) phonon (2LO) and a band observed at ~200 cm^{-1} which was attributed to the LO (Γ) phonon. A kinetic mechanism using the free energy changes Gibbs is proposed.

1. Introduction

PbS nanocrystals are of current interest due to their unique structural, optical and electrical properties which are different from the material in bulk form [1–4]. These nanocrystals exhibit increased strength, hardness, roughness and superior soft magnetic properties in regard to the conventional coarse-grained materials [5]. PbS has a direct band gap (E_g) ~0.41 eV (300 K) which is very suitable for infrared detection applications [6] as well in electronic and optoelectronic devices, infrared photography, photo thermal conversion applications, etc. PbS allows to modify its morphologic, optical, structural and elec-

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trical properties by systematic doping with different ions as alkali metals, transition metals, non-metals, and chalcogenide, to mention just a few: Li^{+}, Cu^{2+}, Hg^{2+}, In^{3+}, Se^{2-}, Bi^{3+} [1–4,7,8], etc. However, there are few studies of this material doped simultaneously with two or more ions, and the experimental results that it presents hybridization of properties associated with the dopant ion and it is of interest to observe simultaneously the optical changes [9]. On the other hand, a parameter of interest in the doping process is that it is also possible to systematically reduce GS at different intervals (~0.4–2.5 eV) depending on the doping-ion used and crystalline growth conditions, etc. [1–4,10,11]. An important feature in this doping process is that also the GS decrease increases E_g towards longer wavelengths, i.e., to greater energy. In this context, quantum confinement has attracted enormous attention due to: (*i*) strong quantum confinement arisen from the large exciton Bohr radius (~18 nm) (*ii*) size-tunable E_g covering wide spectral range from UV–vis regions of electromagnetic spectra. Therefore, the optical and electronic properties are determined by their confined nanocrystal structure, being influenced by their surface properties. PbS nanocrystals have been prepared by different methods, such as sonochemical synthesis [12], colloidal hot-injection routes [13], chemical bath (CB) deposition [14,15], etc. CB is a versatile and extremely simple approach, it is possible to obtain nanocrystals in low deposition temperature ranges (~0–90 °C) and is commonly used to doped PbS in a systematic and straightforward way. On the hand, Er^{3+} ion presents $f \rightarrow f$ electronic transitions and has been investigated by many researchers or the past few decades due to its potential applications in many fields such as bio medical lasers, optical data storage and bar code reading etc., [16,17]. Likewise, the Bi^{3+} ion has the property of inducing a GS decrease [8]. In addition, the salts used as dopants have the advantage of being very soluble in water and this avoids the use of non-aqueous solvents that generally have an undesired effect in the crystalline growth. On the other hand, noteworthy is the fact that PbS nanocrystals are promising photovoltaic materials as their variable E_g can be adjusted to match the ideal ~1.6 eV required for achieving a most efficient solar cell. Size-dependent new physical aspects have generated an on-going thrust for new practical applications and PbS nanocrystals with GS dimensions in the ~5–30 nm range shows a stronger quantum confinement effect when the GS matches the dimension of Bohr exciton. We report herein the synthesis of Er^{3+}-Bi^{3+}/PbS co-doped nanocrystals by CB, adding systematically different proportions of the aforementioned ions, in order to examine the morphological, structural and some optical properties. The properties of PbS and doped samples were studied as a function of doping concentration in the growing solution.

2. Chemical reactions and experimental procedure

A model for the crystal growth of undoped and doped PbS films considering the *Nernst* equation and in turn applying the classical relationship for the calculation of *Gibbs* free energy changes (ΔG°) by the $\Delta G^{\circ} = - n\tau\varepsilon^{\circ}$ equation can be considered, where ε° (V) is the cell potential, *n* the number of equivalents (electrons transferred from one chemical species to another) and τ (~96,500 coul/equiv) the *Faraday* constant. ΔG° changes in the key stages of crystal growth were determined employing the cell potential values in basic media, as reported earlier [1–4,7–9]. In the CB technique, a key parameter to avoid spontaneous precipitation is usually associated with the formation of a complex intermediate $[Pb(NH_3)_4]^{2+}$ ion. The aforementioned ion liberates slowly the Pb^{2+} ions considering the adequate conditions (pH, concentration of reagents, mechanical stirring, etc.) and then further allows the combination with the S^{2-} ions slowly, generating PbS nuclei in the whole volume of the reaction. Under these work conditions, the addition of dopant alters the reaction kinetics by competition generated by such additional ions (in this work: Er^{3+} and Bi^{3+} ions). The following model can be proposed:

Hydrolysis of thiourea, generating carbonate and sulfide ions

$$SC(NH_2)_2 + 3OH^- \Leftrightarrow CO_3^{2-} + HS^- + 6H^+ \quad (1)$$

Dissociation of lead acetate in aqueous solution

$$Pb(CH_3COO)_2 \Leftrightarrow 2CH_3COO^- + Pb^{2+} \quad (2)$$

The complex ion formed in our working conditions generates the slow release of ions Pb^{2+}

$$[Pb(NH_3)_4]^{2+} + S^{2-} \Leftrightarrow PbS + 4NH_3 + 2H^+ \quad \Delta G^{\circ} = +362.88\ \text{KJ} \quad (3)$$

Since $\Delta G^{\circ} > 0$, the reaction is not a spontaneous process.

Now, considering the chemical equilibrium for the dopant

$$Er(OH)_3\hat{U}Er^{3+} + 3OH^- \quad \Delta G^{o} = +130.57\ \text{kJ} \quad (4)$$

$$Bi(OH)_3\hat{U}Bi^{3+} + 3OH^- \quad \Delta G^{o} = -50.13\ \text{kJ} \quad (5)$$

$$[Pb(NH_3)_4]^{2+} + HS^- + Er(OH)_3\hat{U}PbSEr^{3+} + 4NH_3 + H^+ + 3OH^- \quad \Delta G^{o} = +493.45\ \text{kJ} \quad (6)$$

$$[Pb(NH_3)_4]^{2+} + HS^- + Bi(OH)_3\hat{U}PbSBi^{3+} + 4NH_3 + H^+ + 3OH^- \quad \Delta G^{o} = +312.75\ \text{kJ} \quad (7)$$

Adding the reactions (6) and (7), as well as its ΔG^{o} respectively, according to the *Hess* law

$$[Pb(NH_3)_4]^{2+} + SH^- + Bi(OH)_3 + Er(OH)_3\hat{U}PbSEr^{3+}\text{-}Bi^{3+} + 4NH_3 + H^+ + 3OH^- \quad \Delta G^{o} = +806.20\ \text{kJ} \quad (8)$$