Research Article

Synthesis, Characterization, and Photoluminescence on the Glass Doped with AgInS$_2$ Nanocrystals

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We demonstrated a synthetic process on the glass doped with AgInS$_2$ nanocrystals through sol-gel method under a controlled atmosphere. X-ray powder diffraction and X-ray photoelectron spectra revealed that the AgInS$_2$ crystalline phase had formed in the glass matrix. Transmittance electron microscopy showed that these AgInS$_2$ crystals had spherical shape and good dispersed form in the glass matrix, and their diameter distribution was mainly focused on three size regions. Furthermore, the glass doped with AgInS$_2$ nanocrystals exhibited three photoluminescence peaks located at 1.83 eV, 2.02 eV, and 2.21 eV, which were ascribed to the introduction of AgInS$_2$ nanocrystals in the glass.

1. Introduction

In the last two decades, semiconductor nanocrystals have attracted tremendous attention due to their unique electronic and optical properties [1, 2]. Such nanocrystals have potential applications for future photonic devices and electronic devices such as light emitting diodes, solar cell materials, nonlinear optical devices, and biooptical imaging devices [2–4]. Typically of semiconductor materials, II-VI-type semiconductor nanocrystals have drawn more attention due to their considerable fluorescent properties [5]. But, unfortunately, the constituents of these II-VI semiconductors often include some toxic elements such as Cd, As, Pb, Hg, and Se [6, 7], which are not an environmental friendly model. Thus, developing a semiconductor with nontoxic constituents is very important for more wide applications in the future.

One thing worth mentioning is the ternary I-III-VI$_2$-type semiconductors like AgInS$_2$, which has been recognized as an ideal replacement [8–10]. AgInS$_2$ crystals with the bandgap energy of 1.9 eV, specially, exhibit a chalcopyrite structure [11]. Such AgInS$_2$-based materials are often used to develop high-efficiency Cu(In,Ga)Se$_2$ solar cells because the lattice parameter of AgInS$_2$ crystals is almost the same as that of Cu(In,Ga)Se$_2$ crystals [12]. In particular, some studies showed that some AgInS$_2$ crystals with nanolevel size distribution and well-defined spherical morphology exhibited considerable photoluminescence and high quantum yield (∼41%) [13], indicating that the morphology and size distribution of AgInS$_2$ nanocrystals should be controlled effectively in practical applications. Thus, how to achieve a suitable morphology and size distribution of AgInS$_2$ nanocrystals will be very crucial in the synthetic process.

Nanocrystals glasses, namely, by adding nanolevel crystalline particles into the glass matrices, are one of the most interesting issues in materials science. The reason is that glasses seem to be preferable for optical devices because of their ease of fabrication in desirable shapes and sizes, high transparency, good chemical and thermal durability, threshold to optical damage, and so forth [14], which make them promising matrices for loading different nanocrystals, thereby giving glasses some good performances. Consequently, a variety of nanocrystals glasses have been developed for many applications, such as solid state laser [15], nonlinear media [16], and photonic applications [17]. Under this background, researchers have been trying to employ different methods for realizing the development of nanocrystals glasses. In this paper, we demonstrated an effective path to achieve the synthesis of the glass doped with AgInS$_2$.
nanocrystals through sol-gel method under a controlled atmosphere. By adjusting these parameters including temperature, time, and atmosphere, AgInS$_2$ nanocrystals with well-defined spherical morphology and suitable size distribution were successfully doped in the glass matrix. It meant that nanocrystals-glass material, which has both the properties of semiconductor and optical glass, could be realized in the same material system. In addition, microstructure and photoluminescence of the glass doped with AgInS$_2$ nanocrystals were also studied in this paper. We believe that the path will provide a reference to realize the synthesis of different semiconductor nanocrystals in the glass matrices, which is very necessary and significant to study the photonics and optoelectronics in materials science.

2. Experimental Section

In a typical synthetic process, bulk glass doped with AgInS$_2$ nanocrystals was synthesized through sol-gel method under a controlled atmosphere. The stoichiometric composition of the glass was designed for the following: Na$_2$O (7 mol%), B$_2$O$_3$ (23 mol%), and SiO$_2$ (70 mol%) • AgInS$_2$ (1.5 mol%). The synthetic process of the stiff gel agreed with our previous work [18]. Silver and indium nitrate salts were chosen to form AgInS$_2$ nanocrystals. Specific synthetic process of the glass doped with AgInS$_2$ nanocrystals showed the following. Firstly, the yellow-brown stiff gel containing silver and indium ions was heated in oxygen atmosphere at 450°C and kept for 10 h at this temperature. Secondly, the aerogel was exposed to hydrogen atmosphere at 450°C for 10 h to form Ag-In alloy nanocrystals and then the aerogel was further heated in hydrogen sulfide atmosphere up to 600°C. Finally, an indehiscent, well-densified brown glass doped with AgInS$_2$ nanocrystals was obtained, as shown in Figure 1(a). Meanwhile, transparent pure post glass was shown in Figure 1(b).

The crystalline phase was performed on a Germany Bruker X-ray diffractometer from 10° to 70°. The formation of AgInS$_2$ was measured by AXIS ULTRA DLD X-ray photoelectron spectrometer. Transmission electron microscopy was recorded on a FEI Tecnai F20 transmission electron microscope for the morphology, size distribution, and crystalline phase of AgInS$_2$ nanocrystals. The photoluminescence spectra of the as-obtained glass were measured by Horiba Jobin Yvon 6400 Raman scattering spectrometer with a 325 nm laser as the excitation source at room temperature.

3. Results and Discussion

Figure 2 represented an X-ray powder diffraction (XRD) result of the as-obtained glass, in which several characteristic
diffraction peaks corresponding to (120), (002), (121), (122), and (040) of orthorhombic AgInS$_2$ crystals (JCPDS-25-1328) are observed. No other diffraction peaks are observed in the diffraction curve, indicating that the desired product for AgInS$_2$ crystals has formed in the glass matrix. Moreover, the characteristic diffraction peak shapes are broad, suggesting that the as-obtained AgInS$_2$ crystals should be small in size.

Figure 3 represented the high-resolution XPS result of the as-obtained glass, from which the Ag 3d, In 3d, and S 2p XPS spectra are evident. Figure 3(a) shows that the binding energies of Ag 3d$_{3/2}$ and Ag 3d$_{5/2}$ located at 373.6 eV and 367.5 eV with a peak spacing of 6.1 eV, which agreed with the standard reference XPS spectrum of Ag (I). Similarly, the peak spacing of In 3d$_{3/2}$ and In 3d$_{5/2}$ located at 452.4 eV and 444.8 eV is 7.6 eV, matching well with In (III), as shown in Figure 3(b). Figure 3(c) shows that the S 2p is an asymmetric peak, maybe resulting from the recombination of S 2p$_{1/2}$ and S 2p$_{3/2}$. Meanwhile, the Ag 3d and In 3d XPS spectra also reveal that the actual molar ratio of Ag and In is about 0.96 : 1, which is almost approximate to 1 : 1. The XPS result agreed well with the XRD result, indicating that AgInS$_2$ crystals have formed in the glass matrix.

To clarify the morphology, distribution, and crystalline phase of AgInS$_2$ crystals in the glass matrix, transmission electron microscopy (TEM) measurement was performed. Figure 4(a) shows that the precipitated AgInS$_2$ particles appear in a spherical shape and good dispersed form, and the diameter size of these AgInS$_2$ particles mainly focuses on three different regions, as shown in Figure 4(b), including 8~12 nm accounting for 20%, 12~16 nm accounting for 50%, and 16~20 nm accounting for 30%, after counting all particles in Figure 4(a). Figure 4(c) shows the high-resolution TEM result (HRTEM), in which the atomic planes with lattice fringe are observed, indicating a typical crystalline structure. The insets shown in the red square and circle frames are an enlarged image for the lattice fringe, as shown in the main panel of Figure 4(c). The lattice fringe spacing is equal to 0.357 nm corresponding to the (120) plane of AgInS$_2$ crystals in an orthorhombic crystal system (JCPDS-25-1328). Figure 4(d) shows the selected area electron diffraction...
(SAED) pattern taken in a zone filled with nanoparticles. The estimated diffraction radii rings correspond well to AgInS$_2$ lattice planes $(120), (202), (123),$ and $(124)$, respectively. TEM results further confirm the analytical results of XRD and XPS measurements.

Figure 5 represented the photoluminescence result of the pure and as-obtained glasses, which are excited at 325 nm. In a prescribed wavelength scope, it is noticed that no photoluminescence emission peak appears in the pure glass (Curve (a)). However, three photoluminescence emission peaks located at $1.83$ eV, $2.02$ eV, and $2.21$ eV are evident in the as-obtained glass (Curve (b)). Obviously, the different photoluminescence of the two glasses should derive from the AgInS$_2$ nanocrystals in the glass. Interestingly, the photoluminescence emission peaks appear on three different photon energy positions, which could be attributed to the size distribution of AgInS$_2$ nanocrystals in the glass. Figures 4(a) and 4(b) show that the diameter sizes of these AgInS$_2$ nanocrystals are mainly focused on three different regions, indicating that the different photoluminescence emission positions are correlative with the size distribution. Hamanaka et al. and Ogawa et al. had also come to a similar conclusion [10, 19]. They discovered that the photoluminescence peaks of the AgInS$_2$ nanocrystals shifted towards a lower energy with increasing nanocrystals size. Such a size-dependent shift of the emission peak should be attributed to a quantum confinement effect of carriers in AgInS$_2$ nanocrystals. Thus, the photoluminescence should derive from the transition between the lowest quantized levels of the valence and conduction bands in the as-obtained glass. The results also suggest that the as-obtained glass will have better tunability from orange-green to deep red region by adjusting the size distribution of the AgInS$_2$ nanocrystals in the glass. The relevant work is still in progress.

4. Conclusion

We design a path successfully to realize the synthesis of the glass doped with AgInS$_2$ nanocrystals by sol-gel method under a controlled atmosphere. XRD and XPS analysis show that the AgInS$_2$ nanocrystals have formed in the glass, and these AgInS$_2$ nanocrystals have spherical shape, good dispersed form, and three main size distribution regions observed in TEM analysis, which will cause three significant
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Figure 5: Photoluminescence spectra of the as-obtained glasses: (a) pure glass and (b) AgInS$_2$ nanocrystals glass.

Photoluminescence emission peaks located at 1.83 eV, 2.02 eV, and 2.21 eV, respectively. The reason is attributed to a quantum confinement effect of carriers in AgInS$_2$ nanocrystals. We believe that the synthetic path will become a promising technique in the optical glass materials. In particular, the tunability of emission color in the nanocrystals glass will have a potential application in solid laser, LED, nonlinear optics, and so forth.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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