Research Article

Synthesis, Characterization, and Photoluminescence on the Glass Doped with AgInS₂ Nanocrystals

Dewu Yin,^{1,2} Lang Pei,² Zhen Liu,² Xinyu Yang,^{1,2} Weidong Xiang,^{1,2} and Xiyan Zhang¹

¹College of Materials Science and Engineering, Changchun University of Science and Technology, Changchun 130022, China

²Faculty of Chemistry & Material Engineering, Wenzhou University, Wenzhou 325027, China

Correspondence should be addressed to Xinyu Yang; yangxinyu13@126.com and Xiyan Zhang; xiyzhang@126.com

Received 17 August 2014; Accepted 17 September 2014

Academic Editor: Wen Lei

Copyright © 2015 Dewu Yin et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

We demonstrated a synthetic process on the glass doped with AgInS₂ nanocrystals through sol-gel method under a controlled atmosphere. X-ray powder diffraction and X-ray photoelectron spectra revealed that the AgInS₂ crystalline phase had formed in the glass matrix. Transmittance electron microscopy showed that these AgInS₂ 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 AgInS₂ nanocrystals exhibited three photoluminescence peaks located at 1.83 eV, 2.02 eV, and 2.21 eV, which were ascribed to the introduction of AgInS₂ 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-VI₂-type semiconductors like AgInS₂, which has been recognized as an ideal replacement [8–10]. AgInS₂ crystals with the band-gap energy of 1.9 eV, specially, exhibit a chalcopyrite structure [11]. Such AgInS₂-based materials are often used to develop high-efficiency Cu(In,Ga)Se₂ solar cells because the lattice parameter of AgInS₂ crystals is almost the same as that of Cu(In,Ga)Se₂ crystals [12]. In particular, some studies

showed that some AgInS₂ 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 AgInS₂ nanocrystals should be controlled effectively in practical applications. Thus, how to achieve a suitable morphology and size distribution of AgInS₂ 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 AgInS₂

FIGURE 1: Photograph of as-obtained glass: (a) AgInS_2 nanocrystals glass and (b) pure glass.

FIGURE 2: XRD pattern of the as-obtained glass. The JCPDS pattern of AgInS_2 crystals is also shown.

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_2O (7 mol%), B_2O_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

FIGURE 3: XPS pattern of AgInS_2 nanocrystal: (a) Ag 3d core level spectrum; (b) In 3d core level spectrum; (c) S 2p core level spectrum.

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

FIGURE 4: TEM analysis of the as-obtained glass: (a) morphology image; (b) size distribution; (c) HRTEM image; (d) SAED image.

(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

FIGURE 5: Photoluminescence spectra of the as-obtained glasses: (a) pure glass and (b) AgInS₂ 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 AgInS₂ 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.

Acknowledgments

The work was financially supported by the National Natural Science Foundation of China (Grant no. 51202166), the Zhejiang Province Natural Science Foundation of China (Grant no. Y4100233), and the Wenzhou University Innovation and Career Project of China (Grant no. DC2012006).

References

- [1] H. Weller, "Colloidal semiconductor Q-particles: chemistry in the transition region between solid state and molecules," *Angewandte Chemie International Edition*, vol. 32, pp. 41–53, 1993.
- [2] Y. Masumoto and T. Takagahara, *Semiconductor Quantum Dots: Physics, Spectroscopy and Applications*, Springer, Berlin, Germany, 2002, Springer.
- [3] H. S. Nalwa, *Handbook of Thin Film Materials*, Academic Press, San Diego, Calif, USA, 2002.
- [4] L. W. Liu, R. Hu, W. C. Law et al., "Optimizing the synthesis of red- and near-infrared CuInS₂ and AgInS₂ semiconductor nanocrystals for bioimaging," *Analyst*, vol. 138, no. 20, pp. 6144–6153, 2013.
- [5] J. S. Steckel, S. Coe-Sullivan, V. Bulović, and M. G. Bawendi, "1.3 μm to 1.55 μm tunable electroluminescence from PbSe quantum dots embedded within an organic device," *Advanced Materials*, vol. 15, no. 21, pp. 1862–1866, 2003.
- [6] Z. Lingley, K. Mahalingam, S. Lu, G. J. Brown, and A. Madhukar, "Nanocrystal-semiconductor interface: atomic-resolution cross-sectional transmission electron microscope study of lead sulfide nanocrystal quantum dots on crystalline silicon," *Nano Research*, vol. 7, no. 2, pp. 219–227, 2014.
- [7] S. V. Kahane, V. Sudarsan, and S. Mahamuni, "A study of charge transfer mechanism and optical properties of Au-CdS core-shell nanocrystals," *Journal of Luminescence*, vol. 147, pp. 353–357, 2014.
- [8] J. Y. Chang, G. Q. Wang, C. Y. Cheng, W. X. Lin, and J. C. Hsu, "Strategies for photoluminescence enhancement of AgInS₂ quantum dots and their application as bioimaging probes," *Journal of Materials Chemistry*, vol. 22, pp. 10609–10618, 2012.
- [9] M.-A. Langevin, A. M. Ritchey, and C. N. Allen, "Air-stable near-infrared AgInSe₂ nanocrystals," *ACS Nano*, vol. 8, no. 4, pp. 3476–3482, 2014.
- [10] Y. Hamanaka, T. Ogawa, M. Tsuzuki, K. Ozawa, and T. Kuzuya, "Luminescence properties of chalcopyrite AgInS₂ nanocrystals: Their origin and related electronic states," *Journal of Luminescence*, vol. 133, pp. 121–124, 2013.
- [11] J. L. Shay and B. Tell, "Energy band structure of I-III-VI₂ semiconductors," *Surface Science*, vol. 37, pp. 748–751, 1973.
- [12] Y. Akaki, K. Yamashita, and T. Yoshitake, "Characterization of AgInS₂ thin films prepared by vacuum evaporation," *Physica B*, vol. 407, pp. 2858–2860, 2012.
- [13] X. S. Tang, W. B. A. Ho, and J. M. Xue, "Synthesis of Zn-Doped AgInS₂ nanocrystals and their fluorescence properties," *The Journal of Physical Chemistry C*, vol. 116, no. 17, pp. 9769–9773, 2012.
- [14] F. E. P. Dos Santos, C. B. De Araujo, A. S. L. Gomes et al., "Nonresonant third-order nonlinear properties of glasses in the near infrared," *Journal of Applied Physics*, vol. 106, Article ID 063507, 2009.
- [15] P. T. Guerreiro, S. Ten, N. F. Borrelli, J. Butty, G. E. Jabbour, and N. Peyghambarian, "PbS quantum-dot doped glasses as saturable absorbers for mode locking of a Cr: forsterite laser," *Applied Physics Letters*, vol. 71, no. 12, pp. 1595–1597, 1997.
- [16] L. A. Padiha, A. A. R. Neves, E. Rodriguez, C. L. Cesar, L. C. Barbosa, and C. H. Brito Cruz, "Ultrafast optical switching with CdTe nanocrystals in a glass matrix," *Applied Physics Letters*, vol. 86, Article ID 161111, 2005.
- [17] Q. Luo, X. Fan, X. Qiao, H. Yang, M. Wang, and X. Zhang, "Eu²⁺-Doped glass ceramics containing BaF₂ nanocrystals as a potential blue phosphor for UV-LED," *Journal of the American Ceramic Society*, vol. 92, no. 4, pp. 942–944, 2009.
- [18] X. Yang, W. Xiang, H. Zhao, H. Liu, X. Zhang, and X. Liang, "Nonlinear saturable absorption of the sodium borosilicate glass containing Bi₂S₃ nanocrystals using Z-scan technique," *Journal of Alloys and Compounds*, vol. 509, no. 26, pp. 7283–7289, 2011.
- [19] T. Ogawa, T. Kuzuya, Y. Hamanaka, and K. Sumiyama, "Synthesis of Ag-In binary sulfide nanoparticles—structural tuning and their photoluminescence properties," *Journal of Materials Chemistry*, vol. 20, no. 11, pp. 2226–2231, 2010.