γ-Irradiation Route to Nanocrystalline Lead Selenide

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30 nm PbSe has been synthesized for the first time by γ-irradiation method from an ethylenediamine solution containing lead acetate and elemental selenium at room temperature and in ambient pressure.

Recently, the syntheses of binary sulfides and selenides have been the focus of the attention because of their important physical and chemical properties and good commercial application as semiconductors of luminescence.[1] The study on PbSe is meaningful because it could be widely used as IR sensors, solar cell, infrared detectors, chemical sensors and so on.[2-4] Conventionally, metal chalcogenides are synthesized by the reaction of the elements at elevated temperatures, typically 500-600 °C, in evacuated tubes by a solid state metathesis reaction of anhydrous metal halide with $Na_2(S,Se)$ at high temperature, or involved the use of complex and expensive organometallic precursors with highly toxic and malodorous gaseous H_2S and H_2Se.[5-6] Recently, G. H. Henshaw reported room temperature route to metal chalcogenides by a reaction between metal and S or Se in liquid ammonia. But in this method, many operations must be carried out at -77° C. Furthermore, reactions in liquid ammonia are easy to explode and all the operation should be conducted with blast proof and behind safety screen.[7] Here we report a new approach — γ-irradiation — for preparing metal selenides, totally free of using toxic H_2Se or liquid ammonia. In this approach, all procedures are carried out at room temperature and in ambient pressure, which is quite different from other synthesis methods for metal selenides at high temperatures or other extreme conditions.

γ-Irradiation has been developed to be a method to prepare nanocrystalline metals, alloys, metal oxide and glass-metal, silver/polyacrylamide nanocomposite.[8] Recently, nanocrystalline CdS was obtained under γ-irradiation at room temperature in aqueous solution, using sodium thiosulfate as the sulfur source.[9] Here, we first extend γ-irradiation to the preparation of nanocrystalline selenides in non-aqueous solution. Pure nanocrystalline PbSe was successfully obtained from an ethylenediamine solution containing lead acetate and elemental selenium under γ-irradiation at room temperature. Also it is the first report on γ-irradiation of nanomaterials in amine solvents, rather than the preliminary aqueous or alcohol solvents. The successful extension of the irradiating systems will no doubt expand the application of γ-irradiation preparation.

In this approach, the solutions were prepared by dissolving an appropriate amount of analytically pure lead acetate and selenium powders in ethylenediamine. The solutions were irradiated in the field of a 2.59×10^{15} Bq ^{60}Co γ-ray source. Irradiation dose is 3.0×10^4 Gy. The irradiated solutions were kept for several hours to precipitate powders. Black precipitates were collected and washed with absolute ethanol, distilled water and dilute acetic acid in sequence to remove the by-products. The final products were washed with acetone and then dried in vacuum at room temperature for 4 h.

The samples were characterized by X-ray powder diffraction (XRD) patterns employing a scanning rate of $0.05°s^{-1}$, using a Japan Rigaku Dmax γ_A X-ray diffractometer equipped with a graphite monochromatized CuKα radiation (λ= 1.54178 Å). Figure 1 shows the XRD pattern of a typical sample of PbSe, which was prepared by γ-irradiation of a solution containing 0.05 kmol/m^3 lead acetate in the saturated ethylenediamine of selenium. All peaks can be indexed as cubic phase PbSe with the cell constant a= 6.12 Å, which is consistent with the reported value (JCPDS Card File No. 6-354).

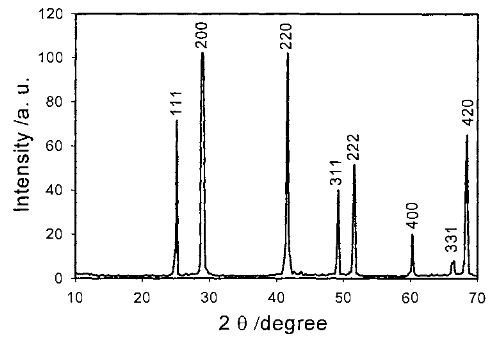

Figure 1. XRD pattern of PbSe prepared by γ-irradiation.

The morphology and particle sizes are determined by Transmission Electron microscopy (TEM), which were taken on a Hitachi Model H-800 Transmission Electron Microscope with an accelerating voltage of 200 kV. A TEM image of the sample as that in Figure 1 is shown in Figure 2. It shows that as-prepared PbSe consists of homogeneously spherical particles with average size of 30 nm.

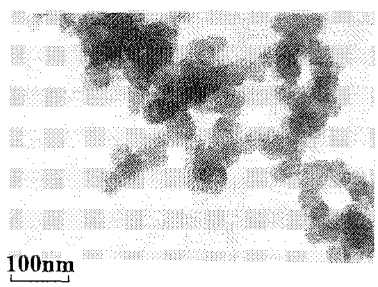

Figure 2. TEM image of the PbSe sample shown in Figure 1.

In the γ-irradiation process, the mechanisms of the formation of nanocrystalline selenide are not known up to now. Few reports have been given on the transformation of the elemental selenium under γ-irradiation. However, some probable reactions may be going on under γ-irradiation. It is known that (1) elemental selenium is rather stable in aqueous solution under γ-irradiation, and (2) amorphous and crystalline selenium powders can be synthesized from irradiated solutions dissolving SeO_2 in hydrochloric acid and NaOH solution, respectively.[10] Here the solvent ethylenediamine probably plays an important role in the formation of PbSe. So, different solvents were also tested in our experiments and the results confirmed that the kinds of solvents were the most effective factor on the quality of nanocrystalline PbSe. In other solvents, such as benzene, tetrahydrofuran, which even can not dissolve the selenium powders, no homogenous solution can be formed and no PbSe can be obtained under γ-irradiation.

Ethylenediamine is chosen as the solvent due to its N-chelation ability to many kinds of metal ions. It can not only bind to and stabilize Pb(II), but also dissolve Se and produced complex, just like some amine solvents produce complex with S and Se.[11] This is also supported by the solution color changes from opaque to dark brown when lead acetate and Se powder dissolve in ethylenediamine. Selenium disperses into ethylenediamine solution, which greatly increases its surface area. So the solvent ethylenediamine enhances the reactivity of Se, and promotes the reaction without the need of high temperature, which greatly differs the γ-irradiation method from solid state reaction. Like most other kinds of the organic system, solvated electrons can be formed in ethylenediamine systems under γ-irradiation.[12] The existence of active solvated electrons which react as reluctant, also probably activates the reaction between Se and lead acetate and made it easily happen at room temperature.

In a summary, γ-irradiation has been used for the first time to prepare nanocrystalline PbSe at room temperature and under ambient pressure. A non-aqueous system was chosen consisting of lead acetate and selenium powders in ethylenediamine solution. The ethylenediamine plays an important role in the formation of PbSe. By appropriate control of the experimental parameters, it is possible to prepare versatile nanocrystalline metal selenides though this new γ-irradiation route.

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References and Notes

1 L. E. Brus, *Appl. Phys. A,* **53,** 465 (1991).
2 V. B. Orletskii, *Ukr. Fiz. Zh.,* **39,** 505 (1994).
3 P. A. Kondas, *Report,* 1993, 6pp.
4 J. N. Zemel, *J. Franklin Inst.,* **296,** 475 (1973).
5 I. P. Parkin, *Chem. Soc. Rev.,* **1996**, 199.
6 A. C. Chang, W. F. Pfeiffer, B. Guillaume, S. Baral, and J. H. Fendler, *J. Phys. Chem.,* **94,** 4284 (1990).
7 G. H. Henshaw, I. P. Parkin and G. Shaw, *J. Chem. Soc. Chem. Commun,* **1996**, 1095.
8 Y. J. Zhu, Y. T. Qian, X. J. Li and M. W. Zhang, *Chem. Commun.*, **1997**, 1081.
9 Y. Yin, X. Xu, G. Xia, X. Ge and Z. Zhang, *Chem. Commun.* **1998**, 1641.
10 Y. J. Zhu, Y. T. Qian, H. Huang, and M. W. Zhang, *Mater. Lett.*, **28,**119 (1996).
11 Y. Cheng, T. J. Emge, and J. G. Brennan, *Inorg. Chem.,* **35,**7339 (1996).
12 T. Shida, *J. Phys. Chem.*, **74,** 3055 (1970).