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A Novel in Situ Oxidization–Sulfidation Growth Route via self-Purification Process to β-In_2S_3 Dendrites

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A novel in situ oxidization–sulfidation growth route via a self-purification process has been developed to synthesize β-In_2S_3 dendrites. To our best knowledge, this is the first example to prepare dendrites of III–VI compounds, which are expected to show particular physical properties. The X-ray analysis (EDXA), X-ray photoelectron spectra (XPS), Raman spectrum and optical properties of β-In_2S_3 dendrites have also been investigated. It is found that the product is pure In_2S_3 and shows the strong quantum confinement of the excitonic transition expected for the In_2S_3 dendrites. © 2002 Elsevier Science (USA)

Key Words: **in situ; self-purification; indium sulfide; raman spectrum; optical properties.**

INTRODUCTION

It is well known that the particle sizes and shapes of materials are important for their physical properties (1, 2), so dendrites as a type of fractal are currently the focus of considerable interest. Since Nittmann and Stanley (3) reported dendritic growth patterns in 1986, many methods have been used for the preparation of inorganic dendrites (4–11), most of which are focused on the metal or alloy field. Most scientists thought that the formation of dendrites is due to non-equilibrium growth and molecular anisotropy (3, 12). In our group, InSb dendrites (9) and Ag, Pd dendrites (10) have been prepared by a sonochemical co-reduction route and an ultrasonically assisted templated route, respectively. Some InSb dendrites were also found in the product via a potassium borohydride reducing solvothermal route (11), which was carried out by ultrasonic diffusion at first. The result of these previous studies (9–11) indicates that the surge, growth, shrink and collapse of ultrasonic cavitate go with the diffusion of its local energy and enhance the mass transport (13–15), which brings out the non-equilibrium growth. Moreover, element-reaction route is easier for the aggregation of anisotropic molecules, which will lead to the occurrence of dendritic growth. It is concluded that the ultrasonic element-reaction route is an effective way to synthesize dendrites. However, the preparation of metal sulfide dendrites is still a challenge to us, due to the fact that metal and sulfur are difficult to react along element-reaction route under ultrasonic conditions. It is thought that metal or alloy dendrites can probably be firstly prepared under ultrasonic conditions and then used as template, in which the oxidization and sulfidation processes are carried out in situ. Therefore, in this paper, InSb dendrites obtained by a sonochemical coreduction route (9) are chosen as precursor to react with sulfur source in situ and grow In_2S_3 dendrites.

β-In_2S_3 as a III–VI compound has been of interest, due to its optoelectronic properties (16), electronic properties (17), optical properties (18, 19), acoustic properties (20) and semiconductor sensitization (21) in recent years. It can also be used as n-type semiconductor with a medium energy gap between 2.00 and 2.20 eV (22), photoconductor (23, 24), materials in the preparation of green and red phosphors and in the manufacture of picture tubes for color televisions (25–27), dry cells (28), and heterojunctions for use in photovoltaic electric generators (29).

EXPERIMENTAL

Preparation

The procedure employed by us for preparing β-In_2S_3 dendrites is as follows. The precursor of InSb dendrites was firstly obtained by a sonochemical coreduction route (9). In subsequence, the mixtures of InSb dendrites (0.473 g, 2 mmol), CS_2 (0.18 mL, 3 mmol), NaOH (0.720 g, 18 mmol) and 30% H_2O_2 (0.60 mL, 6 mmol) were loaded into a 50-mL Teflon-lined autoclave, which was then filled with distilled water up to 90% of the total volume. The autoclave was sealed and maintained at 180°C for 24 h and was then

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cooled to room temperature naturally. The precipitate was filtered off, washed with distilled water and absolute ethanol for several times, and then dried in vacuum at 60°C for 4 h.

Characterization

X-ray diffraction (XRD) patterns were carried out on a Japan Rigaku D/max rA X-ray diffractometer equipped with graphite monochromatized high-intensity Cu $K\alpha$ radiation ($\lambda = 1.54178$ Å). The transmission electron microscopy (TEM) images, electronic diffraction (ED) patterns and energy dispersive X-ray analysis (EDXA) were taken on a Hitachi Model H-800 instrument with a tungsten filament, using an accelerating voltage of 200 kV. The X-ray photoelectron spectra (XPS) were collected on an ESCALab MKII X-ray photoelectron spectrometer, using non-monochromatized Mg$K\alpha$ X-ray as the excitation source. The Raman spectra were performed at room temperature with a LABRAM-HR Confocal Laser Micro-Raman Spectrometer. The 4ultraviolet and visible light (UV-vis) spectra and photoluminescence (PL) spectra were recorded on a JGNA Specord 200 PC UV-vis spectrophotometer and Hitachi 850 fluorescence spectrophotometer, respectively.

RESULTS AND DISCUSSION

Phase and Morphology

Figure 1 shows the XRD pattern of typical sample of β-In_2S_3 dendrites as prepared. All the reflections could be indexed to the β-In_2S_3 phase with lattice parameters $a = (7.613 \pm 0.002)$, $c = (32.326 \pm 0.005)$ Å, which are in agreement with the reported data of $a = 7.619$, $c = 32.329$ Å for In_2S_3 (JCPDS Card Files, 25-390). No characteristic peaks were observed for the other impurities such as In_2O_3, S or $In(OH)_3$.

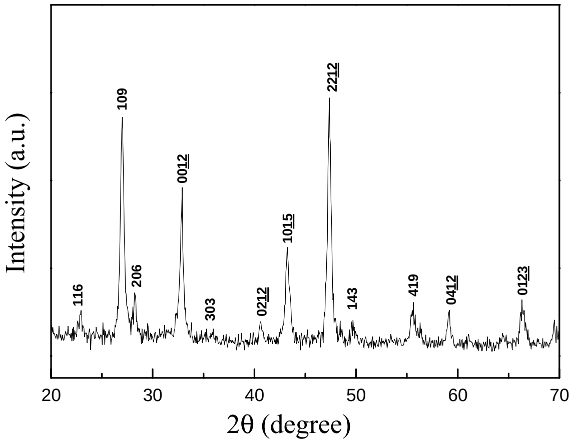

FIG. 1. XRD pattern of β-In_2S_3 dendrites prepared by a novel in situ oxidization–sulfidation growth route via a self-purification process.

Typical TEM images and ED patterns of the precursor of InSb dendrites and as-prepared product of β-In_2S_3 dendrites are shown in Fig. 2. It can be seen that the dendritic pattern of precursor almost remained in the as-prepared product, except that the rapid growth at higher temperatures made the as-prepared In_2S_3 dendrites grow larger and the branch-splitting of as-prepared In_2S_3 dendrites was not as delicate as that of precursor. ED pattern (Fig. 2c) of the as-prepared In_2S_3 dendrites shows that they were tetragonal single crystals. EDXA analysis of the as-prepared dendrites indicates that they were made up of In and S, which gives a ratio of S to In in the products (1.47:1). However, there is a little inconsistency among the results, and this is very true for the stoichiometry of In_2S_3.

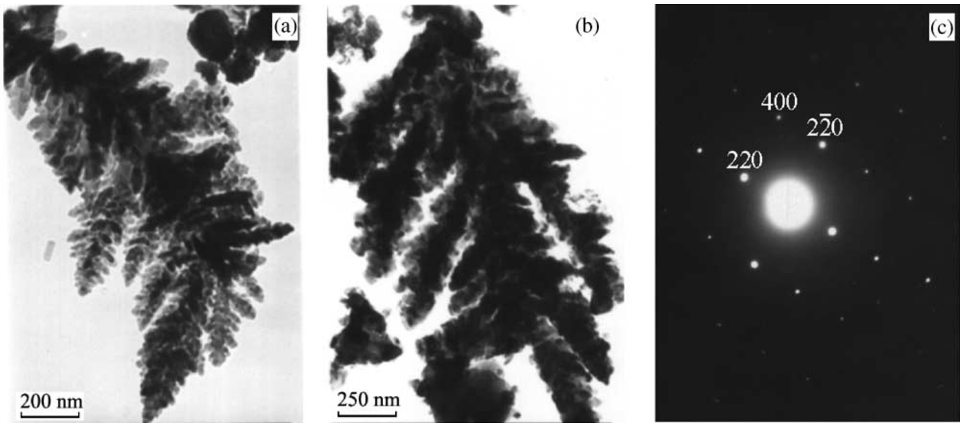

FIG. 2. (a) TEM image of the precursor of InSb dendrites; (b) TEM image of the as-prepared In_2S_3 dendrites; (c) ED pattern of the as-prepared In_2S_3 dendrites.

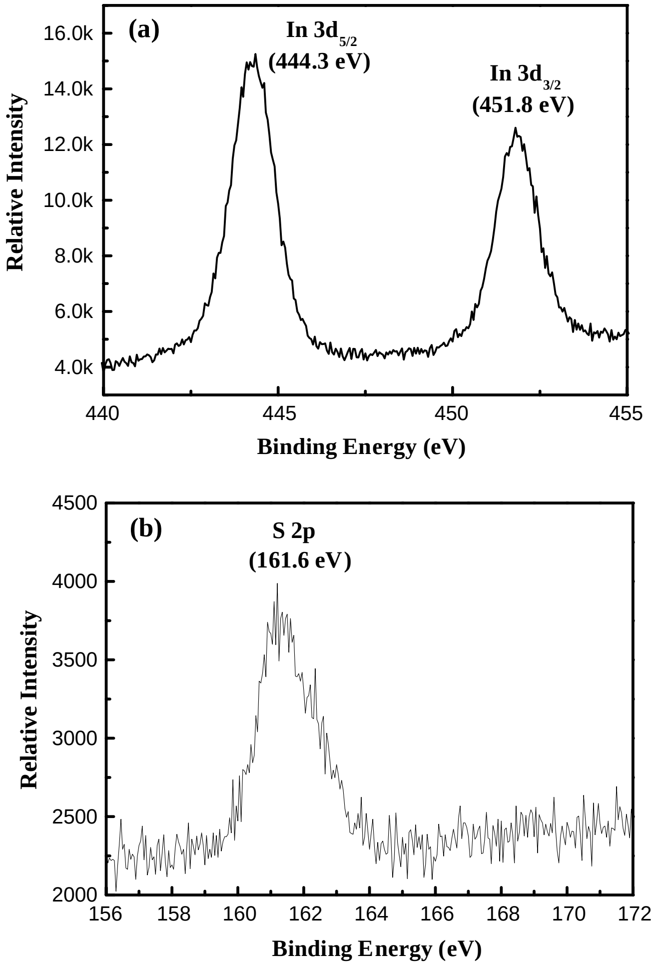

FIG. 3. XPS spectra of the samples: (a) In 3D core level spectrum of In_2S_3; (b) S $2p$ core level spectrum of In_2S_3.

XPS Characterization

Further evidence for the quality and composition of the samples was obtained by the XPS of the products. The binding energies obtained in the XPS analysis were corrected for specimen charging by referencing the C $1s$ to 284.60 eV. The In 3D core level spectrum (Fig. 3a) shows the observed value of the binding energies for In $3d_{5/2}$ (444.3 eV) agree with the reported data in In_2S_3 (444.3 eV) (30). The kinetic energy of the In $M_4N_{45}N_{45}$ peak is 408.0 eV. Therefore, the value of the "modified Auger parameter" (a') is 852.3 eV, which is in agreement with the literature observed in In_2S_3 and far from the data in In_2O_3 (30). The S $2p_{3/2}$ binding energy of In_2S_3 (Fig. 3b), centered at 161.6 eV, is very consistent with those observed in chalcopyrite $CuFeS_2$ (31). The contents of In and S are quantified by In $3d$ and S $2p$ peak areas, and a molar ratio of 1 : 1.46 for In : S is given. No obvious peaks for elemental sulfur or other impurities were observed. So the XPS analysis shows that the product is pure In_2S_3 and has no oxide impurities.

Raman Spectrum

The room temperature stable phase of β-In_2S_3 crystallizes in a defect spinel superstructure with space group $I4_1/\alpha md - D_{4h}$ containing 16 molecules in the unit cell. Indium atoms occupy all octahedral sites as well as $\frac{2}{3}$ of the tetrahedral metal positions of the spinel lattice. One-third of the tetrahedral metal ion sites remains empty and they are ordered in a 4_1 screw axis by alignment of three spinel blocks along the c-axis of the crystal. The primitive unit cell of β-In_2S_3 chosen for the account of the normal modes of vibrations is reduced by one-half along the c-axis unit cell (32–34). The space group isomorphic to the point group of β-In_2S_3 is D_{4h}.

Group theory analysis (35) gives the following predictions for the Raman-active modes at the center of the Brillouin zone.

$$\Gamma_R = 9A_{1g} + 9B_{1g} + 4B_{2g} + 14E_g.$$

With unpolarized light, the Stokes components of the scattered light are displayed in Fig. 4. Assuming that all peaks correspond to a first-order spectrum, the frequency at which each of them occurs would correspond to a normal mode of vibration. Fifteen normal modes of vibrations are thus observed, which correspond exactly to those given by a sample of β-In_2S_3 with unpolarized light (36). The small change of peak intensity and the instability of baseline are due to the influence of fluorescence.

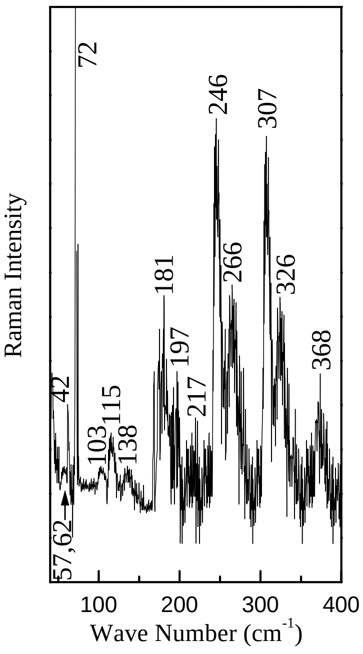

FIG. 4. Raman spectrum of β-In_2S_3 dendrites.

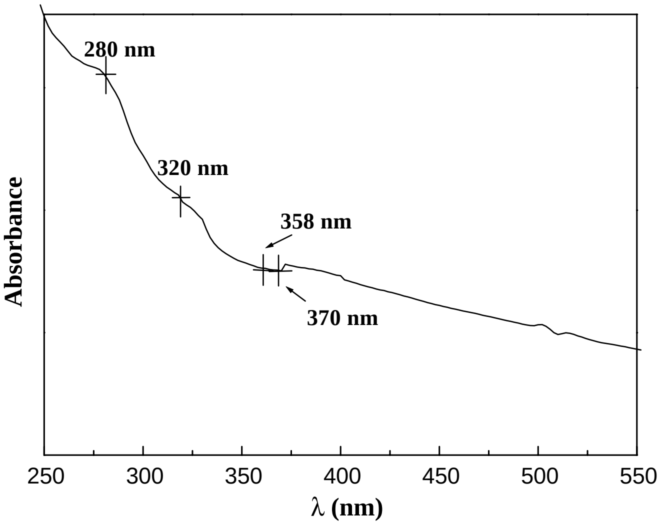

FIG. 5. UV-vis spectra of the as-prepared In_2S_3 dendrites.

Optical Properties

To examine the quantum-confined effect of the products, room-temperature UV-vis spectra and PL spectra are shown, when ethanol is used as a reference. The result of UV-vis spectroscopy (Fig. 5) shows that there is an absorption band at 280–370 nm. Because there is a strong influence from light scattering, the bumps they observe in UV-vis absorption may be difficult to discuss in terms of actual transitions. However, according to the characteristic steplike shape of the band, it should be attributed to the valence-to-conduction-band transition in indium sulfide. In bulk In_2S_3, the band gap (E_g) is reported to be between 2.00 and 2.20 eV with corresponding UV band from 620 to 550 nm (16, 17). Considering the position of the UV-vis onsets estimated as the step median, 330 nm, the band-gap becomes equal to $E_g = 3.76$ eV (corresponding to 330 nm). It is obvious that there is blue shift between the result and the reported data for bulk In_2S_3, which indicates the strong quantum confinement of the excitonic transition expected for the In_2S_3 dendrites. The larger difference between the peak and the onset, which might be related to the width of particle size distribution, is characteristic for the size difference between the branch-splitting and bough of dendrite.

More evidences indicating quantum confinement effect of as-obtained product are provided by the luminescence spectrum. Figure 6a is the PL excitation spectrum of the In_2S_3 dendrites while Fig. 6b represents that of the reference ethanol. Under PL excitation at 330 nm, the In_2S_3 dendrites emit blue light as 358 nm (corresponding to 3.46 eV). It clearly indicates the existence of electronic transition at particular wavelenth(358 nm), and is stronger than in the bulk In_2S_3, which is virtually non-luminescent. The UV peak of In_2S_3 dendrites is accompanied by a shoulder of 0.2 eV to the red from the emission maximum. It is reported that its intensity and position with respect to the main peak is affected by the choice of stabilizer and by the media (37). The closeness of the emission peaks to the absorption onset of the semiconductor indicates that this emission comes from the interband electron–hole recombination. To be corrected with notations, it is necessary to note that the interband transition may actually involve electronic levels in close vicinity to the bottom of the lowest empty band and the top of the highest occupied band, as the case for CdSe (38–40).

Reaction Mechanism

In the reaction process, CS_2 could be attacked by NaOH to release S^{2-}, which provided sulfur source (41). In subsequence, InSb was oxidized by H_2O_2 to In (III) and Sb (III) (41) that then would be combined with S^{2-} to produce In_2S_3 and Sb_2S_3 in situ.

$$In^{3+} + 3e^- \rightarrow In \quad E^0 = -0.34\ \text{V}, \qquad [1]$$

$$SbO^+ + 2H^+ + 3e^- \rightarrow Sb + H_2O \quad E^0 = 0.21\ \text{V}, \qquad [2]$$

$$H_2O_2 + 2e^- \rightarrow 2OH^- \quad E^0 = 0.88\ \text{V}. \qquad [3]$$

The produced Sb_2S_3 could be dissolved in the produced NaOH solution (42) — this is a self-purification process. Simultaneously, the produced In_2S_3 in situ would grow along the former dendritic pattern. Thus the InSb dendrites

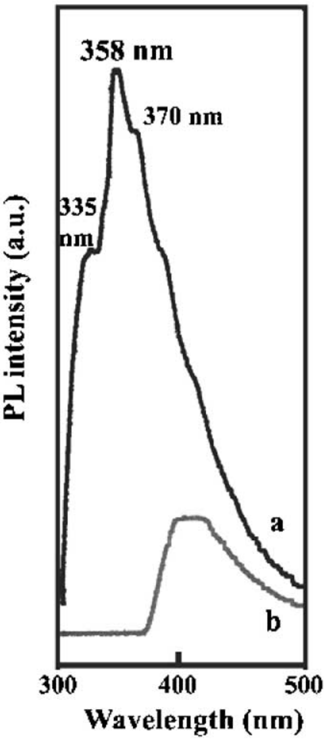

FIG. 6. PL spectra of (a) the as-prepared In_2S_3 dendrites; (b) the reference ethanol.

was transformed to In_2S_3 dendrites in situ. The whole process can be shown as follows:

$$CS_2+6NaOH \rightarrow 2Na_2S + Na_2CO_3+3H_2O, \quad [4]$$

$$2InSb + 6Na_2S + 6H_2O_2 \rightarrow In_2S_3+Sb_2S_3+12NaOH, \quad [5]$$

$$4NaOH + 2Sb_2S_3 \rightarrow NaSbO_2+3NaSbS_2+2H_2O. \quad [6]$$

The existence of Eq. (4) was identified by the following facts: dropping a little $CaCl_2$ solution into the filtered solution after reaction, some white deposit was found in the mixed solution, which then turned clear when adding either CO_2 gas or HCl solution.

CONCLUSIONS

In summary, a novel in situ oxidization–sulfidation growth route via self-purification process was reported to synthesize β-In_2S_3 dendrites. To our best knowledge, this is the first example to prepare dendrites of III–VI compounds, which are expected to show particular physical properties.

The X-ray analysis (EDXA), X-ray photoelectron spectra (XPS), Raman spectrum and optical properties of β-In_2S_3 dendrites have also been investigated. It is found that the product is pure In_2S_3 and shows the strong quantum confinement of the excitonic transition expected for the In_2S_3 dendrites. This technique is expected to synthesize other metal chalcogenide dendrites from alloy (or metal) dendrites or metal chlorides.

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REFERENCES

1. R. Rosetti, S. Nakahare, and L. E. Brus, *J. Chem. Phys.* **79,** 1086 (1983).
2. F. Williams and A. J. Nozik, *Nature* **312,** 21 (1984).
3. J. Nittmann and H. E. Stanley, *Nature* **321,** 663 (1986).
4. S. T. Selvan, *Chem. Commun.* 351 (1998).
5. Y. Zhou, S. H. Yu, C. Y. Wang, X. G. Li, Y. R. Zhu, and Z. Y. Chen, *Adv. Mater.* **11,** 850 (1999).
6. S. Z. Wang and H. W. Xin, *J. Phys. Chem. B* **24,** 5681 (2000).
7. H. Li, G. Zhu, X. Huang, and L. Chen, *J. Mater. Chem.* **10,** 693 (2000).
8. M. Wang, S. Zhong, X. B. Yin, J. M. Zhu, R. W. Peng, Y. Wang, K. Q. Zhang, and N. B. Ming, *Phys. Rev. Lett.* **86,** 3827 (2001).
9. Y. J. Xiong, Y. Xie, G. A. Du, X. M. Liu, and X. B. Tian, *Chem. Lett.* 1038 (2001).
10. J. P. Xiao, Y. Xie, R. Tang, M. Chen, and X. B. Tian, *Adv. Mater.* **13,** 1887 (2001).
11. J. Lu, Y. Xie, X. C. Jiang, W. He, P. Yan, and Y. T. Qian, *Can. J. Chem.* **79,** 127 (2001).
12. E. Ben-Jacob and P. Garik, *Nature* **343,** 523 (1990).
13. T. J. Mason and J. P. Lorimer, "Sonochemistry: Theory, Applications and Uses of Ultrasound in Chemistry." Ellis Horwood Limited, Chichester, UK, 1988.
14. K. Chatakondu, M. L. H. Green, M. E. Thompson, and K. S. Suslick, *Chem. Commun.* 900 (1987).
15. K. S. Suslick and G. J. Price, *Annu. Rev. Mater. Sci.* **29,** 295 (1999).
16. W. T. Kim and C. D. Kim, *J. Appl. Phys.* **60,** 2631 (1986).
17. R. Nomura, S. Inazawa, K. Kanaya, and H. Matsuda, *Appl. Organomet. Chem.* **3,** 195 (1989).
18. N. Kamoun, S. Belgacem, M. Amlouk, R. Bennaceur, J. Bonnet, F. Touhari, M. Nouaoura, and L. Lassabatere, *J. Appl. Phys.* **89,** 2766 (2001).
19. A. A. El Shazly, D. Abd Elhady, H. S. Metwally, and M. A. M. Seyam, *J. Phys.: Condens. Mater.* **10,** 5943 (1998).
20. S. H. Choe, T. H. Bang, N. O. Kim, H. G. Kim, C. I. Lee, M. S. Jin, S. K. Oh, and W. T. Ki m, *Semicond. Sci. Technol.* **16,** 98 (2001).
21. M. Amlouk, M. A. Ben Said, N. Kamoun, S. Belgacem, N. Brunet, and D. Barjon, *Jpn. J. Appl. Phys. Part 1* **38,** 26 (1999).
22. Y. Yasaki, N. Sonoyama, and T. Sakata, *J. Electroanal. Chem.* **469,** 116 (1999).
23. W. Rehwald and G. Harbeke, *J. Phys. Chem. Solids* **26,** 1309 (1965).
24. J. M. Giles, H. Hatwell, G. Offergeld, and J. Van Cakenberghe, *J. Phys. Stat. Sol.* **2,** K73 (1962).
25. Jpn. Patent Appl., *Chem. Abbstr.* **91,** 67384a (1979).
26. Jpn. Patent Appl., *Chem. Abbstr.* **96,** 113316h (1979).
27. Jpn. Patent Appl., *Chem. Abbstr.* **95,** 107324x (1981).
28. E. Dalas and L. Kobotiatis, *J. Mater. Sci.* **28,** 6595 (1993).
29. E. Dalas, S. Sakkopoulos, E. Vitoratos, and G. Maroulis, *J. Mater. Sci.* **28,** 5456 (1993).
30. C. D. Wanger, W. M. Riggs, L. E. Davis, J. F. Moulder, and G. E. Muilenberg, "Handbook of X-ray Photoelectron Spectroscopy." Perkin-Elmer Corp., Eden Prairie, 1978.
31. I. Nakai, Y. Sugitani, K. Nagashima, and Y. Niwa, *J. Inorg. Nucl. Chem.* **40,** 789 (1978).
32. C. Roymans, *J. Inorg. Nucl. Chem.* **11,** 78 (1959).
33. J. Van Landuyt, H. Hatwell, and S. Amelinckx, *Mater. Res. Bull.* **3,** 519 (1968).
34. V. Keramidas, B. De Angelis, and W. White, *J. Solid State Chem.* **15,** 233 (1975).
35. H. Hutz and H. Haueseler, *Z. Naturf.* **26a,** 323 (1971).
36. K. Kambas, J. Spyridelis and M. Balkanski, *Phys. Stat. Sol. B* **105,** 291 (1981).
37. D. K. Nagesha, X. Liang, A. A. Mamedov, G. Gainer, M. A. Eastman, M. Giersig, J. J. Song, T. Ni, and N. A. Kotov, *J. Phys. Chem. B* **105,** 7490 (2001).
38. A. L. Efros, M. Rosen, M. Kuno, M. Nirmal, D. J. Norris, and M. Bawendi, *Phys. Rev. B* **54,** 4843 (1996).
39. M. Nirmal, D. J. Norris, M. Huno, M. G. Bawendi, A. Efros, and M. Rosen, *Phys. Rev. Lett.* **75,** 3728 (1995).
40. D. J. Norris and M. G. Bawendi, *J. Chem. Phys.* **103,** 5260 (1995).
41. N. N. Greenwood and A. Earnshaw, "Chemistry of the Elements." Pergamon Press, Oxford, 1984.
42. J. A. Dean, (Ed.), "Lange's Handbook of Chemistry." McGraw-Hill Book Company, New York, 1972.