

Synthesis of Nanocrystalline Cobalt Selenide in Nonaqueous Solvent

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Cobalt selenide nanocrystals have been synthesized by a solvothermal reaction between metallic cobalt and selenium at 140°C. The products obtained have been characterized by X-ray powder diffraction (XRD) and transmission electron microscopy (TEM). According to the XRD analysis, the as-produced cobalt selenide adopted a NiAs structure analogous to that of Ni_{0.85}As. Therefore, it was termed Co_{0.85}Se. Elemental analysis showed a cation-deficient composition of about Co_{0.844}Se. TEM observation indicated that the obtained Co_{0.85}Se nanocrystals were of foliate morphology. IR analysis suggested that the product was free from contaminants such as ethylenediamine. The influence of various solvents on this synthetic process has been discussed. Ni_{0.85}As has also been synthesized with a similar synthetic process. © 2000 Academic Press

1. INTRODUCTION

Inorganic solids are generally synthesized by repeated grinding and firing at high temperature. High reaction temperature is indispensable to overcoming the long diffusion path in solid reactions. It is difficult to control particle size or phase homogeneity at these temperatures. Recently, there has been a marked trend to lower reaction temperatures to prepare technologically important materials with tailored properties (1). Much attention has been focused on lower-temperature approaches such as the sol-gel method (2) and soft chemistry including cationic exchange, dehydration, dehydroxylation, hydrolysis, redox, intercalation, and deintercalation (3). Intermediate-temperature synthetic techniques, including flux and hydrothermal methods, have also been developed to prepare novel materials with unusual electronic, optical, and catalytic properties. The solvothermal method, one of the most promising intermediate-temperature synthetic techniques, has recently been extensively applied to the synthesis and design of materials with novel structures and properties (4).

Generally, cobalt selenide is synthesized by the common solid-state reaction (5), selenization of aqueous solutions

containing cobalt cations (6), or molecular precursors (7). Either the composition fails to be controlled or only amorphous products are obtained. The electronic structure and magnetic and optical properties of cobalt selenide have been reported (8). In this work, we apply this solvothermal method, analogous to the method we reported previously (9), to the synthesis of cobalt selenide. The elemental reaction between metallic cobalt and selenium results in the formation of monophasic cobalt selenide nanocrystals in nonaqueous solvents. The structure and composition of the product will be discussed. The influence of the solvents has been also studied.

2. EXPERIMENTAL PROCEDURES

Metallic cobalt powder (2 mmol) and equivalent metallic selenium powder (99.99%) were ground together in an agate roller. The mixed precursors were added to a Teflon-lined autoclave of capacity 40 ml, which was then filled with anhydrous ethylenediamine up to 90% of the total volume. The autoclave was maintained constantly at 140°C for 12 h and then cooled to room temperature naturally. A black product was collected, filtered, washed with absolute ethanol three times, and finally dried in a vacuum box at 60°C for 4 h. The yield of the product was about 92%, based on the molar weight of selenium.

The obtained samples were characterized by X-ray powder diffraction (XRD). The XRD analysis was carried out with a Japan Rigaku D/max-γ rotation anode X-ray diffractometer, using Ni-filtered CuKα radiation ($\lambda = 1.5418 \text{ \AA}$). A scanning rate of 0.05°/s was used to record the patterns in the 2θ range 20°–80°. Transmission electron microscopy (TEM) was used to determine the morphology and particle size of products. The images were taken with a Hitachi H-800 transmission electron microscope, using an accelerating voltage of 200 kV. The infrared (IR) spectra were recorded on a Magana IR-750 FT spectrometer at room temperature using KBr pressed pellets as self-supporting wafers. Elemental analysis of the sample was carried out on a Perkin-Elmer/6500 ICP-AES (inductive coupling plasma-atomic emission spectroscopy) instrument. The obtained

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samples were also characterized by X-ray photoelectron spectra (XPS). XPS measurements were performed on an ESCLAB MKII with $MgK\alpha$ ($h\nu = 1253.6$ eV) as the exciting source. The binding energy obtained in the XPS analysis was corrected for specimen charging by referencing the C1s to 284.5 eV.

3. RESULTS AND DISCUSSION

A typical XRD pattern of the as-obtained sample is shown in Fig. 1. The XRD Bragg reflection data are listed in Table 1. All the peaks could be indexed as for a hexagonal structure. No other impurities, such as metallic cobalt or selenium, were detected in the XRD pattern. After refinement, the cell constants are given as $a = 3.615(0)$ Å, $c = 5.283(2)$ Å, $c/a = 1.460$ (space group, $P6_3/mmc$ (194)). This structure is analogous to that of hexagonal $Ni_{0.85}Se$ with NiAs structure (JCPDS 18-888). Therefore, the as-formed product is termed $Co_{0.85}Se$. The broadening of peaks in the XRD pattern indicates the nanocrystalline nature of the sample. The crystallite size is about 19 nm, as estimated according to (101) reflection by the Scherrer equation with a shape factor of 0.9 applied (10).

The morphology and particle size of the as-obtained samples were characterized with TEM. The image shows a larger particle size than that estimated with the Scherrer equation. If discriminated carefully, these crystallites have a foliate shape. This morphology is very common in crystallites with NiAs structure (11). On the other hand, it could explain the difference between the Scherrer estimation and TEM observation for crystal size because of the lack of spherical symmetry. These foliate crystallites are also very inclined to stack on each other.

The obtained cobalt selenide has a NiAs structure. Although the cobalt and selenium have the same coordination

TABLE 1
X-Ray Diffraction Data of the As-Obtained $Co_{0.85}Se$
($\lambda = 1.54178$ Å)

$d/\text{Å}$	I/I_0	hkl
2.6912	100	101
2.0241	74	102
1.8037	59.7	110
1.5316	23.4	103
1.4985	23.4	112
1.3443	22.1	202
1.3213	10.2	004

number, they do not have the same coordination environment in this NiAs structure. The cobalt and selenium are both six-coordinate. The selenium atoms have a hexagonal close-packed arrangement, and the cobalt atoms occupy the octahedral interstitial sites (O sites) with the tetrahedral sites (T_+ and T_+ sites) empty. The selenium atoms have six cobalt neighbors arranged as a trigonal prism. It is a characteristic feature for this structure to show a variable composition. The product obtained with this solvothermal method is about $Co_{0.844}Se$, as determined by atomic emission spectroscopy (AES) measurements. This result was also confirmed by the XPS analysis. These experimental results showed that the obtained cobalt selenide is a little cation-deficient.

IR analysis of the as-formed products was carried out to investigate attachment of ethylenediamine to cobalt selenide, as shown in Fig. 2. The absorption peaks at about 3431 and 1633 cm^{-1} , which correspond to the O–H stretching vibration [$\nu(O-H)$] and H–O–H bending vibration [$\delta(OH_2)$], respectively, could be due to absorption by H_2O absorbed on these samples. In fact, absorption by water is very common for powder samples with high surface area which have been exposed to atmosphere. These results

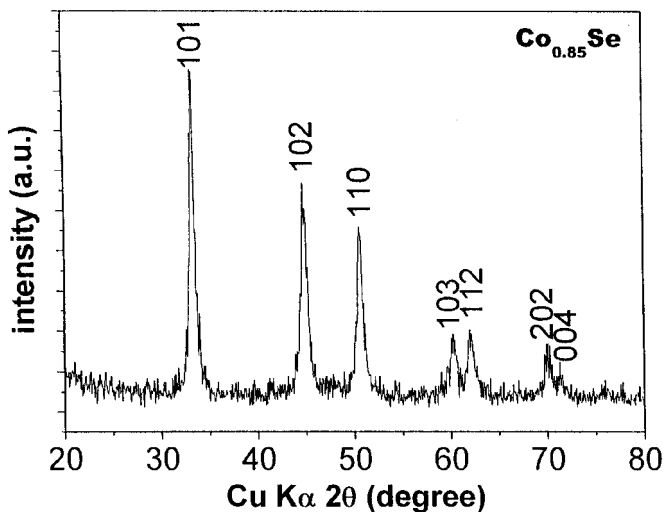


FIG. 1. XRD pattern of the obtained $Co_{0.85}Se$.

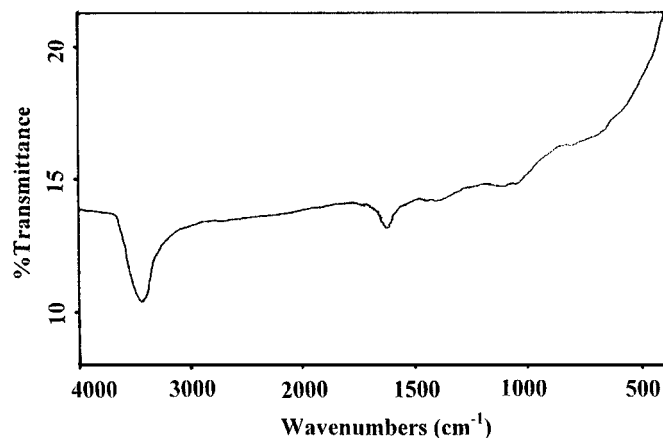


FIG. 2. IR spectrum of the obtained sample.

suggest that the as-obtained products are free from ethylenediamine.

The synthetic procedure has also been carried out at temperatures ranging from 120 to 180°C. The reaction could proceed rapidly with the elevation of the reaction temperature, but the experiments showed that the reaction temperature had no drastic influence on the composition of the obtained products.

To investigate their influence on the reaction, we replaced ethylenediamine with other solvents such as benzene, triethylamine, and pyridine, keeping other reaction factors constant. No obvious reaction was observed in the case of benzene, for a large amount of cobalt remained in the product. It was necessary to prolong the reaction time with triethylamine or pyridine substituting for ethylenediamine. It has been reported that the low-temperature elemental reaction of metals with chalcogens could be promoted in coordinating alkylamine solvents, as these solvents could activate the metal or chalcogen surface, effectively allowing good contact between the elements (12–14). Accordingly, it was reasonable that no obvious reaction occurred in benzene. Ethylenediamine could promote the reaction faster than triethylamine and pyridine since it is a bidentate chelating agent and has stronger coordinating ability. Consequently, ethylenediamine was selected as the synthetic medium in this solvothermal process.

4. CONCLUSIONS

A solvothermal process has been used to prepare nanocrystalline cobalt selenide by elemental reaction between cobalt and selenium at 140°C. The XRD characterization shows that the obtained product has a hexagonal NiAs structure, analogous to that of Ni_{0.85}As. Hereby, the obtained cobalt selenide was termed Co_{0.85}Se. IR analysis indicated that the product was not contaminated in this synthetic process. The results of elemental analysis show that the obtained product has a composition of Co_{0.844}Se, which deviates from the stoichiometric composition of NiAs structure. TEM observations show that the obtained cobalt

selenide nanocrystals have a foliated morphology. This morphology is generally observed in compounds with NiAs structure. In this synthetic process, various solvents have a considerable influence on the formation of cobalt selenide. The coordinating alkylamine is favorable for the reaction. Chelating ethylenediamine is especially favorable. By a similar synthetic approach, nickel selenide has also been produced with a structure as reported in the literature (Ni_{0.85}Se, JCPDS 18-888).

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