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Mechanochemical Route for the Preparation of Nanosized Aluminum and Gallium Sulfide and Selenide

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Aluminum and gallium chalcogenides are promising, yet relatively underexplored photoelectric and semiconducting materials. Many studies confirmed the applicability of gallium sulfides and selenides in photovoltaics and as electrode materials. In present work, a simple and convenient mechanochemical method has been developed for preparation of aluminum and gallium sulfide and selenide from elemental powders. The products have been characterized by X-ray powder diffraction (XRPD) and transmission electron microscopy (TEM), including energy-dispersive X-ray spectroscopy (EDX). The following products have been obtained: Al₂S₃, Al₂Se₃, Ga₂S₃, and Ga₂Se₃, with crystallite sizes in the range 8–12 nm.

Keywords Aluminum; Chalcogenides; Diffraction; Gallium; Mechanochemistry; Microscopy; Nanocrystalline; Selenides; Semiconductors; Sulfides.

INTRODUCTION

Nanosized metal chalcogenides have been extensively studied over the past decade due to their promising semiconducting and optoelectronic properties. While most of the research has focused on 11–16 and 12–16 compounds, most notably copper and cadmium chalcogenides, compounds of the 13–16 group have also been shown to be promising materials for application such as semiconductors and infrared optical devices [1]. The traditional method for the preparation of these compounds in a bulk form is joint melting of elemental precursors at elevated temperatures for several hours [2]. However, like most of high-temperature solid-state reactions, the process is difficult to control, unsuitable for the preparation of nanosized products, while long reaction times combined with high temperatures may often cause contamination of products with impurities from reactor walls [1]. One alternative approach is the reaction between metal oxides or hydroxides and hydrogen sulfide/hydrogen selenide, but the drawback of this method is the use of highly toxic gaseous precursors.

Aluminum sulfide, Al₂S₃, is a colorless solid with a variety of crystalline structures [3]. It is sensitive to moisture and hydrolyzes readily in contact with water and slowly in moist air, generating gaseous H₂S. Nevertheless, it has been successfully tested as solid lithium ionic conductor in the Li₂S–Al₂S₃–GeS–P₂S₅ system,

showing high ionic conductivities [4]. Alternative approaches for the synthesis of aluminum sulfide involve the low-temperature synthesis in hydrocarbon solution [3], preparation by explosive loading reaction [5], and synthesis from aluminum(III) iodide with elemental sulfur in a quartz reactor [1]. Aluminum selenide, Al₂Se₃, is the least studied of the group 13 chalcogenides [6]. The bandgap of Al₂Se₃ at about 3.1 eV makes it a promising material in photoemission/photocollector systems. Due to close lattice matching to silicon, Al₂Se₃ has also attracted attention for the preparation of heterostructures combining 13–16 semiconductors with Si [7]. In addition, Al₂Se₃ is an interesting precursor to the preparation of the new quaternary semiconductor Cu(InAl)Se₂ with improved electrical and transport properties [8].

Gallium sulfides and -selenides are important intrinsic semiconducting materials due to their defect structure with various existing phases. Ga₂S₃ has been reported to be a wide-band-gap semiconductor with band-gap values above 3 eV, while Ga₂Se₃ exhibits a direct band gap around 2–2.5 eV [9, 10]. Chalcogenide glasses based on Ga₂S₃ have recently attracted much interest due to their applications in optoelectronics and photovoltaics [11, 12], while interesting optical [13] and photoluminescent [14] properties have been reported for nanocrystalline Ga₂S₃. Many preparation methods for the synthesis of Ga₂S₃ have been reported, including chemical vapor transport [9], boron-sulfur-metallic oxide reaction [13], reaction of gallium(III) iodide with sulfur in a quartz glass reactor [15], and room temperature reaction of gallium(III) chloride with sodium thiosulfate in water [16]. Gallium selenide, Ga₂Se₃, has been investigated as a negative electrode material for lithium-ion batteries [17] and has recently attracted attention due to its role as a precursor to the preparation of ternary CuGaSe₂

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[18] and even more important copper-indium-gallium-selenide (CIGS) quaternary semiconductors, which are among the most promising materials for the fabrication of thin film solar cells [19]. Besides the traditional methods mentioned earlier, syntheses of Ga_2Se_3 by solvothermal method [20] and from single-source precursors using selenoether complexes [21] were reported recently.

Mechanochemistry, often also referred to as mechanical alloying, is a solid-state powder processing method involving repeated cold welding, fracturing, and rewelding of powder particles using a high-energy ball mill. Originally developed in the 1970s for the fabrication of superalloys for the aerospace industry, this method has been recently used for the production of advanced alloys like NiTi(Al) , Fe-Cr-Al , and TiC [22–24] and ceramic materials such as $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ with giant dielectric properties [25]. The first mechanochemical syntheses of transition metal chalcogenides from elements were reported in the 1990s, focusing mainly on copper sulfides, selenides, and tellurides [26, 27]. In 2003, Tan et al. reported on the first mechanochemical synthesis of a cadmium chalcogenide, CdTe [28], while in 2006, Godočikova et al. published a paper reporting the mechanochemical preparation of copper sulfide by a metathesis reaction from $\text{Cu}(\text{CH}_3\text{COO})_2$ and Na_2S [29]. More recently, our group reported on the mechanochemical preparation of the whole family of nanosized copper and cadmium chalcogenides (CuS , CuSe_2 , Cu_7Te_5 , CdS , CdSe , and CdTe) from elemental precursors [30]. Campos et al. reported the synthesis of GaSe by mechanical alloying a $\text{Ga:Se} = 50:50$ mixture by high-energy ball milling [31], applying milling times from 30 min to >10 h. Ball milling technology has also been applied for the fabrication of copper-indium-gallium-diselenide (CIGS) layers from the binary nanoparticles of In_2Se_3 , Ga_2Se_3 , and CuSe [19] and for the preparation of amorphous solid electrolytes in the system $\text{Li}_2\text{S-Al}_2\text{S}_3\text{-SiS}_2$ [32], while to the best of our knowledge, the mechanochemical synthesis of Al_2E_3 and Ga_2E_3 ($\text{E} = \text{S, Se}$) has not been reported as yet.

MATERIALS AND METHODS

Elemental aluminum (99.9%, Kemika Zagreb), gallium (99.99%, Aldrich), sulfur (99+%, Merck), and selenium powder (99.5%, Aldrich) were used as purchased without further purification. The mixtures were milled in an SPEX 8000 M ball mill using stainless steel vial and milling balls. The ball mass was approximately 20 g, and the mass of the starting mixture was 1 g during all experiments to obtain the ball to powder mass ratio of 20:1. In a typical procedure, 0.360 g ($=13.33 \cdot 10^{-3} \text{ mol}$) of aluminum and 0.640 g ($=20.0 \cdot 10^{-3} \text{ mol}$) of sulfur were milled together using milling times from 1 h to 8 h. The other chalcogenides were synthesized following the same procedure, always using molar ratios $\text{M:E} = 2:3$ ($\text{M} = \text{Al, Ga}$; $\text{E} = \text{S, Se}$) and ball to powder mass ratio 20:1. Due to the moisture sensitivity of Al_2S_3 and Al_2Se_3 , we performed some of the milling experiments by filling the vial under nitrogen inside a

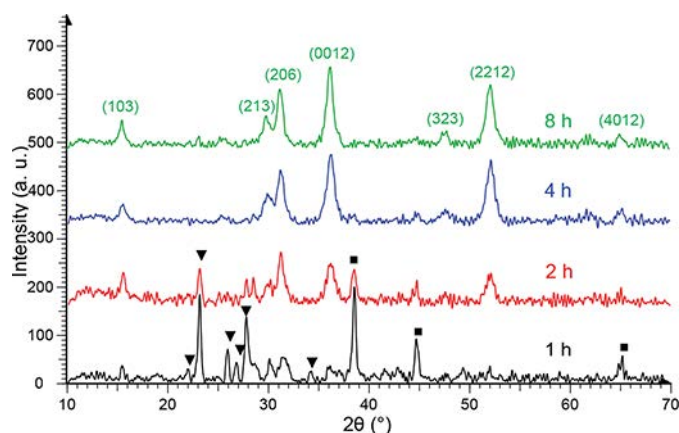


FIGURE 1.—X-ray powder patterns of Al_2S_3 nanoparticles prepared by mechanical milling after 1 h, 2 h, 4 h and 8 h milling time. ■ = Al, ▼ = S.

glove box (GS Campus T2, <10 ppm H_2O) and closing it airtight before transferring into the mill.

All as-obtained products were characterized by X-ray powder diffraction (XRPD) using an AXS-Bruker/Siemens model D5005 X-ray powder diffractometer. The samples were attached to an Si-single crystal holder and measured in the range $10^\circ \leq 2\theta \leq 70^\circ$ using graphite monochromated $\text{CuK}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) with a step size of 0.0358° and time/step = 1 s. The crystallite size was estimated from the average of three strongest diffraction peaks, using the Scherrer formula, after subtracting the effects of instrumental broadening. A JEOL 2100 TEM microscope operating at 200 kV was used for transmission electron microscopy (TEM) measurements. The nanoparticles were dispersed in ethanol using an ultrasonic bath and placed on a carbon-coated Cu grid.

RESULTS AND DISCUSSION

Figure 1 presents the XRPD patterns of the products, obtained by milling of aluminum powder with sulfur in molar ratio 2:3 for 1–8 h. After 1 h milling time, the

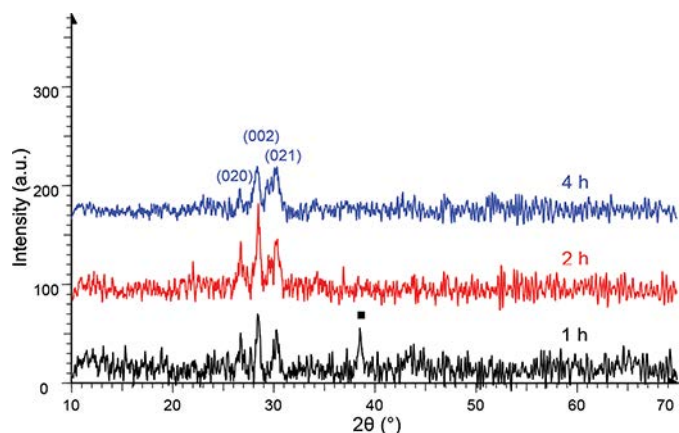


FIGURE 2.—X-ray powder patterns of Al_2S_3 nanoparticles prepared by mechanical milling after 1 h, 2 h, and 4 h milling time. ■ = Al.

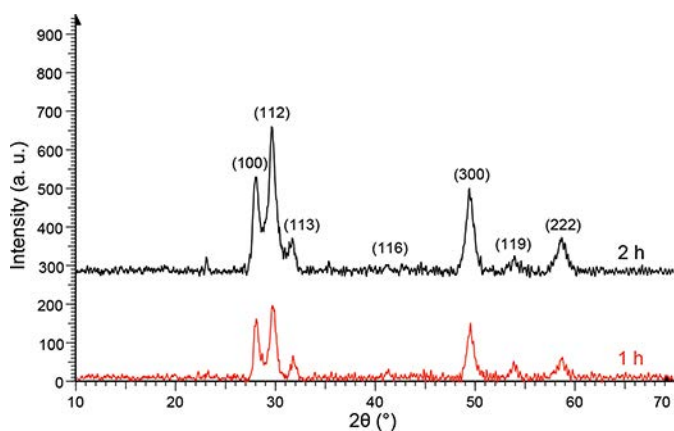


FIGURE 3.—X-ray powder patterns of Ga_2S_3 nanoparticles synthesized by mechanical milling after 1 h and 2 h milling time.

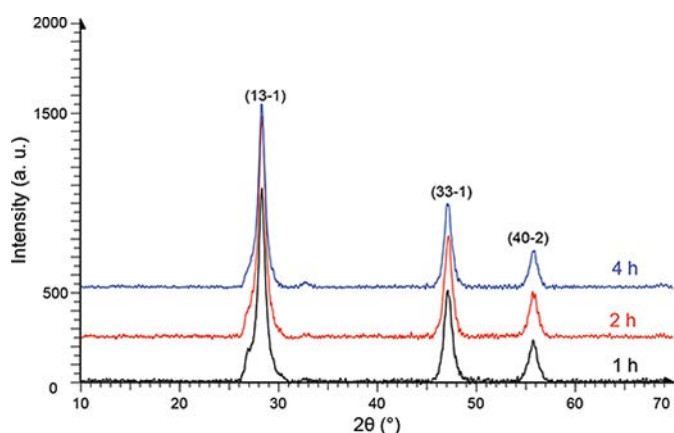


FIGURE 4.—X-ray powder patterns of Ga_2S_3 nanoparticles synthesized by mechanical milling after 1 h, 2 h and 4 h milling time.

powder mixture is composed mainly of both precursors Al and S, although some small peaks of Al_2S_3 are already visible. After 2 h milling time, peaks belonging to Al_2S_3 are clearly visible next to those of both precursors. After 4 h and 8 h milling time, only peaks of tetragonal Al_2S_3 (JCPDS No. 00-024-0014) were visible.

XRPD patterns of powders, prepared by ball milling of aluminum powder with selenium (molar ratio 2:3), are shown in Fig. 2. The as-obtained products are low crystalline, but nevertheless, the main peaks of monoclinic Al_2Se_3 (JCPDS No. 00-019-0048) are observable in all three patterns. The peak of elemental Al at 38.6° , which can be observed after 1 h, indicating that the reaction is not complete, is hardly visible after 2 h and has completely disappeared after 4 h milling time, indicating that the reaction is completed. By using longer milling times of 6 h and 8 h (patterns not shown), the peaks belonging to Al_2Se_3 become less pronounced, and after 12 h no peaks are observable in the as-milled powder, which could be explained with the formation of an amorphous product by prolonged mechanical alloying.

XRPD patterns of powders, which were prepared by ball milling of gallium with sulfur and selenium using different milling times, are presented in Figs. 3 and 4, respectively. Hexagonal $\beta\text{-Ga}_2\text{S}_3$ (JCPDS No. 00-015-0104) and monoclinic Ga_2Se_3 (JCPDS No. 00-044-1012) with no detectable peaks of precursors or impurities like oxides were prepared after 1 h milling time and the composition and crystallite size of the products remained unchanged by prolonging the milling times. The XRPD patterns of the products are identical, regardless of whether the vial was filled and closed under nitrogen inside the glove box or in open air. It should be pointed out that to the best of our knowledge, this is the first case where the β -form of Ga_2S_3 was formed at room temperature. While Ga_2S_3 is known to exist in several polymorphic modifications, the most stable form at room temperature is the α -form [33]. However, the polymorphic form produced is strongly dependent on the preparation method. The unique reaction conditions inside the high-energy ball mill, involving strong mechanical forces and local heating during the ball collisions, seem to enable the synthesis of polymorphs, which could be prepared only at elevated temperatures when using traditional methods.

TEM images of Ga_2S_3 nanoparticles, obtained by mechanical milling after 2 h milling time, are displayed in Fig. 5(a) and (b). The primary spherical nanoparticles with diameters in the range of 20–40 nm are

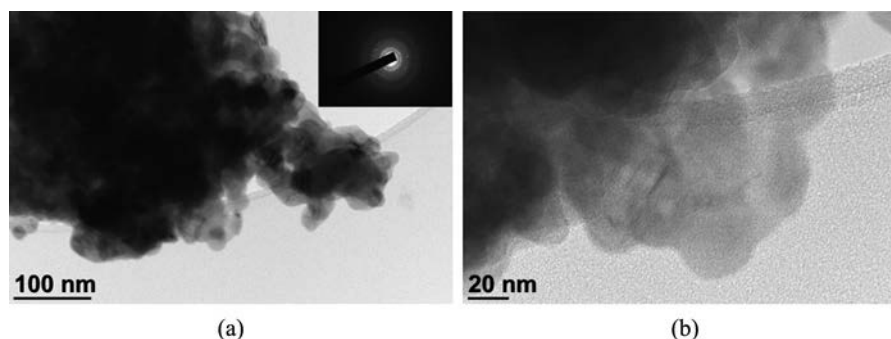


FIGURE 5.—TEM images of Ga_2S_3 nanoparticles synthesized by mechanical milling after 2 h milling time at different magnifications.

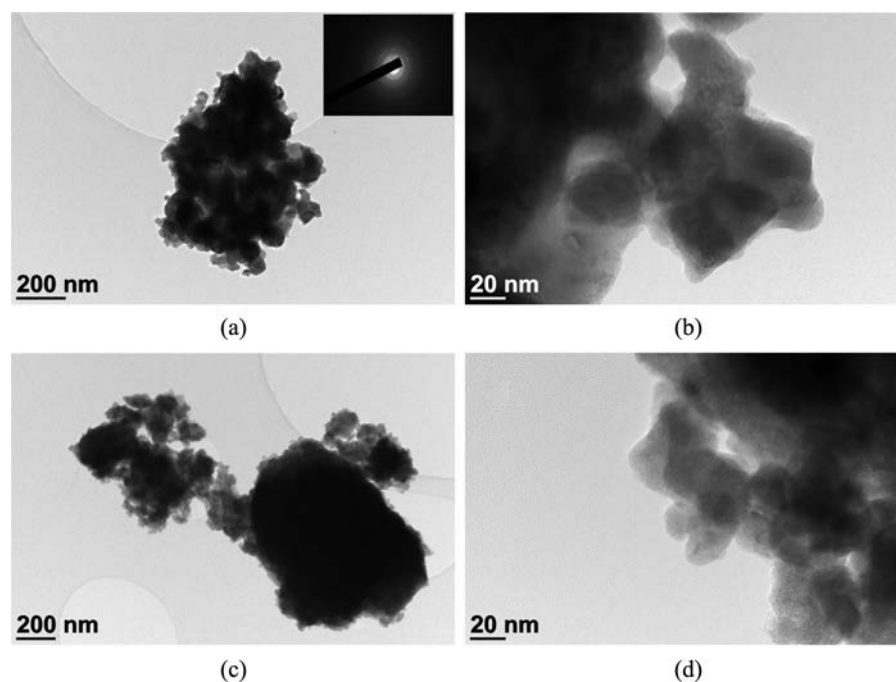


FIGURE 6.—TEM images of Ga_2Se_3 nanoparticles synthesized by mechanical milling after 1 h (a) and (b) and 4 h (c) and (d) milling time at different magnifications.

embedded within an amorphous matrix and strongly agglomerated into clusters. The EDX analysis revealed the Ga:S ratio approaching 2:3, with no evidence of gallium oxides in the product. The nanoparticles of Ga_2Se_3 obtained after 1 h milling time (Fig. 6(a) and (b)) are also strongly agglomerated, making a reliable particle size distribution analysis difficult. As could be expected, products obtained by longer milling times (Fig. 6(c) and (d)) are composed of smaller individual nanoparticles, roughly 10–15 nm in diameter, which are again agglomerated into clusters. The results are in fair agreement with the crystallite size estimated by Scherrer equation, taking into account the strong agglomeration of the primary nanoparticles. A summary of reaction conditions and as-prepared products is provided in Table 1.

CONCLUSIONS

Aluminum, gallium sulfide, and selenide have been prepared using mechanochemical approach from elemental precursors. Nanoparticles with crystallite sizes between 8 and 12 nm, agglomerated into clusters, have been obtained. The method is simple, compared to most reported preparation method, and environment-friendly due to the absence of elevated temperatures, organic solvents and toxic precursors. Further research will be focused on using different molar ratios of precursors during the synthesis, which is expected to enable the preparation of chalcogenides with different stoichiometries, as well as on studying the application of surfactants during the synthesis, which may prevent the agglomeration of nanoparticles during the high-energy milling process.

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TABLE 1.—Precursors, reaction conditions, and products of the mechanochemical syntheses.

Metal	Chalcogen	Molar ratio	Milling time	Atmosphere	Product	Crystallite size
Al	S	2:3	4 h	N_2	Al_2S_3	11 nm
			8 h			10 nm
Al	Se	2:3	4 h	N_2	Al_2Se_3	9 nm
Ga	S	2:3	1 h	air	Ga_2S_3	12 nm
			2 h			10 nm
Ga	Se	2:3	1 h	air	Ga_2Se_3	11 nm
			2 h			8 nm
			4 h			9 nm

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