

Microwave-Assisted Preparation, Morphological, and Photoacoustic Studies of the Na_4SnSe_4 , $\text{K}_4\text{Sn}_2\text{Se}_6$, and $\text{K}_4\text{Sn}_3\text{Se}_8$, Zintl Molecular Sn–Se Oligomers

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The Zintl compounds Na_4SnSe_4 , $\text{K}_4\text{Sn}_2\text{Se}_6$, and $\text{K}_4\text{Sn}_3\text{Se}_8$ were prepared for the first time using the microwave-assisted solid-state reaction method. The heteroanions of these phases represent oligomeric group of (zero-dimensional) molecular anions: $[\text{SnSe}_4]^{4-}$, $[\text{Sn}_2\text{Se}_6]^{4-}$, $[\text{Sn}_3\text{Se}_8]^{4-}$. The compounds were characterized using Powder XRD, SEM-EDS, and their electronic properties were studied using photoacoustic spectroscopy. The microwave method was found to be simple, fast and efficient for the preparation of these Zintl compounds. © 2002

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INTRODUCTION

In recent years, Zintl compounds have attracted considerable interest due to their intriguing structural diversity and rich chemistry (1). Zintl compounds are a group of solids in which a strong electron donor such as an alkali or alkaline earth metal is bonded with main group elements or even transition metals which serve as acceptors. Structurally, the main group elements form zero- to three-dimensional nets using covalent bonds. The alkali metals donate their electrons to these nets, thus forming cations, which are electrostatically attracted to these negatively charged nets. Thus, the bonding mode of the Zintl compounds is both ionic and covalent in character (2). It is anticipated that many of these compounds may demonstrate semiconducting and thermoelectric behavior (3–5).

The pseudo-zero-dimensional Zintl compounds are of special interest because: (a) they represent basic building blocks for the formation of the higher dimensional

compounds; and (b) they may serve as precursors for the “soft chemistry” synthesis of the intermetallic compounds (6–13). Substitution of ligands such as P^{3-} , or Se^{2-} for O^{2-} in the silicate or other anions results in units like $[\text{SiP}_4]^{8-}$ or $[\text{SiSe}_4]^{4-}$, where the negative charge is balanced by the alkali metal cations, for example K^+ or Ba^{2+} . This results in Zintl compounds with isolated tetragonal or trigonal heteroanions (14). Few compounds with this structure, such as Na_8SnSb_4 , K_8SnAs_4 , and K_3GaTe_3 (15–17), are known. The condensation of these heteroanions to form dimers or even trimers has been reported. This condensation is conducted via the common edges, with preservation of the pseudo-zero-dimensional order of the overall structure. Examples of such structures are $[\text{Ge}_2\text{S}_6]^{4-}$, $[\text{Ga}_2\text{Sb}_6]^{12-}$, and a few others (18–20). A tetramer $[\text{Sn}_4\text{Se}_{10}]^{4-}$ was synthesized previously; however, it is not a pseudo-zero-dimensional solid (21–22).

At least two synthetic methods have been used for the preparation of Zintl compounds: (a) high-temperature reaction of the elements (2); and (b) the flux method, where salts with a relatively low melting point are both the precursor and solvent for the preparation of the more complex compounds (23). Both methods have disadvantages. The high-temperature reaction method requires prolonged heating (many hours or days), and in a few cases special container materials are needed to protect ampoules from the high reactivity of the reactants. The flux method also requires prolonged heating. Another drawback of the flux method is the need to use liquid ammonia for the preparation of the precursors (4). These drawbacks motivated the development of a new synthetic method, which overcomes these problems and facilitates product

formation. The microwave-assisted reaction presented here does not suffer from the disadvantages of the other synthetic routes.

Microwave-assisted chemical reactions have only recently been developed, but they have already been shown to be superior to other synthetic techniques in the fields of organic and analytical chemistry (24–32). Their extension to inorganic chemistry was much slower, but there are already a few examples of the application of microwave heating to inorganic synthesis (33–40). We recently developed a microwave-assisted polyol reduction method in solution for the preparation of the binary and ternary nanosized chalcogenides (41, 42). The current work is a continuation of this effort towards the application of microwave heating to solid state chemistry.

This report describes the synthesis and characterization of an attractive and rich group of Zintl compounds, based on alkali–Sn–Se ternary compounds. This study was motivated by the recent demonstration (9) that $[\text{SnSe}_4]^{4-}$ could be used as efficient precursor for the synthesis of mesoporous semiconductor compounds. They analyzed only the mesoporous products, which contained surfactant in addition to monomeric $[\text{SnSe}_4]^{4-}$. The anion was not examined separately by these authors. The Sn–Se binary unit is of interest because it contains three oligomeric units: monomer— $[\text{SnSe}_4]^{4-}$, dimer— $[\text{Sn}_2\text{Se}_6]^{4-}$, and trimer— $[\text{Sn}_3\text{Se}_8]^{4-}$. This oligomeric group is the subject of this paper. In particular, the electronic properties of this group were studied using photoacoustic spectroscopy (PAS). This is a very efficient technique for the examination of semiconductors, especially those which are highly moisture and air sensitive, such as the current Zintl compounds (43).

MATERIALS AND METHODS

Reagents

Chemicals were used as obtained: (1) tin powder, 99.98% purity, –100 mesh, Aldrich Co.; (2) selenium powder, 99.5% purity, and sodium and potassium metal, both 99% purity, Aldrich Co. Because of the high sensitivity of the alkali metals and resulting products to moisture and oxygen, all manipulations were conducted in an Ar-filled glove-box, with less than 1 ppm of O_2 and H_2O .

Synthesis

Control reactions were carried out by the classical high temperature method.

High-temperature method. Stoichiometric amounts of thoroughly mixed Na or K, Sn, and Se were heated in an evacuated quartz tube at 750°C for 24 h. The heating rate was $30^\circ\text{C}/\text{h}$ and cooling was natural (total reaction time:

50 h). For example, for the synthesis of Na_4SnSe_4 in a quartz ampoule (14 mm o.d. and 11 mm i.d.), the following quantities were used: Na—0.24 g, Sn—0.3 g, and Se—0.8 g. Some reaction with the quartz container was observed.

Microwave synthesis. Identical quantities of the elements were sealed in an evacuated quartz ampoule. The ampoule was placed in a modified microwave oven, which is described below. All microwave reactions took 2 min at 70% power. Only minor reaction with the quartz container was detected. All of the reactions were reproducible.

Equipment

The microwave oven was a modified Kenwood 900 W. At 70% power the oven works in a cycling mode: 15 s on, 5 s off. The high-temperature reaction was carried out in a horizontal-tube oven with an ampoule rotation attachment built by Carbolite. The X-ray diffraction patterns of the products were recorded with a Bruker AXS D8 Advance powder X-ray diffractometer (using $\text{CuK}\alpha$ $\lambda=0.15418$ nm radiation) operating at 40 kV/40 mA, with a graphite reflected-beam monochromator and variable divergence slits. During measurements, compounds were sealed in a home-built, air-free PXRD cell. EDS measurements were made using an X-ray microanalyzer (Oxford Scientific) built on a JSM-840 scanning electron microscope (JEOL). ZAF correction was applied for precise quantitative measurements. For SEM measurements samples were carbon coated. Elemental analysis (carbon and oxygen) was done with an EA 1110 CHNS-O instrument. Photoacoustic measurements were obtained with a homemade instrument which has been described elsewhere (44). The photoacoustic method consists of illuminating the sample with chopped monochromatic light in an airtight cell connected to a microphone. The light is absorbed and converted to heat. The chopped heat then flows to the surface of the sample where it produces an acoustic wave. The wave is detected with a lock-in voltmeter. The signal, which is acquired as a function of wavelength, is normalized against the absorption of carbon black powder, which is a 100% absorber. The wavelength coverage of the instrument is 300 to 1600 nm. The spectrum is independent of the physical condition of the sample, unlike reflectance spectroscopy, where the nature of the surface can have a marked effect on the spectrum. It is particularly useful for particulate matter, whose turbidity and scattering make conventional absorption spectroscopy difficult as best. In addition, PAS is completely nondestructive. Photoacoustic spectra of such difficult specimens often show features that are much better resolved than with conventional absorption spectroscopy (45).



FIG. 1. Photographs of the reaction for the preparation of one of Zintl compounds ($\text{K}_4\text{Sn}_2\text{Se}_6$) taken during microwave reaction. Insert: higher magnification image.

RESULTS AND DISCUSSIONS

Microwave Reactions

Figure 1 shows a snapshot of the reaction occurring in the microwave oven during the synthesis of $\text{K}_4\text{Sn}_2\text{Se}_6$.

After only 3–4 s, an intense yellow glow appears inside the ampoule and is observed during the entire reaction period (2 min) while the oven is in the “on” part of the cycle. When the oven is in the “off” part of its cycle, the glow disappears. The temperature is estimated to be around 900°C , based on the color of the glow. Reactions conducted at 100% microwave power also result in products, but sometimes cracks are observed on the ampoule walls. For this reason, 70% power was used in all reactions. This power level was found to be optimal for avoiding ampoule defects, while maintaining reproducibility. On the other hand, reactions conducted at lower power, for example 40%, resulted in mixed phases of the products, with the main impurity being tin selenide. Under these conditions, the glow is less intense.

The color of the products (at 70% power) is yellow for Na_4SnSe_4 and $\text{K}_4\text{Sn}_2\text{Se}_6$ and yellow-brown for $\text{K}_4\text{Sn}_3\text{Se}_8$. These colors are similar to those of the products obtained using regular heating.

PXRD Measurements

The results of the powder XRD measurements are shown in Figs. 2a–2c. Pure phases were obtained for all the

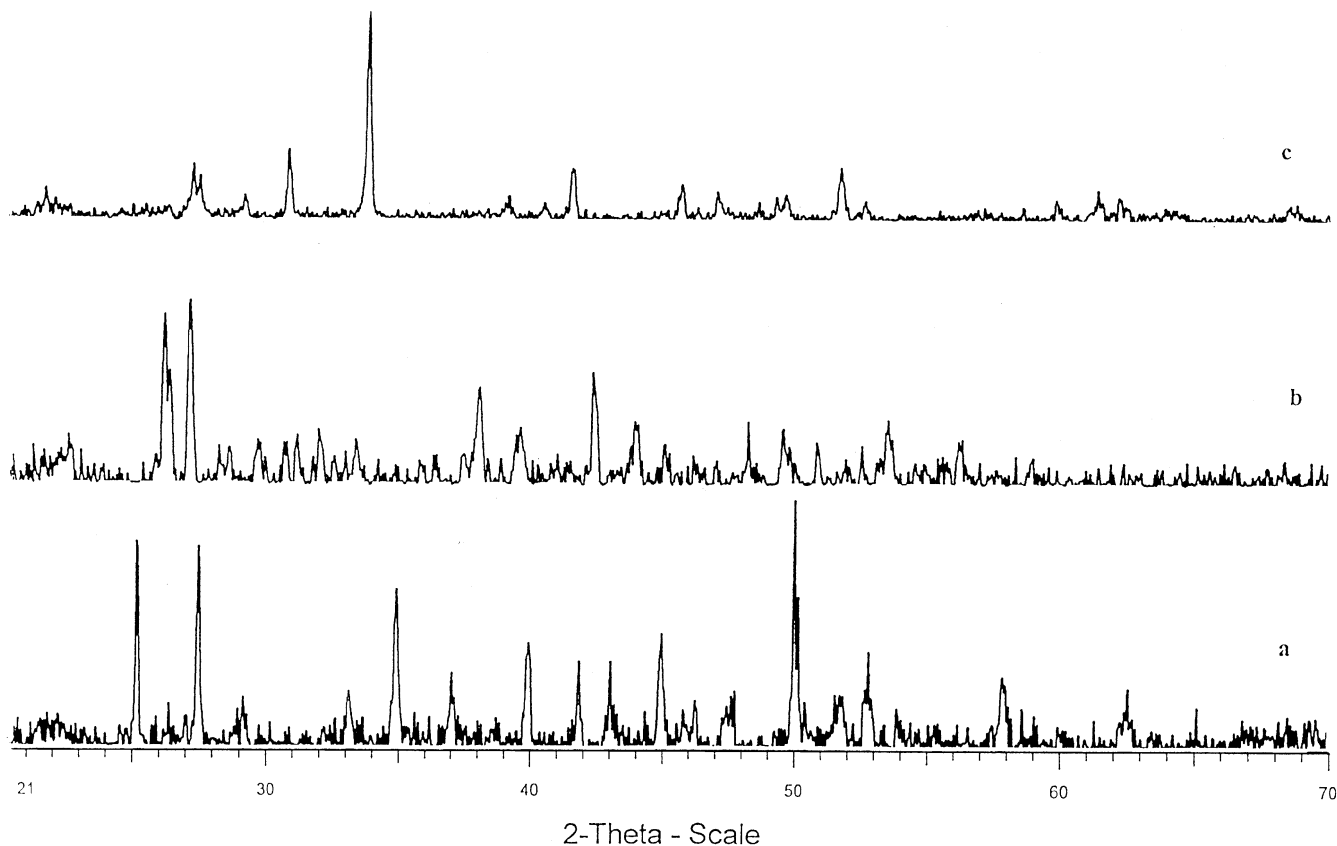


FIG. 2. Powder XRD patterns of the Zintl compounds prepared using microwave irradiation: (a) Na_4SnSe_4 ; (b) $\text{K}_4\text{Sn}_2\text{Se}_6$; and (c) $\text{K}_4\text{Sn}_3\text{Se}_8$.

products. The diffraction patterns are in agreement with the data available in the PDF database: Na_4SnSe_4 PDF# 81-1017 (tetragonal unit cell, calculated lattice parameters are $a=8.169$, $b=8.169$, $c=7.265$ —see Fig. 2a), $\text{K}_4\text{Sn}_2\text{Se}_6$ PDF 84-2342 (triclinic unit cell; $a=8.625$, $b=7.609$, $c=6.951$, $\alpha=67.6$, $\beta=74.5$, $\gamma=75.4$ —see Fig. 2b) and for the $\text{K}_4\text{Sn}_3\text{Se}_8$ PDF 78-1228 (orthorhombic unit cell; $a=27.771$, $b=8.192$, $c=8.185$ —see Fig. 2c). The XRD patterns of the compounds prepared using conventional heating are similar to the patterns of the microwave-

synthesized materials. One of the compounds, $\text{K}_4\text{Sn}_3\text{Se}_8$, was prepared for the first time using the high temperature method. Previously, it was prepared using the methanolothermal method with a synthesis time of 10 days (46).

The composition of the prepared compounds was examined using EDS spectroscopy. The experimental values are similar to the theoretical values, and no deficit in the alkali metal was observed. This proves that the alkali metal did not react with the ampoule walls. In other reports of Zintl compound synthesis, an excess of alkali metals was

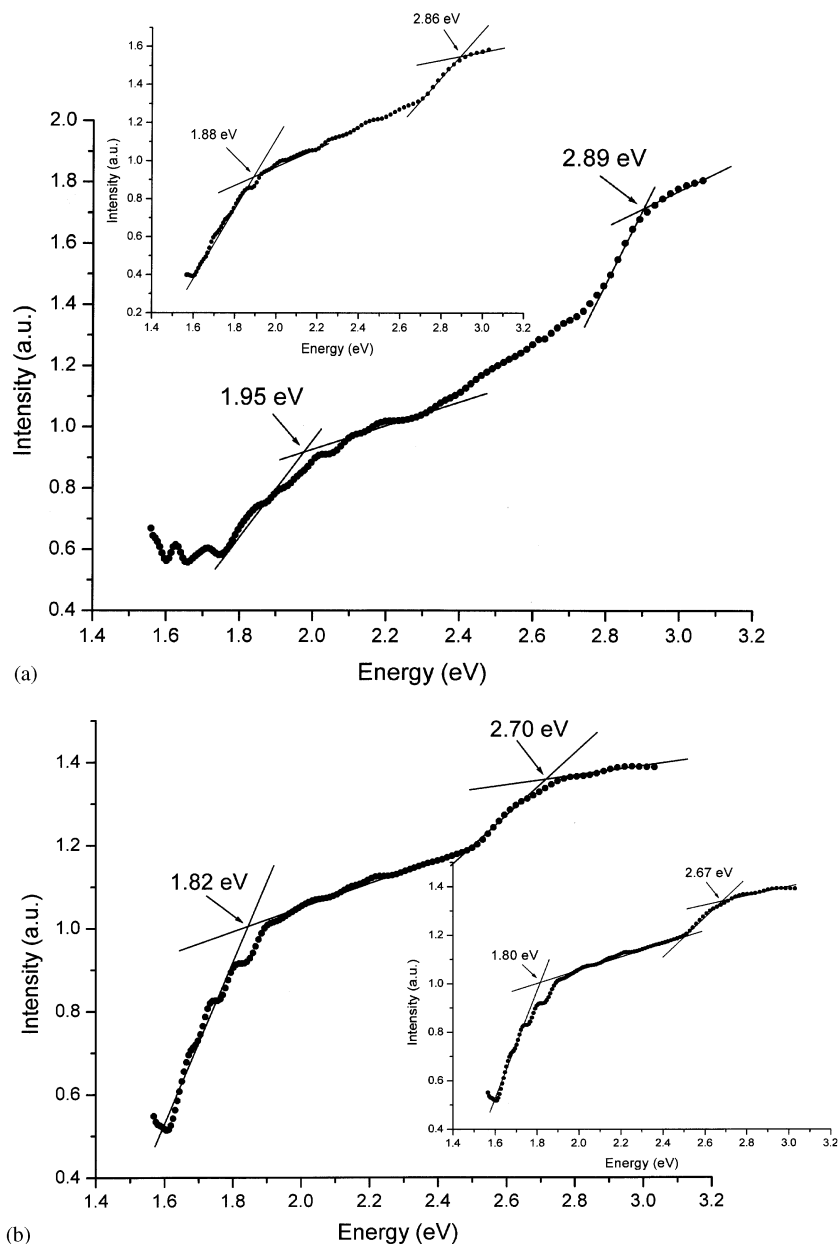


FIG. 3. Photoacoustic spectra of the Zintl compounds prepared using microwave irradiation: (a) Na_4SnSe_4 (insert—PAS of the same compound prepared by regular heating); (b) $\text{K}_4\text{Sn}_2\text{Se}_6$ (insert—PAS of the same compound prepared by regular heating); and (c) $\text{K}_4\text{Sn}_3\text{Se}_8$ (insert—PAS of the same compound prepared by regular heating).

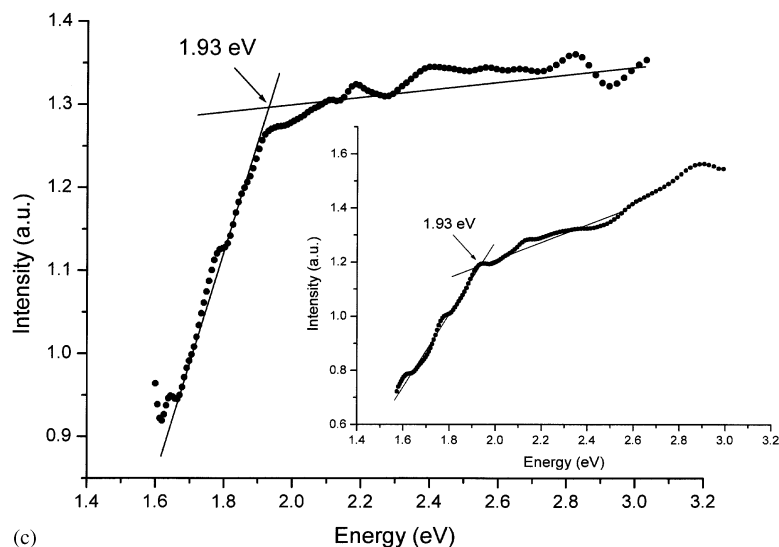


FIG. 3—Continued.

used to compensate for the loss of metal due to reaction with the walls. Silicon and oxygen impurities were never observed in microwave reactions, as opposed to the high-temperature procedures, where small quantities of Si and O are detected sometimes.

Photoacoustic Measurements

Photoacoustic spectra of the microwave prepared materials are shown in Figs. 3a–3c (the inserts are the respective spectra of the high-temperature products). The band-gaps calculated from the PAS spectra for all the products are summarized in Table 1. To the best of our knowledge this is the first report of the electronic properties of these materials. The band-gap values for the compounds prepared by microwave and the high temperature processes are within the experimental error. This supports our claim that the Zintl compounds prepared using microwave irradiation are identical to those obtained using conventional techniques.

Reaction Mechanism

Despite the widespread belief that metals inside a microwave cavity cause strong plasma discharges, Whitaker and Mingos have shown that that metal powders can very efficiently couple with the microwave field and heat up to very high temperatures in very short periods of time without discharging (33, 36). This phenomenon enables the use of microwave power as an efficient promoter for solid state reactions. The precise mechanism of this heating is still unclear, but possibilities include the conduction and domain friction mechanisms (47, 48).

In order to determine which of the elements is the best susceptor for microwave irradiation, three ampoules filled with either pure sodium (or potassium), Se, and Sn were heated separately in the microwave oven. Se was found to be susceptible to microwave heating, but its heating rate is slower than the reaction rate. On the other hand, the alkali metals (both Na and K) and Sn are very strong susceptors for microwave irradiation, and even after a few seconds (2 s for alkali metals, and 6 s for tin) a yellow flame appeared and the metals melted immediately. This result suggests that microwave heating of the alkali metals and tin is the driving force for the start of this reaction.

The risk of contamination of the high-purity elements by the quartz ampoule is reduced when microwave heating is used. Unlike conventional heating, microwave heating is a volumetric heating method, so that heat is generated within the material and not supplied by the thermal conductivity from an external source. This volumetric heating and the “thermal runaway” effect, which are generally observed

TABLE 1
Band-Gaps of the Zintl Compounds Prepared by Both Methods Calculated from the Photoacoustic Spectra (PAS): dir. = Direct, ind. = Indirect Band-Gap

| Compound | Method | Band-gap |
|------------------------------------|-----------------|--------------------------------|
| Na_4SnSe_4 | MW | 1.95 eV (ind.); 2.89 eV (ind.) |
| Na_4SnSe_4 | Regular heating | 1.88 eV (ind.); 2.86 eV (ind.) |
| $\text{K}_4\text{Sn}_2\text{Se}_6$ | MW | 1.82 eV (dir.); 2.70 eV (ind.) |
| $\text{K}_4\text{Sn}_2\text{Se}_6$ | Regular heating | 1.80 eV (dir.); 2.67 eV (ind.) |
| $\text{K}_4\text{Sn}_3\text{Se}_8$ | MW | 1.93 eV (dir.) |
| $\text{K}_4\text{Sn}_3\text{Se}_8$ | Regular heating | 1.93 eV (dir.) |

during microwave reactions, result in very high temperatures.

The reaction between the three liquids (Na or K, Sn, and Se) will depend on their fluidity. Microwave overheating decreases the viscosity of these liquid elements, and as a result the reaction rates will increase.

Conclusions

The solid state MW method described in this paper offers a considerable reduction of the reaction time from days to 2 min. The reaction can serve as a general method for the preparation of known Zintl compounds. The quality of the products is superior to the conventional heating method. We attribute the lack of container impurities to the short reaction time and the volumetric heating.

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