

A fast synthesis for Zintl phase compounds of Na_3SbTe_3 , NaSbTe_2 and K_3SbTe_3 by microwave irradiation

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Abstract

The microwave irradiation technique was used to prepare three Zintl phase compounds Na_3SbTe_3 , NaSbTe_2 and K_3SbTe_3 . The as-prepared products were analyzed and characterized by XRD, EDX and SEM techniques. Higher microwave oven power and shorter irradiation time are required for the synthesis of Na_3SbTe_3 , whereas lower oven power and longer irradiation time are needed for NaSbTe_2 . Moderate microwave irradiation conditions facilitate the formation of pure K_3SbTe_3 . Pure phase of Na_3SbTe_3 are directly obtained by this technique for the first time. Compared with the traditional high-temperature solid-state synthesis, the microwave reaction required a considerable shortened reaction time for the preparation of the three Zintl compounds. The initial driving force for these reactions originates from the interaction of microwave electric field with alkali metals (Na and K) and Sb powders.

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1. Introduction

Solid-state reactions are often plagued by extremely long reaction times caused by slow diffusion rates in solids. Consequently, a constant interest has remained in exploring a variety of methods in order to achieve higher reaction rates. Various starting materials, including fluxes, or alternative heating techniques such as induction heating, arc furnaces, and microwave heating have been attempted for this purpose. It was recently demonstrated that microwave-assisted solid-state synthesis is a simple, fast and energy-efficient, as well as environmentally friendly technique. The fast synthesis is attributed to the nature of the microwave volumetric heating and to the thermal runaway effect associated with the microwave heating. The method, which has been recently reviewed [1], is applicable to the fast syntheses of chalcogenides [2,3], chalcopyrite semiconductors [4], carbides [5], nitrides [6–8], complex oxides [9–12], silicides [13,14], apatite [15], glasses [16], etc. In

our group, a microwave-assisted solid-state synthesis involving metals with low boiling point has been developed, and was successfully applied to the syntheses of Zintl phase compounds of Na_4SnSe_4 , $\text{K}_4\text{Sn}_2\text{Se}_6$ and $\text{K}_4\text{Sn}_3\text{Se}_8$ [17], and of a series of intermetallic compounds such as $\text{Li}_{21}\text{Si}_5$, $\text{Li}_{17}\text{Sn}_4$, Li_3Bi and Li_3Sb [18,19]. In this report, we have extended this technique to the fast preparation of another group of Zintl compounds of Na_3SbTe_3 , NaSbTe_2 and K_3SbTe_3 .

Zintl compounds have attracted considerable interest due to their intriguing structural diversity and rich chemistry [20]. In Zintl compounds, a strong electron donor such as alkali or alkaline earth metal is bonded with main group elements or even transition metals that serve as acceptors. Structurally, the main group elements form zero- to three-dimensional nets using covalent bonds, i.e., polyatomic anions. The alkali metals donate their electrons to these nets, thus forming cations, which are electrostatically attracted to these negatively charged nets. The bonding mode of the Zintl compounds is both ionic and covalent in character [21]. The pseudo-zero-dimensional Zintl compounds represent basic building blocks for the formation of the

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higher-dimensional compound, and they can serve as precursors for the “soft chemistry” synthesis of the intermetallic compounds [22–27].

Conventional high-temperature solid-state synthesis routes to Zintl phase compounds usually required high temperatures and long synthesis times that can make the synthesis tedious. Zintl phase Na_3SbTe_3 was first mentioned by Lazarev et al. [28] during an investigation of the phase diagram of the ternary Na–Sb–Te system, but they did not provide any information about its characterization and structure. In order to grow Na_3SbTe_3 single crystals, Lin and Miller [29] used an elemental mixture with an excess of Sb which is reacted at 1070 K for 24 h, and subsequently cooled to room temperature for 24 h. As a result, a mixture of gray-colored Na_3SbTe_3 and elemental Sb is derived. After mechanically separating, the amount of pure Na_3SbTe_3 single crystals obtained sufficed only for the determination of its structure. Therefore, a pure phase of Na_3SbTe_3 has never been directly obtained so far. K_3SbTe_3 was prepared by Jung et al. [30] using a direct reaction of the elements through a 6-h 550°C heating and subsequent 28-h cooling process. Microwave heating offers several advantages over conventional heating methods in the synthesis of Zintl compounds, the most important being the greatly shortened reaction times [17] which includes the heating and subsequent cooling which are both extremely rapid (up to 100°C/s). Such high heating and cooling rates could potentially lead to the fabrication of kinetic controlled phases that could not be easily obtained by other routes [7]. Here we report on a novel microwave irradiation technique for the syntheses of Zintl compounds of Na_3SbTe_3 , NaSbTe_2 and K_3SbTe_3 . The as-prepared Zintl phase compounds were characterized by PXRD, SEM and EDX techniques.

2. Experimental procedures

2.1. Reagents and equipment

Antimony powders (99.5% purity, –100 mesh), tellurium powders (99.8% purity, –200 mesh), sodium and potassium metal with both 99% purity were purchased from the Aldrich Co. All chemicals were directly used without further treatments. Because of the high sensitivity of the alkali metals and the 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 .

The microwave oven was a modified Kenwood 900 W. At 80% power the oven works in a cycling mode: 13 s-on, 3 s-off. 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. Morphology and EDX analyses were performed on a JEOL-JSM-840 scanning microscope.

2.2. Synthesis procedures

A typical element ratio for the preparation of Na_3SbTe_3 is as follows: 0.16 g (0.0069 mol) sodium, 0.204 g (0.0017 mol) antimony, and 0.64 g (0.005 mol) tellurium are put into a carbon-coated quartz ampoule. The ampoule is evacuated up to 5×10^{-5} Torr, and after that sealed by oxygen-gas flame. The sealed ampoule is placed in a microwave cavity and is exposed to microwave irradiation for a given time. After completion of the synthesis, the ampoule is opened inside an argon-filled glove box. Similar procedures are adopted for compounds of NaSbTe_2 and K_3SbTe_3 . Their typical reagents ratios are 0.065 g (0.0028 mol) sodium, 0.305 g (0.0025 mol) antimony powders and 0.64 g (0.005 mol) tellurium powders for the synthesis of NaSbTe_2 , and 0.24 g (0.061 mol) potassium, 0.204 g (0.0017 mol) antimony powders and 0.64 g (0.005 mol) tellurium powders for the synthesis of K_3SbTe_3 . All products are gray bulks with metallic luster, these colors are similar to those of Na_3SbTe_3 , NaSbTe_2 and K_3SbTe_3 obtained by the conventional high-temperature solid-state reaction. After grounding, the powders of Na_3SbTe_3 and NaSbTe_2 are dark gray, whereas K_3SbTe_3 is dark red.

3. Results and discussions

Na_3SbTe_3 is reported to be a stable solid phase below 703 K, but is known to decompose into Na_2Te and NaSbTe_2 above 703 K, before the onset of melting [28]. This implies that lower oven power and/or shorter irradiation time may be required for the formation of Na_3SbTe_3 . In general, it is well documented that higher microwave oven powers and/or longer irradiation times, lead to higher irradiation temperatures. Table 1 lists some experimental results under different microwave irradiation conditions. At 60% oven power, 1 or 2 min irradiation lead to the formation of NaSbTe_2 and Sb_2Te_3 , but no Na_3SbTe_3 is obtained. However, 80% oven power, and 3 min irradiation produced a mixture of Na_3SbTe_3 and NaSbTe_2 , whereas 4 min of irradiation resulted in another mixture of NaSbTe_2 and Na_2Te . When 90% oven power is used, after 3 min of irradiation a multiphase mixture of Na_3SbTe_3 , NaSbTe_2 and Na_2Te is obtained. The results presented in Table 1 demonstrate that lower oven powers and/or longer irradiation time favor the formation of NaSbTe_2 , and that higher oven power and shorter irradiation time facilitate the

formation of Na_3SbTe_3 . It appears that in the system of Na–Sb–Te, NaSbTe_2 is the thermodynamically preferential phase, whereas Na_3SbTe_3 may be the kinetically controlled phase, which could be easily obtained by microwave rapid heating and rapid cooling process [7].

Based on our experimental observations and solid-state reaction thermodynamics, a full oven power and shorter irradiation time are applied for the synthesis of Na_3SbTe_3 , in contrast to a lower oven power and longer irradiation time required for the synthesis of NaSbTe_2 . The experiments turned out the expected results (Table 1), namely, at a full oven power and 1.5 min irradiation time a pure phase of Na_3SbTe_3 is obtained. This is also the first time where pure Na_3SbTe_3 is directly obtained without a need for further separation. However, at the same oven power, after 2 min irradiation a multiphase mixture of Na_3SbTe_3 , NaSbTe_2 and Na_2Te is obtained. The formation of this multiphase mixture can be ascribed to the decomposition of Na_3SbTe_3 formed under microwave irradiation. A support for this assumption is observed, when the sample was exposed to irradiation for more than 2 min, it has remained red and hot, indicating that as-formed Na_3SbTe_3 can couple well with microwave, at least at high temperatures. This longer irradiation leads to the formation of NaSbTe_2

and Na_2Te . In the case of NaSbTe_2 , at 60% oven power, a pure phase of NaSbTe_2 is obtained after 6 min of irradiation, a shorter irradiation time of 2.5 min produced a mixture of NaSbTe_2 and Sb_2Te_3 .

Recently, a simple solution synthetic technique has been proposed for the fabrication of various binary or ternary intermetallic chalcogenides that cannot be prepared by other routes (e.g., [22,23]). The reaction consists of electron transfer from a Zintl polyanion precursor with high chemical reactivity to a transition metal cation, which results in the rapid precipitation of the neutral solid product. Zintl phase has become a crucial precursor for the synthesis of intermetallic compounds. Among them, Zintl compound K_3SbTe_3 can easily be dissolved in several polar solvents (e.g., H_2O , DMF, DMSO, formamide and ethylenediamine) to form K^+ cations and $[\text{SbTe}_3]^{3-}$ anions, and has been successfully used as the precursors for the soft chemistry

Table 1
Preparation conditions and phase composition of products by microwave irradiation

Compound	Oven power (%)	Irradiation time (min)	Phase composition
(1) Na_3SbTe_3	60	1	$\text{NaSbTe}_2 + \text{Sb}_2\text{Te}_3$
	60	2	$\text{NaSbTe}_2 + \text{Sb}_2\text{Te}_3$
	80	3	$\text{Na}_3\text{SbTe}_3 + \text{NaSbTe}_2$
	80	4	$\text{NaSbTe}_2 + \text{Na}_2\text{Te}$
	90	3	$\text{NaSbTe}_2 + \text{Na}_2\text{Te} + \text{Na}_3\text{SbTe}_3$
	100	1.5	Na_3SbTe_3
(2) NaSbTe_2	60	2	$\text{Na}_3\text{SbTe}_3 + \text{NaSbTe}_2 + \text{Na}_2\text{Te}$
	60	2.5	$\text{NaSbTe}_2 + \text{Sb}_2\text{Te}_3$
	60	6	NaSbTe_2
(3) K_3SbTe_3	60	3	$\text{Sb}_2\text{Te}_3 + \text{K}_2\text{Te} + \text{Te}$
	80	2	K_3SbTe_3
	100	2	$\text{K}_3\text{SbTe}_3 + \text{Sb}_2\text{Te}_3$

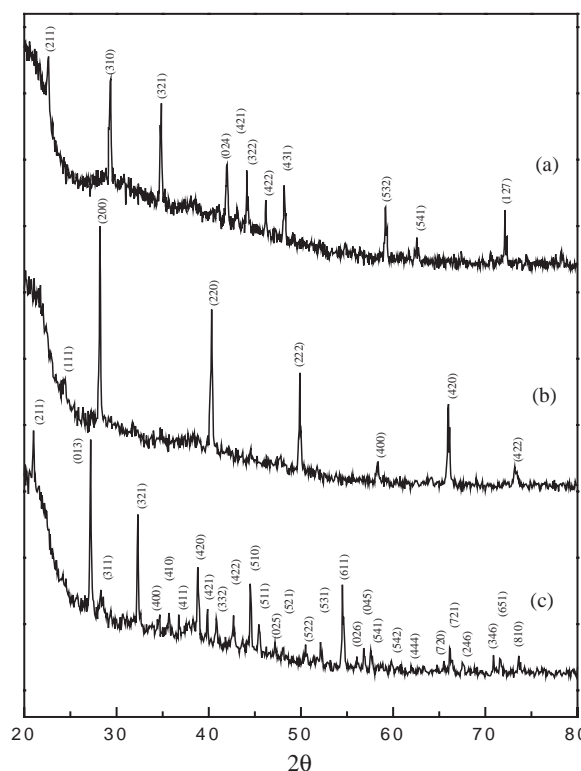


Fig. 1. XRD patterns of Na_3SbTe_3 (a), NaSbTe_2 (b), and K_3SbTe_3 (c) prepared by microwave irradiation.

Table 2
Lattice parameters of the Zintl phase compounds prepared by microwave irradiation

Compound	Crystal system	Time of microwave irradiation (min)	Oven power (%)	Lattice parameters (\AA) ^a	Ref.
Na_3SbTe_3	Cubic	1.5	100	9.6208(7) [9.6114(9)]	[29]
NaSbTe_2	Face-centered cubic	6	60	6.3471 [6.34500]	JCPDF No. 34-1175
K_3SbTe_3	Cubic	2	80	10.3174(8) [10.306(1)]	[30]

^aThe literature values are given in square brackets.

syntheses of $\text{Ni}_3(\text{SbTe}_3)_2$, $\text{Fe}_3(\text{SbTe}_3)_2$ and $\text{Co}_3(\text{SbTe}_3)_2$ [22,27,30]. Therefore, it is just natural that the above-mentioned fast process was extended to the synthesis of the Zintl compound K_3SbTe_3 . The synthetic experimental results are also presented in Table 1. At 60% oven power, 3 min irradiation leads to an uncompleted reaction, whereas at 100% oven power, a mixture of K_3SbTe_3 and Sb_2Te_3 is obtained after 2 min of irradiation. The optimal conditions for the synthesis are found to be 80% oven power and 2 min irradiation, where only one product, K_3SbTe_3 , is obtained.

The typical XRD patterns of the Zintl phase compounds prepared at different conditions by microwave irradiation are depicted in Fig. 1. Compared with their respective JCPDF files (Na_3SbTe_3 : JCPDF No. 82-1424; NaSbTe_2 : JCPDF No. 34-1175; Na_3SbTe_3 : JCPDF No. 80-2477), the diffraction patterns can be indexed as corresponding cubic Na_3SbTe_3 , face-centered cubic NaSbTe_2 , and cubic K_3SbTe_3 , respectively. The calculated lattice parameters are listed in Table 2, which match with the reported data (29, JCPDF No. 34-1175, 30).

SEM images of Na_3SbTe_3 , NaSbTe_2 and K_3SbTe_3 from microwave irradiation are depicted in Fig. 2. The images of Figs. 2A–C show that the products prepared by this method are homogeneous, and that the morphology of the particles is of closely irregular plates in all cases.

The stoichiometric ratios of the elements composing the as-prepared products are evaluated using EDX measurements. For Na_3SbTe_3 and NaSbTe_2 , the measured atomic ratio of Na:Sb:Te are 3.10:1:3.17 and 0.98:1:2.06, respectively. For both compounds the measured ratios are close to their theoretical stoichiometry. Similarly, the measured atomic ratio of K:Sb:Te is 2.93:1:3.03, which also is close to the expected theoretical stoichiometric ratio of K_3SbTe_3 . These analytical results are also in agreement with XRD analyses.

We also observed that during the preparation of Na_3SbTe_3 , NaSbTe_2 and K_3SbTe_3 , several strong yellow flashes are produced inside the ampoule after 2–5 s of irradiation. These yellow flashes appear through the entire reaction period when the microwave oven is in the “on” part of the cycle. The strong flash formation causes a little amount of alkali metal Na or K to evaporate to the upper part of the ampoule, and thus in our synthetic experiments a little excess in alkali metal Na or K must be considered in order to obtain the stoichiometric ratios.

The precise mechanism of microwave solid-state reaction is still unclear and whether there is an athermal effect of microwave on specific chemical reaction is in controversy, despite the extensive application of microwave radiation in organic or inorganic synthetic chemistry. In general, the driving force of microwave

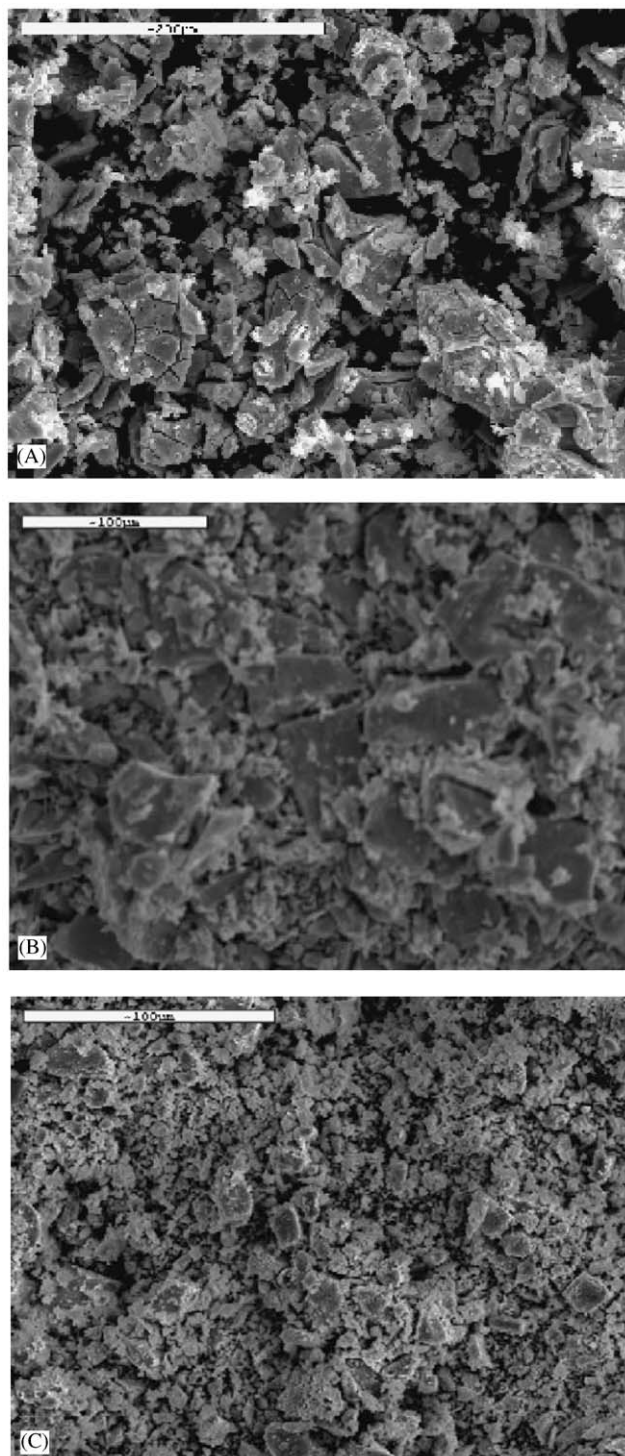


Fig. 2. SEM images of Na_3SbTe_3 (A), NaSbTe_2 (B), and K_3SbTe_3 (C) prepared by microwave irradiation.

irradiation synthesis arises from the interaction of reactants with microwave electronic field. This requires that one of the reactants must be a microwave susceptor. Previous investigations have shown that alkali metals Na and K can couple well with microwave, as reflected in the yellow glowing sparks [17]. In addition, Sb

powders can also couple well with microwave [19], while Te powders is not a good microwave susceptor [3,31]. The appearance of above-reported yellow glow at the start of the reaction suggests that interactions of alkali metals and Sb powders with microwave is the reaction driving force for these reactions in both systems of Na–Sb–Te and K–Sb–Te.

4. Conclusions

In summary, microwave irradiation technique was successfully applied to the fast preparation of Zintl phase compounds of Na_3SbTe_3 , NaSbTe_2 and K_3SbTe_3 . A significant short reaction time (a few min) was required compared with the conventional high-temperature solid-state synthesis technique. A pure phase of Na_3SbTe_3 was obtained for the first time by this technique. The start driving force for these reactions originates from the interaction of microwave electric field with alkali metals and Sb powders.

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