Semiconducting Behavior in the Polymeric Zintl Phase Material $K_2Ga_2Sb_4$

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A ternary Zintl phase material of the formula $K_2Ga_2Sb_4$ has been prepared directly from reaction of the elements following a high temperature procedure. The compound consists of potassium ions and planar ribbons of $(Ga_2Sb_4^{-2})_\infty$ consisting of five membered $[Ga_2Sb_3]$ rings bridged by Sb atoms. The variable temperature specific resistivity measurements show the material to be an intrinsic semiconductor.

Introduction

Main-group compounds containing metallic and semi-metallic elements yield a variety of compositions and structures that are achieved in the so-called Zintl phase. Attempts to rationalize these types of compounds have been based on concepts developed first developed by Zintl and then extended by others to explain the structures of compounds that arise when alkali or alkaline earth metals are reacted with other post transition main group metals or metalloids[1]. In our labs, we have been studying some ternary Zintl phase materials, and primarily those phases that contain semiconducting elements. The I-III-V Zintl phases are especially interesting because of possible applications to semiconduction.

The semiconducting industry is actively searching for new types of semiconducting phases as well as new techniques for the preparation of crystalline and thin film forms of known semiconducting phases. Of particular interest are the IV and III-V type semiconductors. A great deal of research has been reported on the methods of preparation of III-V type semiconductors[2]. Most of these techniques involve some sort of vapor phase deposition to form structured films. For example, (AlGa)As/GaAs[3-7] and InP.(InGa/As), (InGa)(AsP)[8-10] have been deposited via molecular beam epitaxy (MBE) and (AlGa)As/GaAs[11,12] have been prepared via organometallic vapor phase epitaxy (OMVPE). The usual form of arsenic used for these preparations is AsH_3 or AsR_3 (where R is an organic group)[13,14]. Other alternatives involve adducts of Ga-As complexes[15-18] or arsenic-organosilanes[19]. Because of the problems associated with AsH_3 new approaches to the formation of GaAs films are desirable.

An alternate approach to the synthesis of III-V semiconductors is through the use of I-III-V Zintl phase materials as precursors. The reactivity of Zintl phase materials affords the possibility of solution phase deposition of semiconducting films and perhaps the layering of metal-semiconductor deposition[20,21].

Besides their potential for solution chemistry, the ternary Zintl phase materials are inherently interesting. In recent years a large number of crystal structures of ternary Zintl phase materials have been reported[22-25]. These materials display a wide range of structures, from discreet molecular units to one- or two-dimensional polymeric arrays. Despite the wealth of structural information which is unfolding, little is being done to explore the physical properties of these materials.

We have undertaken the synthesis of a series of I-III-V ternary Zintl phase materials, both as a preliminary step in the investigation of new synthetic routes to the preparation of III-V type semiconductors, and for the purpose of investigating their electrical and magnetic properties. Several I-III-V Zintl phase materials have already appeared in the literature: $KGaSb_2$[26], $K_3Al_2As_3$[27], $Na_7Al_2Sb_5$[28], $Na_2Al_2Sb_3$[29], $K_3Ga_3As_4$[30], $K_4In_4As_6$[31], and $K_4In_4Sb_6$[31]. Our previous syntheses of $K_3Ga_3As_4$, $K_4In_4As_6$, and $K_4In_4As_6$ resulted in insulating layered materials. The compound of potassium gallium antimonide ($K_2Ga_2Sb_4$) has been reported by Schaeffer and coworkers[26] in which $GaSb_2^{2-}$ polyanions are isosteric with BS_2 in the polymeric modification of BS_2. In our current rent study we have measured the electrical properties of $K_2Ga_2Sb_4$ over the 15-300K temperature region and have observed semiconducting behavior.

Experimental

Synthesis. $K_2Ga_2Sb_4$ was prepared by direct combination of the elements at elevated temperatures. A dry quartz or Vycor tube was charged with a stoichiometric amount of the elements. The sample tube was evacuated at a pressure of approximately 0.005 torr for at least 1.5h, then sealed under vacuum. The sample tube was placed inside a larger diameter tube, which was similarly evacuated and sealed. The sample was heated at 750°C in a tube furnace for 10h, then cooled to ambient temperature over a 40h period. A metallic grey crystalline product was obtained and can be isolated in approximately 85% yield.

Resistivity Measurements. Resistivity measurements on pressed pellets were made using a linear four-probe method[32]. The current was supplied by a Keithley model 224 Programmable Current Source and the voltage drop across the sample was measured using a Keithley model 181 Digital Nanovoltmeter.

Results and Discussion

The structure of $K_2Ga_2Sb_4$ is composed of ribbons of $(Ga_2Sb_4^{-2})_\infty$ propagated in the c direction[26]. The planar ribbons are composed of five membered Ga_2Sb_3 rings bridged by Sb atoms. A schematic diagram of the monomeric segment of $(Ga_2Sb_4^{-2})_\infty$ is shown in Figure 1. All of the atoms in each ribbon chain are constrained to planarity with the atoms lying on a crystallographic mirror plane. The typical bond between Sb-Ga is a covalent bond that has a relatively short bond-distance in the range of 2.6-2.5 A. It is also found that
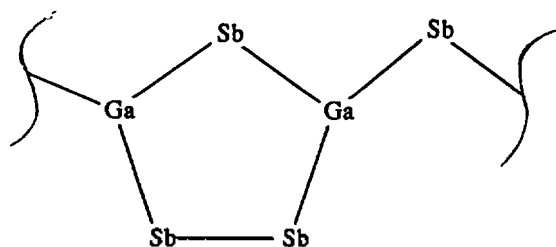
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Figure 1. Schematic diagram of the Ga$_2$Sb$_4^{2-}$ monomeric unit.
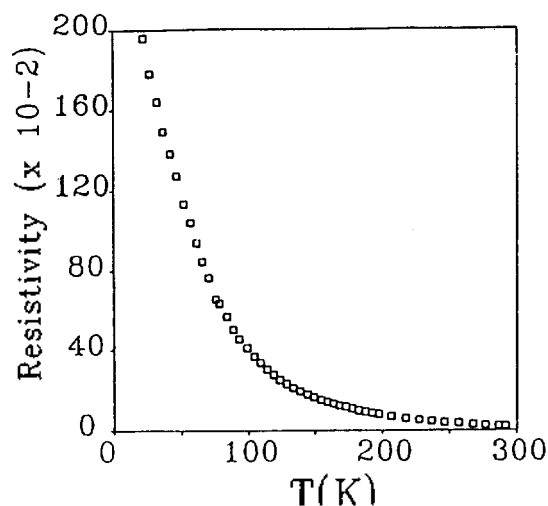

Figure 2. Specific resistivity of a pellet of K$_2$Ga$_2$Sb$_4$ plotted as a function of temperature over the 15-300K temperature range.

the Sb-Sb covalent bond has a bond length of 2.8394[5] A, which is slightly longer than Sb-Ga bond length.

According to the Zintl bonding rules, a Zintl phase material is expected to follow the 8-N rule which requires that the octet rule be followed in the formation of covalently bonded anionic clusters. In other words, it should be possible to draw a Lewis structure for a Zintl hetero-poly anion [eg., (Ga$_2$Sb$_4^{-2}$)$_\infty$]. In order to satisfy the octet, it is necessary to allow the delocalization of lone pairs of electrons on two antimony atom into the empty orbital on the gallium atoms to form two quasi-double bonds in the monomeric unit. One resonance structure of these π-delocalizations has a configuration that forms a one dimensional conjugated polymer. The planarity that is observed in the crystal structure determination is consistent with the conjugated electron delocalization scheme that is proposed.

The other reported I-III-IV Zintl phase analogs exhibit layered structures that consist of a network of single covalent bonds. Those materials have also been shown to be insulating materials when such measurements have been recorded. Electrical conductivity of K$_2$Ga$_2$Sb$_4$ is shown in Figure 2. The increase in the specific resistivity of as a function of temperature is consistent with the behavior of an intrinsic semiconductor. An analysis of the resistivity data gives an estimate of the activation energy of 2 eV, based on the slope of the log resistivity versus temperature plot.

Conclusion

The material K$_2$Ga$_2$Sb$_4$ has been shown to be an intrinsic

semiconductor following the standard temperature dependent resistivity behavior. This property may arise from the delocalization of antimony electrons into empty gallium p-orbitals to form a conjugated (Ga$_2$Sb$_4^{-2}$)$_\infty$ ribbons. The conjugated electron configuration is also consistent with the 8-N rule for Zintl phases, since each atom in the (Ga$_2$Sb$_4^{-2}$)$_\infty$ ribbons maintains an octet of electrons.

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