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Synthesis and Characterization of a New Amorphous Alloy Mn3(SbTe3)2

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In recent publications we have reported the synthesis and characterization of a series of ternary intermetallic chalogenide compounds.[1] These ternary metal chalcogens are prepared from a simple metathesis reaction between a Zintl phase material and a divalent transition metal halide. Zintl materials are valence compounds; the metals and metalloids that comprise the material transfer or share electrons in order to achieve an octet in the outmost electron shell.[2] This often results in the formation of covalently bonded polyatomic anionic units, referred to as Zintl anions. The ionic character that may arise in Zintl phase may be sufficient to allow the solvation of salt like ions (cations and Zintl anions) in polar solvents (*e.g.* KSn dissolves in liquid NH_3, and K_5InTe_4 dissolved in H_2O). We have recently synthesized two new ternary Zintl compounds composed of elements from groups I-V-VI of the periodic table, K_3SbTe_3[3] and $LiSbTe_2$.[4] These Zintl phases were prepared from the direct combination of the elements at high temperatures. Although the $LiSbTe_2$ compound is found to be insoluble in all polar solvents because of increased covalency in the crystalline lattice, the K_3SbTe_3 forms solutions with DMSO, DMF, formamide, ethylenediamine, and H_2O solvents, and therefore shows promise for the preparation of intermetallic solids *via* the metathesis procedure. Although most amorphous solids are prepared by rapid thermal quenching, or by pyrolytic or sputtering techniques, chemical methods involving rapid precipitation also can produce non-crystallin solids in certain types of materials. In this paper we report a systematic examination of the magnetic and conducting properties as functions of temperature for a new amorphous $Mn_3(SbTe_3)_2$ material.

Results and Discussion

The new amorphous intermetallic compound, $Mn_3(SbTe_3)_2$, is prepared by using the same rapid precipitation metathesis procedure that we have employed to prepare other types of intermetallic solids.[4] An ORTEP diagram of the unit cell of the precursor Zintl phase material, K_3SbTe_3, is illustrated in Figure 1.[3] The structure consists of an ionic lattice of K^+ cations and discrete $[SbTe_3]^{-3}$ Zintl anions. The ionic character of K_3SbTe_3 permits the Zintl phase to form an ionic solution in polar solvents. It is reported that the tetra-
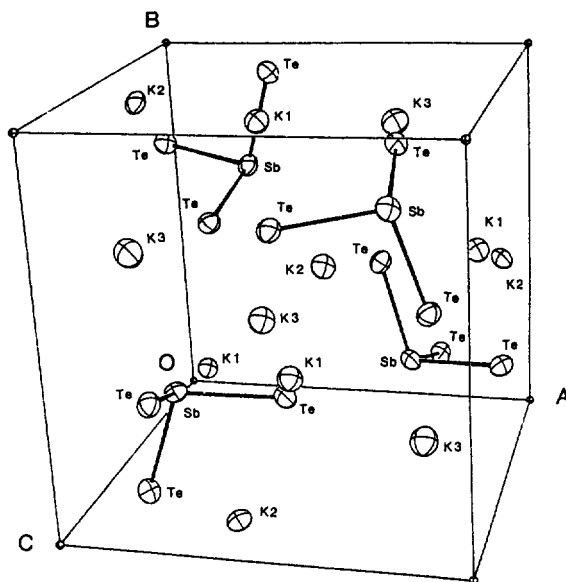

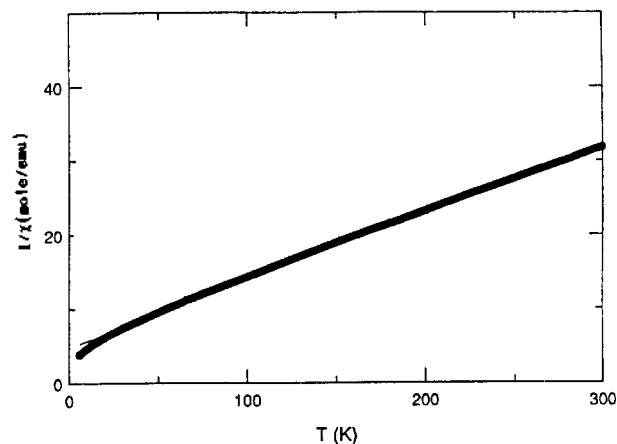**Figure 1.** ORTEP diagram of the unit cell of K_3SbTe_3.

Figure 2. Plot of the inverse susceptibility of $Mn_3(SbTe_3)_2$ as a function of temperature.

hedral structure of the $SnTe_4$ unit comprising the Zintl anion in Mn_2SnTe_4 remains intact when the intermetallic solid is formed. Therefore we can expect the $Mn_3(SbTe_3)_2$ solid to contain the intact $SbTe_3$ pyramidal units. Figure 2 shows the inverse magnetic susceptibility as a function of temperature with Curie-Weiss fits for $Mn_3(SbTe_3)_2$. The least square fit of $1/\chi = (T-\Theta)/C$, in the temperature range 30-300 K gives $\Theta = -51.7$ K. The negative Θ value is apparent that the dominant magnetic exchange interaction is antiferromagnetic in this material.[5] The specific conductivity of this material is highly temperature dependent as shown in the plot of log σ versus $1/T$ in Figure 3. The plot shows two linear regions. A linear least-squares fit of conductivity data to the relationship, $\sigma = C \exp(-Ea/K_BT)$ gives the activation energies for conduction, $Ea = 0.12$ eV in the temperature region 300-160 K and $Ea = 0.08$ eV in the region 160-80 K. In Figure
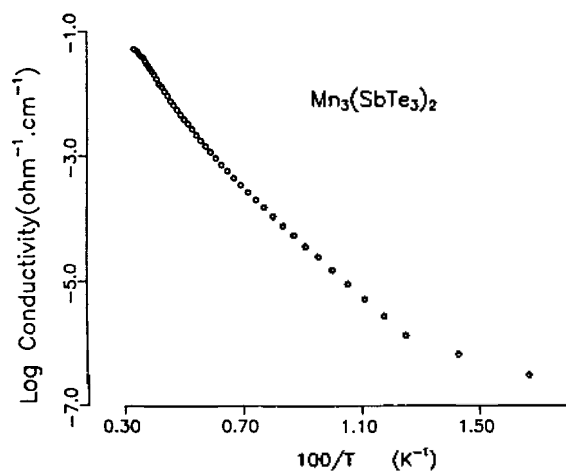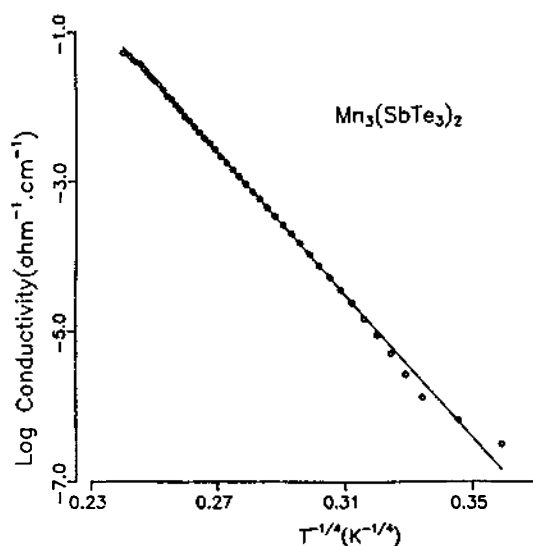
Figure 3. Plot of log conductivity *vs.* 100/T.

Figure 4. Plot of log conductivity *vs.* $1/T^{1/4}$.

4, a straight line in the plot of log σ versus $1/T^{1/4}$ is consistent with the variable range hopping mechanism.[6] A hopping transport mechanism has been observed in many mixed valence semiconductors such as the simple $3d$ oxides, glasses containing $3d$ ions,[7,8] and amorphous semiconductor.[9] From the magnetic measurement each Mn ion has a magnetic moment of 3.55 μB decreased to the normal values of 5.9 μB for Mn^{2+}. Therefore, it is likely that the hopping conductivity in $Mn_3(SbTe_3)_2$ results from the amorphous structure instead of electron transfer between the ions of different valence states. The scattering of the data from log $\sigma - 1/T^{1/4}$ below 70 K is probably due to the effect of the antiferromagnetic correlations developed gradually between the moments.

Experimental Section

Synthesis. All of the reactions are extremely air sensitive. Preparation and sample manipulations were performed under the argon filled glovebox containing less than 1 ppm of oxygen. K_3SbTe_3: The ternary Zintl material K_3SbTe_3 was prepared as described previously.[3] $Mn_3(SbTe_3)_2$: The transi-

tion metal compound was prepared by the metathesis reaction of K_3SbTe_3 with $MnCl_2$ in degassed water. In a typical preparation, while stirring the $MnCl_2$ solution (20 m*l*, 0.05 M), a stoichiomrtric quantity of the K_3SbTe_3 solution (50 m*l*, 0.03 M) was slowly added. A fine black precipitate was immediately formed, separated by solution filtration, washed with degassed water and acetone, and dried overnight under vacuum.

Elemental Analysis. The presence of the only three elements in the sample and the homogenity of the sample were confirmed with an EDS equipped AMRAY Model 1820 scanning electron microscope. The quantitative elemental analysis for this material was carried out on a IL-S-12 AA Spectrometer, Themo Jarrell Ash Corp. The atomic absorption standards were purchased from John-Matthey. The experimental results gave the following chemical composition: $Mn_{2.96}Sb_{2.0}Te_{6.20}$. Within the error of analysis, the material can be represented by the formula corresponding to Mn_3 $(SbTe_3)_2$. The atomic absorption spectroscopy also revealed that the sample also exhibited contamination by residual solvent molecules and the KCl metathesis coproduct.

Resistivity Measurements. Resistivity measurements for all the materials were performed on pressed pellets over the temperature range 30-300 K using a van der Pauw four probe method.[10] The pressed pellets were made under a pressure of 16,000 psi. The current was supplied by a keithley Model 224 programable current source and the voltage drop across sample was measured with a Keithley Model 181 digital nanovoltmeter. Electrical contacts to the samples were made using gold wires attached with silver paint.

Magnetic Measurements. The dc magnetic susceptibility and magnetization measurements were conducted on a SHE Corp. VTS-50 superconduction susceptometer that is interfaced to an IBM XT computer system. Measurements and calibration techniques are reported elsewhere.[11] In the susceptibility measurement, two different procedures were used: (i) zero field coopling, where the sample was slowly cooled in zero field to the lowest measured temperature at which the field was switched on and the $M(T)$ was measured as temperature was raised: (ii) field cooling, where the field was turned on at a high temperature and the sample was cooled in the field.

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Synthesis and Characterization of Poly[(5,6-dideoxy-α-D-xylo-hex-5-enofuranose)-*alt*-(maleic acid)]

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There has been considerable interest in the application of polymers in medicine either as polymer drugs or as polymeric drug carriers[1]. The synthetic polyanions containing carboxylate groups are one kind of polymer drugs[2], which exhibit a broad range of biological activities. They are particulary active against bacteria, viruses, and tumors. Recently we have reported that, among the polyanions, the alternating copolymers of dihydropyran or dihydrofuran rings with maleic anhydride showed very high antitumor activity[3-7].
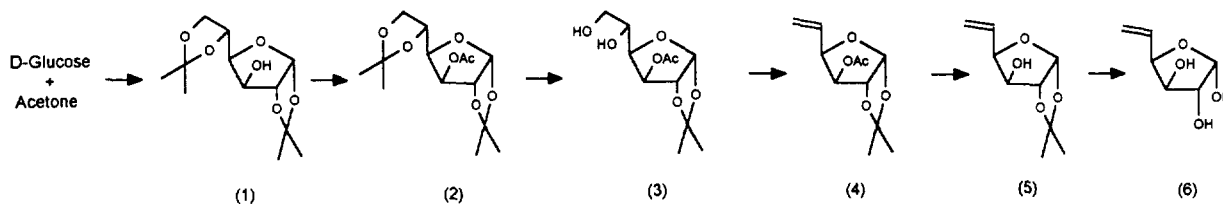
In this paper we report on the synthesis and characterization of monomers, 3-O-acetyl-5,6-dideoxy-1,2-O-isopropylidene-α-D-xylo-hex-5-enofuranose (4) and its derivatives 5 and 6, and their alternating copolymers with maleic anhydride 8, 9, 10, and 11 as shown in Scheme 1. Since polymer 11 is a polyanion, composed of furanose sugar and maleic acid, it may show high biological activities and be applicable for the backbone of polymeric carrier in the liver-specific delivery system. Recently it was found that sugar derivatives attached on the polymer chain had high affinities to liver hepatocyte as its membrane contains a receptor which recognizes them[8-10]. For example, galactose has been used as a homing device in the liver-specific delivery of polymeric antitumor agents[10].
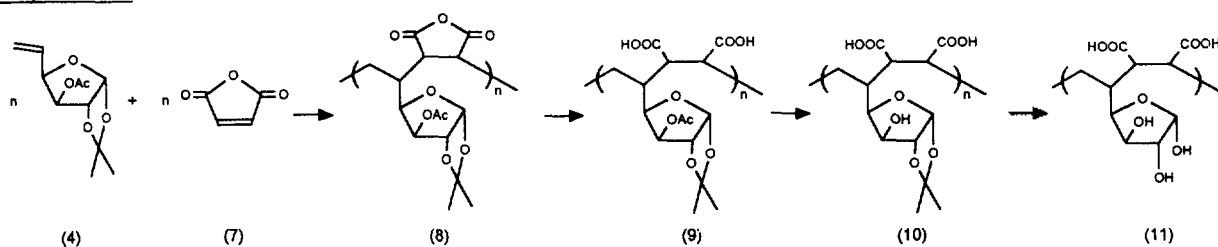
Experimental

Materials and measurement. D-glucose (Aldrich Co.) and N,N-dimethyl formamide dimethyl acetal were used as delivered. Maleic anhydride was sublimed under vacuum. Acetone was distilled over P_2O_5. AIBN was recrystallized from methanol. Other commercially available reagent chemicals were used without further purification. ^1H and ^{13}C-NMR spectra were recorded on a Varian T-60 or a Bruker AMX-500 spectrometer. IR spectra were obtained with a Perkin-Elmer Model 238B spectrometer. UV spectra were recorded with a Hitachi Model 200-20 spectrometer. CD and ORD spectra were obtained with a Jobin-Yvon spectrometer. Measurements of Mn were carried out in acetone at 40°C using a vapour-pressure osmometer (Knauer Co.). Elemental analysis was performed at KRICT.

Synthesis of 3-O-acetyl-5,6-dideoxy-1,2-O-isopropylidene-α-D-xylo-hex-5-enofuranose (4). N,N-dimethylformamide dimethyl acetal (20.0 ml, 15.0 mmol) was added to the solution of 3[13] (6.6 g, 28.9 mmol) in 20 ml of methylene chloride, and the mixture was stirred at room temperature for 3 h. After evaporation under reduced pressure, the residue was redissolved in 40 ml of acetic anhydride. The solution was refluxed for 100 min and then neutralized with

Synthesis of Monomer

Polymerization

Scheme 1.