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High-Pressure Spinel Type Al_2S_3 and $MnAl_2S_4$

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New spinel type forms of Al_2S_3 and $MnAl_2S_4$ were prepared at pressures from 2 to 65 kb. The Al_2S_3 was shown to exhibit a structure similar to β-In_2S_3 in which ordered vacancies result in a super lattice with a tetragonal cell. The cell dimensions are $a = 7.026 \pm 0.001$ Å, $c = 29.819 \pm 0.001$ Å. Electrical measurements show semiconducting behavior with $\rho_{298°K} = 10^9$ Ω cm, $Ea = 0.3$ eV. The spinel form of $MnAl_2S_4$ exhibits a range of stoichiometry as indicated by a range of cell dimension from $a = 10.092 \pm 0.001$ Å to $a = 10.010 \pm 0.001$ Å. Resistivity and magnetic measurements indicate semiconducting and paramagnetic behavior.

Introduction

The compound Al_2S_3 is known to form three polymorphs (*1*): a hexagonal α form, a related hexagonal β form that has a defect wurtzite-type structure, and a γ form having the corundum type structure. The coordination of Al in the α and β forms is tetrahedral, while it is octahedral in the corundum type. These are prepared at ambient pressure. A cubic spinel-type ($a = 9.93 \pm 0.1$ Å) Al_2S_3 is reported (*2*) to form when 2 at. % As is substituted for Al. The β form of indium sesquisulfide is known as a defect spinel-type structure (*3*, *4*). It contains ordered vacancies that result in a superlattice; consequently, the unit cell dimensions are $a = 7.61$, $c = 32.24$ Å.

A large series of thiospinel compounds is known; however, the compound $MnAl_2S_4$ is reported to form a rhombohedral structure when prepared at ambient pressure (*5*). In this study the systems Al_2S_3 and $MnAl_2S_4$ were studied at high pressure.

Experimental

Reactions to prepare Al_2S_3 were carried out, starting with 4*N* purity Al powder, 50/200 mesh, and sulfur of 6*N* purity. To prepare $MnAl_2S_4$, the same reagents and either MnS or Mn and S were used.

Experiments run at 3000 atm or less were done in a vessel pressurized with compressed argon and internally heated by a platinum resistance furnace. The reactants were sealed *in vacuo* in heavy walled Pyrex® tubing (9-mm o.d., 6-mm i.d.) that was contained in a platinum jacket. The Pyrex is soft at 700°C and translates the pressure while acting as an inert container. Reaction cycles were typically as follows: 200 atm, heat to 700°C, increase pressure to 3000 atm or less, increase temperature to 1000°C, hold for the desired length of time, program cool, and quench. Quenching is cooling from operating temperature to room temperature in about five minutes. Reactions done at pressures higher than 3000 atm were performed in a tetrahedral anvil press of National Bureau of Standards design (*6*). The operating procedure has been described elsewhere (*7*).

The products of all reactions were studied by x-ray powder diffractometry using Debye–Scherrer and Guinier techniques. Unit cell dimensions were refined using a computerized least-squares technique.

Resistivity measurements were done by a four probe technique described elsewhere (*8*). Magnetic susceptibility measurements were made using a vibrating sample magnetometer in fields of 16 kOe at temperatures from 77–298°K.

Results and Discussion

A. Al_2S_3

The elements were mixed in the ratio of 1Al:2S since excess S was found to enhance crystal growth and impede reaction of Al with the Pyrex tube.