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0030-0950/79/0004-0186/\$1.00/0

## BRIEF NOTE

MUTUAL SOLUBILITIES OF  $ZnGa_2S_4$  AND  $MnGa_2S_4$  AT 800 °C<sup>1</sup>

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OHIO J. SCI. 79(4): 186, 1979

Manganese gallium sulfide,  $MnGa_2S_4$ , exists in two crystalline forms (Viswanadham and Edwards 1973; Pardo *et al* 1975). The low temperature  $\alpha$ -form, stable below 950 °C, is green. It was assigned a cubic unit cell by Viswanadham and Edwards and a monoclinic unit cell by Pardo and coworkers. The latter assignment was based on studies of single crystals and is the more dependable one. The high temperature  $\beta$ -form, stable from 950 °C to the melting point, 995 °C, is pink with a tetragonal unit cell.

Zinc gallium sulfide has one crystalline form (Hahn *et al* 1955). It is gray with a tetragonal unit cell in space group  $S_4^2$  or  $D_{2d}^{11}$ . A very close similarity between the structure of  $ZnGa_2S_4$  and the high-temperature structure of  $MnGa_2S_4$  was noted by Viswanadham and Edwards. Our paper describes an investigation of the similarity of the two structures as determined by the extent of solid solubility of  $MnGa_2S_4$  in  $ZnGa_2S_4$  at 800 °C.

Gallium (99.999%) and manganese (99.99+%) from Atomergic Chemetals, zinc (99.999%) from New Jersey Zinc, and sulfur (99.9999%) from Electronic Space Products were used as starting materials. The appropriate stoichiometric amounts of the elements were weighed on a Mettler semimicrobalance, then transferred directly to a 14 mm o.d. Vycor tube with one end closed by fusing.

The tube containing the elements was attached to a vacuum system, evacuated, and sealed by fusing such that its final length was about 10 cm. The sealed tube was heated in stages in a resistance furnace, first at 400 °C until most of the sulfur reacted, then at 700–800 °C for several days. The tube was removed from the furnace, cooled, and opened in a glove bag under dry nitrogen. The sample was removed in a glove bag, placed in an agate mortar and ground, then placed in another Vycor tube, all under dry nitrogen. The tube was stoppered, removed from the glove bag, and attached to a vacuum system with minimal exposure of the sample to the atmosphere. The tube was sealed, as described previously, placed in a resistance furnace, and heated at 700–800 °C for 3 to 4 days. At the end of this heating, the tube was quenched from 800 °C.

Fifteen compositions of  $Mn_xZn_{1-x}Ga_2S_4$  were prepared ( $x=0.000, 0.100, 0.200, 0.300, 0.400, 0.500, 0.600, 0.700, 0.800, 0.850, 0.870, 0.900, 0.950, 0.970, \text{ and } 1.000$ ). Each sample was examined visually and with a Debye-Scherrer X-ray diffractogram. The diffractograms were measured and analyzed to deduce the phase-composition of the samples.

All samples of  $Mn_xZn_{1-x}Ga_2S_4$  were powders with some small pink crystals interspersed in the powder in samples with the values of  $x$  larger than 0.4, except with  $x=1.000$ . The color of the powder changed smoothly with increas-

<sup>1</sup>Manuscript received 31 March 1977 and in revised form 21 February 1979 (#77-32).

ing  $x$  up to 0.850. For  $x=0.000$ ,  $\text{ZnGa}_2\text{S}_4$ , the powder was light gray in line with previous descriptions, and for  $x=0.850$  it was a light brown or brownish orange. For  $x=1.000$ ,  $\text{MnGa}_2\text{S}_4$ , the sample was a light green powder in line with previous descriptions (Viswanadham and Edwards 1973).

The Debye-Scherrer X-ray diffractograms revealed that for  $x=0.000$  to  $x=0.850$  the samples contained only one phase and that the structure was that of  $\text{ZnGa}_2\text{S}_4$  with only small changes in cell parameters with changes in  $x$ . For  $x=1.000$  the structure was that of  $\text{MnGa}_2\text{S}_4$ . For  $x=0.870$ , 0.900, 0.950 and 0.970 two phases were found in the samples, one phase with the  $\text{ZnGa}_2\text{S}_4$  structure, *mutatis mutandis*, and one phase with structure identical to that of  $\alpha\text{-MnGa}_2\text{S}_4$ . The small pink crystals found interspersed in some of the samples, when crushed, produced powders identical in color and phase to the rest of the sample.

Figure 1 is a portion of the temperature-composition phase diagram. The abscissa is the mole fraction of  $\text{MnGa}_2\text{S}_4$  or value of  $x$  in  $\text{Mn}_x\text{Zn}_{1-x}\text{Ga}_2\text{S}_4$ . The left side of the diagram represents pure  $\text{ZnGa}_2\text{S}_4$  and the right side represents pure  $\text{MnGa}_2\text{S}_4$ . All points from this study are on the 800 °C isotherm, the temperature from which they were quenched. At  $x \leq 0.850$  the  $\text{ZnGa}_2\text{S}_4$  structure appears, at  $x=1.000$  the  $\text{MnGa}_2\text{S}_4$  low-temperature structure appears, and between  $x=0.870$  and 0.970, both structures appear. Previously known melting and transition points are represented by closed circles (Viswanadham and Edwards 1973). The dashed line in figure 1 represents the left-hand boundary of the two-phase region between the two saturated solid solutions. This is proposed from two known points, the transition from  $\alpha$ - to  $\beta$ - $\text{MnGa}_2\text{S}_4$  at 950 °C and the point at 800 °C between  $x=0.850$  and  $x=0.870$  where the two-phase bound-

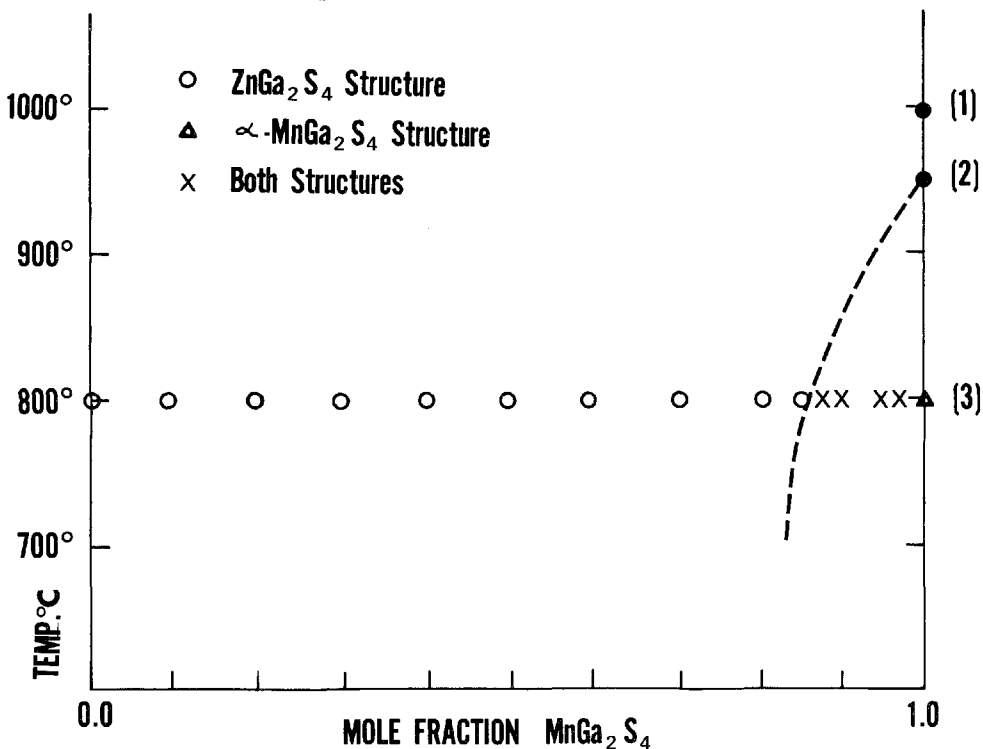


FIGURE 1. Partial Phase Diagram of the  $\text{Mn}_x\text{Zn}_{1-x}\text{Ga}_2\text{S}_4$  System. (1) Melting point of  $\text{MnGa}_2\text{S}_4$ , 995 °C. (2) Transition point of  $\text{MnGa}_2\text{S}_4$ , 950 °C. (3) Results from present studies. The dashed line represents a phase boundary known at two points: the boundary between high and low temperature  $\text{MnGa}_2\text{S}_4$  and at 85% to 90%  $\text{MnGa}_2\text{S}_4$  and 800 °C.

ary was found. The fact that the X-ray diffractogram of the  $\text{MnGa}_2\text{S}_4$ -phase in the two-phase mixtures was indistinguishable from that of  $\alpha$ - $\text{MnGa}_2\text{S}_4$  reveals that the right-hand boundary of the two-phase region is very close to  $x = 1.000$ . Hence, that boundary is not seen in figure 1.

The tendency of  $\text{MnGa}_2\text{S}_4$  to have the structure of  $\text{ZnGa}_2\text{S}_4$  is revealed by two facts: it transforms to that structure at 950 °C, and it accommodates to that structure even at low temperatures in solid solutions with as much as 85 mole-%  $\text{MnGa}_2\text{S}_4$ . This tendency can be related to the fact that the electronic structure of  $\text{Zn}^{2+}$  is  $d^{10}$  and that of  $\text{Mn}^{2+}$  is  $d^5$  high-spin (Viswanadham and Edwards 1973), hence both are spherically symmetric with zero crystal field stabilization energy. The ionic radii are nearly the same, namely 0.74 Å for Zn and 0.82 Å, for Mn. No tendency of  $\alpha$ - $\text{MnGa}_2\text{S}_4$  to accommodate  $\text{Zn}^{2+}$  ions was found.

The transition from  $\beta$ - to  $\alpha$ - $\text{MnGa}_2\text{S}_4$  was shown in other work (Edwards and Gates 1977) to be associated with a net loss to the vapor of gaseous  $\text{Ga}_2\text{S}$  with respect to  $\text{S}_2$ , which loss could produce a change in the  $\text{Ga}_2\text{S}/\text{S}_2$  molar ratio as large as 0.05%. A similar transition was found in  $\text{Ga}_2\text{S}_3$  (Roberts and Searcy 1977). No transition or nonstoichiometry was found in extensive studies of  $\text{ZnGa}_2\text{S}_4$  (Gates and Edwards 1978). The similarity of  $\beta$ - $\text{MnGa}_2\text{S}_4$  to  $\text{ZnGa}_2\text{S}_4$ , revealed by their extensive mutual solubility, would indicate that it is also stoichiometric. Thus,  $\alpha$ - $\text{MnGa}_2\text{S}_4$  appears to be sulfur rich.

The present results resemble those at low pressures in the  $\text{ZnS-MnS}$  system

(Neuhaus and Steffen 1970). There, at 800 °C, a solid solution, with the wurtzite structure, of 48 mol %  $\text{MnS}$  exists in equilibrium with pure  $\alpha$ - $\text{MnS}$ , with the NaCl structure; no solubility of  $\text{ZnS}$  in  $\alpha$ - $\text{MnS}$  is detectable at low pressures. The color of  $\alpha$ - $\text{MnS}$  is green and that of  $\gamma$ - $\text{MnS}$ , with the wurtzite structure, is red.

*Acknowledgments.* The authors thank Mr. Robert Tadsen of Maumee High School and Dr. Gordon Parker of The University of Toledo for arranging the joint program under which this work was done. The authors from Maumee High School acknowledge financial support from The University under a Summer Faculty Research Grant to the first Author.

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