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NOTE

Subsolidus Equilibria in the System ZnS–MnS–$CuInS_2$*

Data on the bounding binary systems have been previously reported (*1*). No previous data on the ternary system have been reported; therefore subsolidus relations were determined at 600, 850, and 1050°C, due to the importance of the ternary compositions as yellow and orange pigments (*2*). The experimental procedures used were the same as previously reported for the bounding binary systems (*1*). In the three ternary systems shown, the heavy lines represent phase boundaries, the lines of intermediate width are tie lines in two-phase regions, and the light lines are "iso-*d* value" lines which show the relationship between the major diffraction peaks of binary and ternary zincblende and wurtzite solid solutions. In each diagram, the relationships in the $CuInS_2$ (chalcopyrite) corner are incomplete and uncertain, mainly for two reasons. First, the interesting yellow, orange, and maroon colors are found in the portion of the system containing less than 50% $CuInS_2$ and more than 40% $ZnZnS_2$. Second, the experimental difficulties are substantial in the region near $CuInS_2$ due to the problem of distinguishing zincblende solid solutions from chalcopyrite solid solutions. Liquid formation and sluggishness of the reactions are secondary reasons for doing only a limited amount of experiments in this area.

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1. The 600°C Section

The region of zincblende solid solution extends to a considerable distance toward MnS in the ternary system. The wurtzite solid solution region is relatively small, but its extension to the binary system MnS–$CuInS_2$ confirms the data previously obtained on the stabilization of γ-MnS or wurtzite binary solid solution (*1*).

Some representative tie lines are shown in the two-phase regions. It was possible to position these tie lines by observing the relationship between the *d* value of the major peak (3.123) for binary and ternary zincblende solid solutions and similar data on the two major peaks for binary and ternary wurtzite solid solutions. The *d* values of the major peak for binary wurtzite solid solutions are shown on the ZnS–MnS side of the system, whereas two peaks are shown within the ternary system and for one binary composition in the system MnS–$CuInS_2$. The light lines in the two major solid-solution regions show the relationship of the *d* values most clearly.

In the high $CuInS_2$ corner, a small region of $CuInS_2$ solid solution exists and the probable coexistence of three phases is indicated by the symbols. Coexistence of zincblende and chalcopyrite solid solutions near the binary system ZnS–$CuInS_2$ is also indicated.

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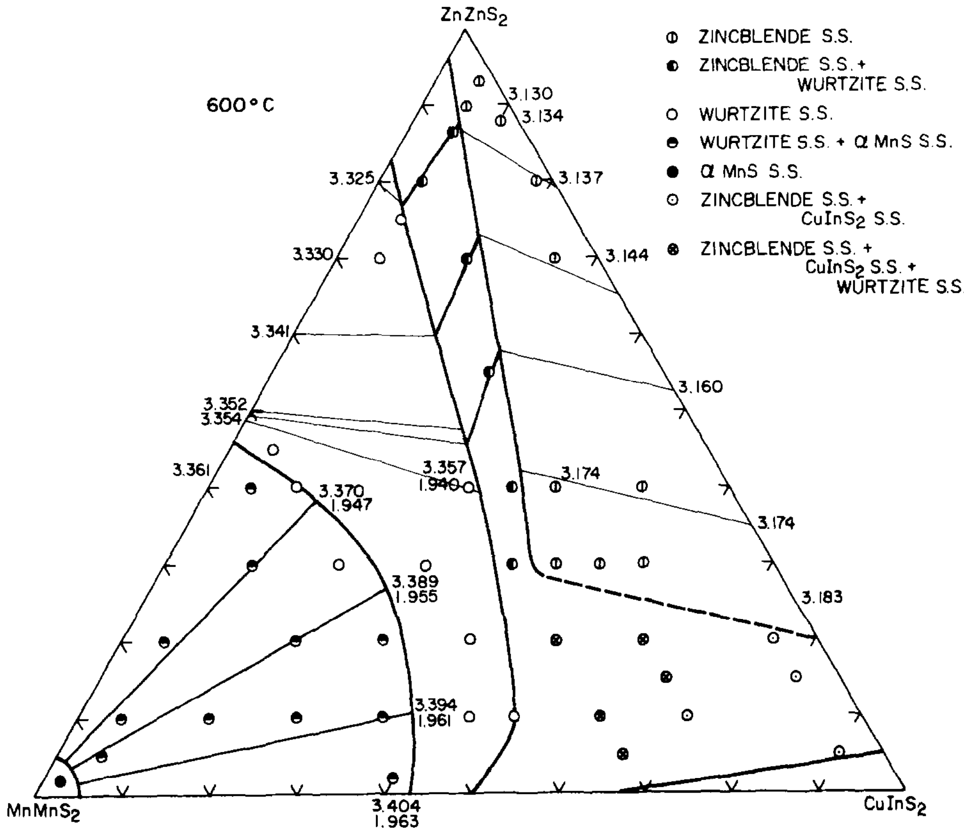

FIG. 1. Isothermal section at 600°C.

2. The 850°C Section

The extent of the zincblende solid solution region has decreased, the wurtzite solid-solution region has become substantially larger, and the regions of the two-phase coexistence have changed their positions accordingly.

In the $CuInS_2$ corner, there is some evidence for the coexistence of zincblende and $CuInS_2$ solid solutions and wurtzite and $CuInS_2$ solid solutions near the respective binary systems ZnS–$CuInS_2$ and MnS–$CuInS_2$, but much uncertainty remains in the compositional region between 55–75% $CuInS_2$ and 10–20% $ZnZnS_2$.

3. The 1050°C Section

At this temperature, the wurtzite solid solutions dominate the system, consistent with the configurations shown in the binary diagrams (*1*). The area of zincblende solid solutions is confined to a narrow region near the binary system ZnS–$CuInS_2$. The region of coexistence of zincblende and wurtzite solid solution is very small and the size of the wurtzite + rock salt solid-solution region has

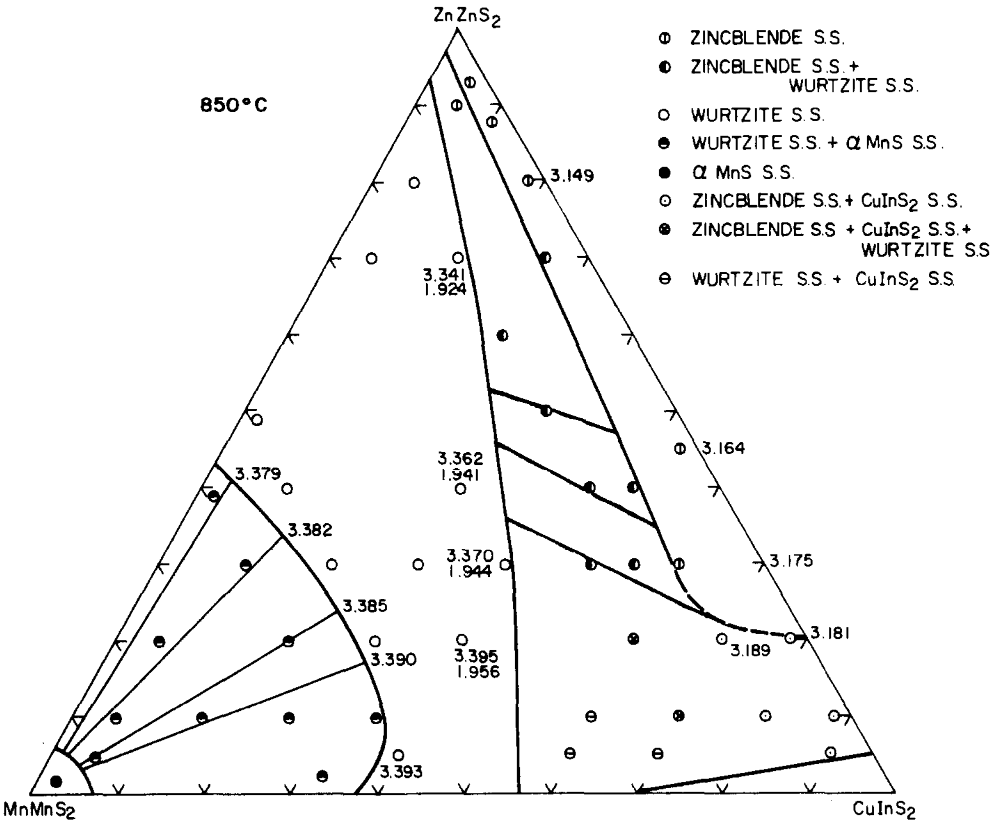

FIG. 2. Isothermal section at 850°C.

reached a minimum relative to its size at the two lower temperatures.

Representative tie lines are again shown in the two-phase regions. It was possible to position these tie lines by plotting the *d* values for the major peak of the binary zincblende solutions and two of the major peaks of the binary and ternary wurtzite solid solutions, as shown in the diagram.

In the $CuInS_2$ corner of the diagram there was substantial evidence for the coexistence of zincblende and $CuInS_2$ solid solutions in five compositions as indicated by the symbols.

In summary, ZnS–MnS–$CuInS_2$ forms a solid-solution-type ternary system, whose configuration is dictated by the relationships in the binary systems. No ternary compounds form and at high temperatures such as 1050°C, the system is dominated by a wurtzite solid-solution region. At lower temperatures such as 600–850°C, a region of zincblende solid solution becomes prominent. The extent of the chalcopyrite region in the ternary system remains relatively constant at all temperatures. Those readers who are interested in detailed data on compositions, heat treatment, phase analyses, and color should refer to Table IV in the thesis (*3*).

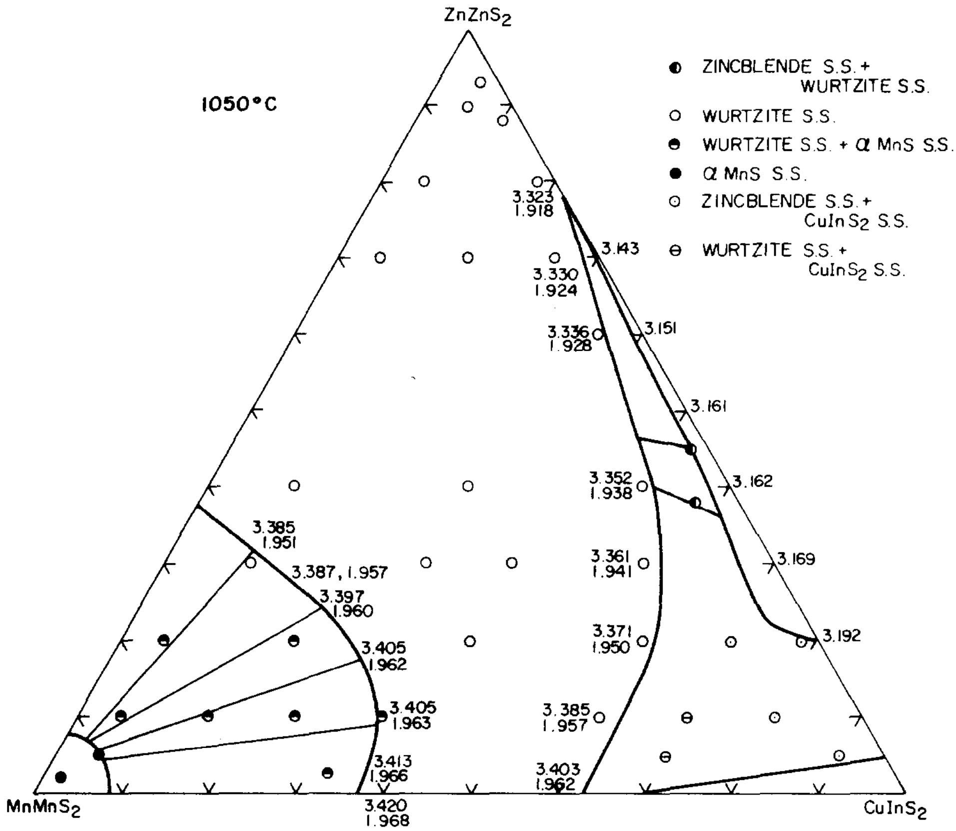

FIG. 3. Isothermal section at 1050°C.

References

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