Subsolidus phase relations in the system $ZnWO_4$–$ZnMoO_4$–$MnWO_4$–$MnMoO_4$[1]

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Summary. Subsolidus phase relations in the systems $ZnWO_4$–$MnWO_4$, $ZnWO_4$–$ZnMoO_4$, $MnMoO_4$–$ZnMoO_4$, and $MnWO_4$–$MnMoO_4$ were investigated by using the quenching technique. A complete series of solid solutions forms in the system $ZnWO_4$–$MnWO_4$ above 840° C, whereas limited solid solubilities were found in the other three. The various limits of solubility are, at 620° C, 4·0 mole % $ZnMoO_4$ in $ZnWO_4$ and 4·0 mole % $ZnWO_4$ in $ZnMoO_4$, 13·0 mole % $ZnMoO_4$ in $MnMoO_4$ and 12·0 mole % $MnMoO_4$ in $ZnMoO_4$, 9·0 mole % $MnMoO_4$ in $MnWO_4$ and 6·0 mole % in $MnWO_4$ in $MnMoO_4$; and at 1000° C, 15·0 mole % $ZnMoO_4$ in $ZnWO_4$ and 15·0 mole % $ZnWO_4$ in $ZnMoO_4$, 36·0 mole % $ZnMoO_4$ in $MnMoO_4$ and 29·0 mole % $MnMoO_4$ in $ZnMoO_4$, 15·0 mole % $MnMoO_4$ in $MnWO_4$ and 27·0 mole % $MnWO_4$ in $MnMoO_4$.

Subsolidus phase relations in the system $ZnWO_4$–$ZnMoO_4$–$MnWO_4$–$MnMoO_4$ were studied at 900° C. The solubility of molybdenum in the $(Zn,Mn)WO_4$ series increases from both end members to a maximum of 27·0 mole % at the composition $Mn_{35}Zn_{65}$. Both molybdates also have limited ranges of solid solutions, and a three-phase region occupies the central portion of the system defined by three points with compositions of 41 mole % $ZnMoO_4$, 26 mole % $MnMoO_4$, 33 mole % $MnWO_4$; 57 mole % $ZnMoO_4$, 10 mole % $MnMoO_4$, 35 mole % $MnWO_4$; and 27 mole % $ZnMoO_4$, 34 mole % $MnWO_4$, 39 mole % $ZnWO_4$.

THE interests of subsolidus phase relations in the system $ZnWO_4$–$ZnMoO_4$–$MnWO_4$–$MnMoO_4$ are twofold. Mineralogically, the system $ZnWO_4$–$MnWO_4$ is composed of the only pair among three wolframite-type tungstate minerals (Mn, hübnerite; Zn, sanmartinite; and Fe, ferberite) whose phase relations require experimental study, since the system $ZnWO_4$–$FeWO_4$ is expected to have a complete series of solid solutions from a crystal-chemical consideration, and it is known from chemical analyses of natural materials that there is no immiscibility gap existing in the system $MnWO_4$–$FeWO_4$. The mineral, wolframite, represents solid solutions with compositions ranging from $Mn_{80}Fe_{20}$ to $Mn_{20}Fe_{80}$.

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Crystallochemically, the non-isomorphism of molybdates of small divalent cations (cations with ionic radius between 0·65 and 0·80 Å) with the wolframite-type tungstates offers an ideal situation for studying the substitution between the two chemically similar hexavalent cations in different crystal structures. Unlike tungstates, molybdates can not be systematically grouped into two structural types based on the size of the divalent cation they contain. Molybdates of larger divalent cations do have scheelite-type structure, but crystal structures vary among molybdates of small divalent cations. Some of them, such as $NiMoO_4$, $CoMoO_4$, and $MnMoO_4$, are monoclinic, and some, such as $FeMoO_4$ and $ZnMoO_4$, are triclinic (Smith, 1962; Smith and Iber, 1965; Abrahams and Reddy, 1965). Even within the same symmetry system, they do not have similar structure. For example, both nickel and molybdenum are in distorted octahedral positions in $NiMoO_4$, whereas in $MnMoO_4$, manganese and molybdenum occupy six- and four-coordinated positions, respectively.

Experimental results on subsolidus phase relations in the temperature range between 625 and 1025° C are reported in this note.

Experimental procedures. The preparation of samples and the procedures of heat treatment were performed as described previously (Chang, 1967), except that it is necessary to prepare molybdates below 500° C because MoO_3 decomposes at temperatures much lower than does WO_3. X-ray diffraction was used to identify phases resulting from thermal runs, and both 'lattice parameter' and 'disappearing' methods (Barrett, 1952) were used to establish the limits of solid solubility.

Results and discussion. The subsolidus phase relations in the four binary systems are shown in fig. 1. Although mutual solid solubilities were found in all systems, only $ZnWO_4$–$MnWO_4$ has complete solid solubility. In this system (fig. 1*a*), both tungstates are of the wolframite-type structure and solubility is completed above 840° C. The solvus is quite symmetrical, but at any particular temperature in the range where the immiscibility gap exists, $MnWO_4$ can always take more Zn into its solid solution than vice-versa. This is a reflection of the difference in ionic size between the two divalent cations involved. If a comparison with phase relations in the system $FeWO_4$–$MnWO_4$ is made, the different behaviour of the equal-sized zinc and ferrous iron in the formation of solid solutions with manganese in their tungstates is obvious. Since zinc has the electronic structure of Group IIB cation, differing distinctly from that of a transition cation, it behaves much like a smaller cation, magnesium, in crystal chemistry (Wells, 1962).

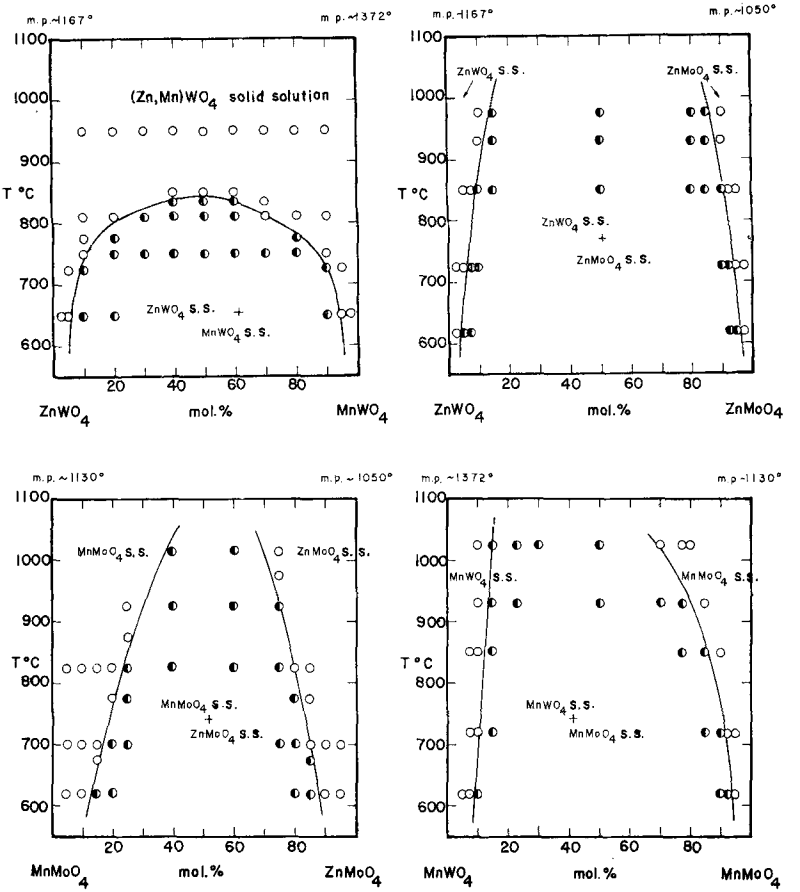

FIG. 1. Subsolidus phase relations in the systems: *a* (top left), $ZnWO_4$–$MnWO_4$; *b* (top right), $ZnWO_4$–$ZnMoO_4$; *c* (bottom left), $ZnMoO_4$–$MnMoO_4$; and *d* (bottom right), $MnWO_4$–$MnMoO_4$.

The phase relations in the systems $ZnWO_4$–$ZnMoO_4$ and $ZnMoO_4$–$MnMoO_4$, as shown in fig. 1*b* and *c*, are very alike. Limited mutual solid solutions exist at both ends in each system, and increase in amount with increasing temperature, up fairly close to the melting points of the end members. In the system $ZnWO_4$–$ZnMoO_4$, equal ranges of solid solutions form at both ends, from 4·0 mole % at 625° C, to 6·0 mole % at 725° C, to 9·0 mole % at 850° C, and to 13·5 mole % at 975° C, whereas in the system $ZnMoO_4$–$MnMoO_4$, the solvus in the Mn-rich side rises from

13·0 mole % at 625° C to 38·0 mole % at 1025° C, and in the Zn-rich side from 12·0 mole % at 625° C to 30·0 mole % at 1025° C.

The phase relations in the system $MnWO_4$–$MnMoO_4$ are shown in fig. 1*d*. On the tungstate side, the amount of molybdenum taken into solid solution is almost a constant over the range of temperatures studied, but on the molybdenum side, the solubility of tungsten increases rapidly with the temperature, from 6·0 mole % at 625° C to 30·0 mole % at

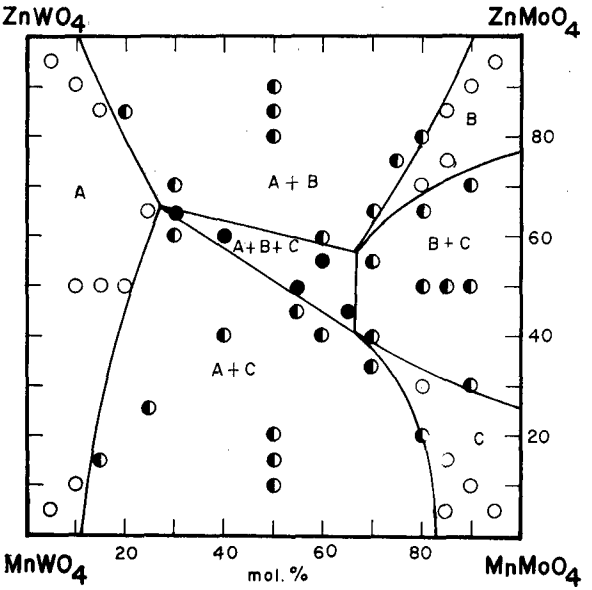

FIG. 2. Subsolidus phase relations in the system $ZnWO_4$–$ZnMoO_4$–$MnWO_4$–$MnMoO_4$ at 900° C. In the figure, A denotes the wolframite-type $(Zn,Mn)WO_4$ solid solution, B, triclinic $ZnMoO_4$-type solid solution, and C, monoclinic $MnMoO_4$-type solid solution.

1025° C. Such differences in solid solubilities may be explained on the basis of crystal structure. The molybdate has a relatively 'open' structure with molybdenum located in the distorted tetrahedral positions as compared with $MnWO_4$ in which tungsten is octahedrally coordinated. The pressure-dependent phase transition from the low-pressure form of $MnMoO_4$ to the high-pressure wolframite-type $MnMoO_4$ (Young and Schwartz, 1963) indicates that only under high pressure does molybdenum assume octahedral positions occupied by tungsten cations in the wolframite-type structure. At moderate temperature, the reverse

situation of tungsten occupying molybdenum positions can occur much more easily.

Subsolidus phase relations in the system $ZnWO_4$–$ZnMoO_4$–$MnWO_4$–$MnMoO_4$ are shown in fig. 2. At 900° C, the complete series of solid solutions formed in the binary system $ZnWO_4$–$MnWO_4$ extends into the field of the system with the solubility of molybdenum increasing from both ends of the tungstates toward the solid solution, $(Zn_{65}Mn_{35})WO_4$, with a maximum of 27·0 mole %. Two other single-phase regions were also found in the system, consisting of solid solutions of monoclinic $MnMoO_4$- and triclinic $ZnMoO_4$-type structures. The solubilities of tungsten in both molybdates increase more or less along the joins, $MnMoO_4$–$ZnWO_4$ and $ZnMoO_4$–$MnWO_4$, from $MnMoO_4$ and $ZnMoO_4$, respectively.

The three single-phase regions are separated by three two-phase regions, consisting of $MnWO_4+MnMoO_4$, $MnMoO_4+ZnMoO_4$, and $ZnMoO_4+ZnWO_4$, which extend from their respective binary system into the four-component system and give rise to a three-phase region occupying the central portion of the diagram. The three-phase region is defined by compositions, 41 mole % $ZnMoO_4$, 26 mole % $MnMoO_4$, 33 mole % $MnWO_4$; 57 mole % $ZnMoO_4$, 10 mole % $MnMoO_4$, 33 mole % $MnWO_4$; and 27 mole % $ZnMoO_4$, 34 mole % $MnWO_4$, 39 mole % $ZnWO_4$.

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References

Abrahams (S. C.) and Reddy (J. M.), 1965. Journ. Chem. Phys., vol. 43, p. 2533.
Barrett (C. S.), 1952. Structure of metals, New York, McGraw-Hill, p. 196.
Chang (L. L. Y.), 1967. Amer. Min., vol. 52, p. 427.
Smith (G. W.), 1962. Acta Cryst., vol. 15, p. 1054.
—— and Iber (J. A.), 1965. *Ibid.*, vol. 19, p. 269.
Wells (A. F.), 1962. Structural inorganic chemistry, 3rd edn, Oxford University Press, p. 506.
Young (A. P.) and Schwartz (C. M.), 1963. Science, vol. 141, p. 248.

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