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SOLID SOLUTIONS OF SCHEELITE WITH OTHER $R^{II}WO_4$-TYPE TUNGSTATES

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ABSTRACT

Solid solutions of scheelite with other $R^{II}WO_4$-type tungstates were determined in the temperature range between 550° and 1150°C using the quenching technique. In the scheelite-wolframite systems, only $MnWO_4$ has a significant range of solid solution with scheelite. At 1100°C, 10.0 mole percent $MnWO_4$ is soluble in $CaWO_4$ and 2.5 mole percent $CaWO_4$ is soluble in $MnWO_4$.

In the $CaWO_4$-$BaWO_4$ system, the solid solubility of $CaWO_4$ in $BaWO_4$ increases from 4.5 mole percent at 550°C to about 10.0 mole percent at 1150°C, whereas only 3.5 mole percent $BaWO_4$ can be dissolved in $CaWO_4$ at 1150°C. Complete solid solutions exist in the systems $CaWO_4$-$SrWO_4$ and $CaWO_4$-$PbWO_4$ above 825° and 815°C, respectively.

In the $CaWO_4$-$CdWO_4$ system, an extensive range of solid solution with a maximum of 55 mole percent $CdWO_4$ at 1150°C was found in the Ca-rich side. The solid solubility of $CaWO_4$ in $CdWO_4$ at 1150°C is 10.0 mole percent.

Lattice parameters in the systems $CaWO_4$-$SrWO_4$, $CaWO_4$-$PbWO_4$, and $CaWO_4$-$CdWO_4$ were found to vary linearly with compositions.

INTRODUCTION

Among tungstates of the $R^{II}WO_4$-type, schellite is the most important because of four aspects: (1) it is the type crystal structure for other minerals and inorganic compounds; (2) it is a major ore for the most refractory metal, tungsten; (3) it is one of the best known fluorescent materials, and (4) it has maser applications.

Extensive studies have been made on both natural and synthetic scheelites, but no information is available on subsolidus equilibrium relations with other $R^{II}WO_4$-type tungstates. Information of this kind will lead to a more complete understanding of the physical and chemical properties of scheelite. Experiments to obtain this information form the subject of this paper.

EXPERIMENTAL

Tungstates of respective divalent cations were prepared by reacting reagent-grade carbonates of calcium, strontium, barium, and manganese, and oxides of magnesium, zinc, nickel, and lead with purified tungstic anhydride in the temperature range between 600° and 900°C. Binary mixtures were then prepared by blending the synthetic tungstates in an automatic grinder under acetone. Samples of the binary mixtures were then cold-pressed into pellets and fired in covered platinum crucibles. Two grindings and firings were performed for each run. Generally, a

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period of 12 hours was used for runs made above 900°C, 48 hours for runs in the temperature range 750°–900°C, and 150 hours for runs below 750°C. Temperatures above 800°C were measured with platinum-10% rhodium thermocouples and chromel-alumel thermocouples were used for lower temperatures. The error in measurement is considered to be less than ±10°C. The samples were quenched in air and the resulting phases were identified using both X-ray diffraction and petrographic microscopy.

Lattice constants were calculated from measurements of d made on a Tem-Pres Model XD-1 diffraction system, in the region $2\theta = 35°–55°$. The 110 line of metallic tungsten at $2\theta = 40.26°$ ($a = 2.1648$, Swanson and Tatge, 1953) was used as an internal standard.

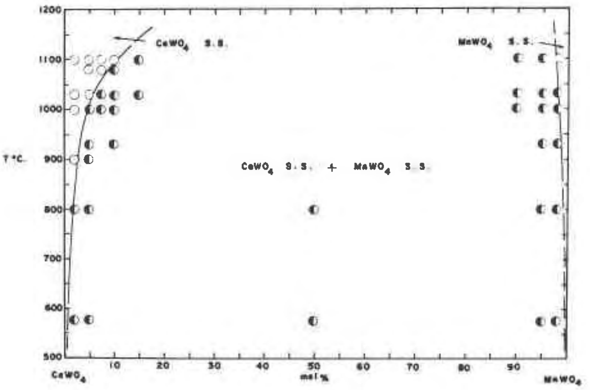

FIG. 1. Phase relations in the system $CaWO_4$-$MnWO_4$.

EXPERIMENTAL RESULTS

The subsolidus phase equilibria in the systems of scheelite with other $R^{II}WO_4$ tungstates (R: Mg, Ni, Zn, Mn, Sr, Ba, Pb, and Cd) were determined in the temperature range between 550° and 1150°C. Results are presented in diagrammatic form. All tungstates involved have been well characterized previously and no difficulty was encountered in phase identification.

The Scheelite-Wolframite Systems. The phase relations in the systems of scheelite with four wolframites are shown in Figures 1 and 2. The cations represent the entire range of ionic sizes which form a wolframite-type tungstate, from manganese (0.80 Å), through zinc (0.74 Å) and nickel (0.69 Å), to magnesium (0.65 Å).

The system $CaWO_4$-$MnWO_4$ (Fig. 1) is the only one of these four systems to show mutual solid solubility. The solvus raises from 575°C with no detectable amount of $MnWO_4$ in $CaWO_4$ to 10.0 mole percent $MnWO_4$ in solution at 1100°C. On the Mn-rich side, the range of solid solution is less extensive with 2.5 mole percent $CaWO_4$ soluble in $MnWO_4$ at 1100°C.

In the other three systems (Fig. 2), the phase relations are similar. Most compositions produced two-phase equilibrium assemblages in the temperature range of this investigation. Only those compositions of $CaWO_4$ with 2 mole percent of each of $MgWO_4$, $NiWO_4$ and $ZnWO_4$ gave rise to a single phase when they were quenched from 1100°C. Phase encountered in the equilibrium assemblages are the end members only with cell dimensions almost identical to those of the synthetic starting materials.

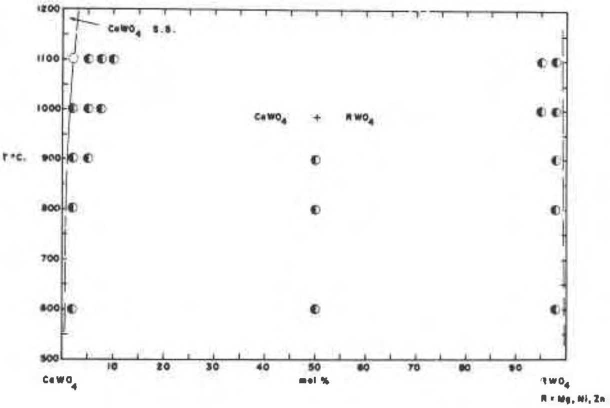

FIG. 2. Phase relations in the systems $CaWO_4$-$ZnWO_4$, $CaWO_4$-$NiWO_4$ and $CaWO_4$-$MgWO_4$.

The System $CaWO_4$-$SrWO_4$. The phase relations in the system $CaWO_4$-$SrWO_4$ are shown in Figure 3. The solid solubilities, very limited below 600°C, increase rapidly above 600°C, and a complete series of solid solutions forms above 825°C. The solvus is asymmetrical with a maximum in the compositional range between $Ca_{80}Sr_{20}$ and $Ca_{70}Sr_{30}$. With $CaWO_4$ and $SrWO_4$ melting at 1580° and 1535°C respectively (Chang, Scroger and Phillips, 1966), this series of solid solutions is expected to be moderately refractory. No sign of melting was observed in three runs made at 1400°C with compositions of $Ca_{60}Sr_{40}$, $Ca_{40}Sr_{60}$, and $Ca_{20}Sr_{80}$.

The variations of lattice parameters in the system $CaWO_4$-$SrWO_4$ are shown in Figure 4 as a function of composition. The calculations were

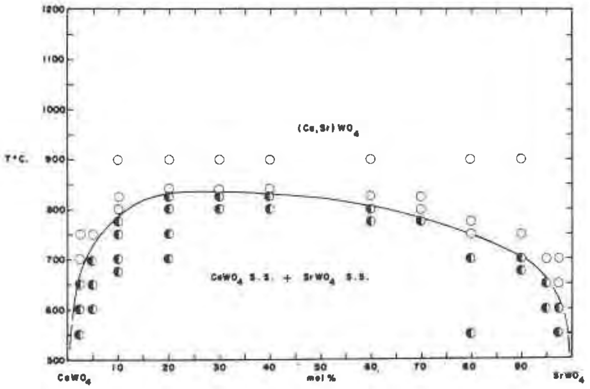

FIG. 3. Phase relations in the system $CaWO_4$-$SrWO_4$.

made from measurements of the shift of diffraction lines (220) and (116) of the scheelite-type structure. The parameter a_0 increases from $CaWO_4$ linearly toward $SrWO_4$, whereas the parameter c_0 shows a slight positive deviation from Vegard's law.

The System $CaWO_4$-$BaWO_4$. The phase relations in the system $CaWO_4$-$BaWO_4$ are shown in Figure 5. No solid solution of $BaWO_4$ can be detected in $CaWO_4$ up to 1000°C in the quenching experiment, but the shift

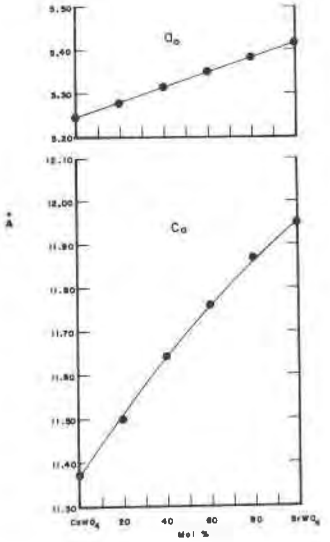

FIG. 4. Variation of lattice parameters in the system $CaWO_4$-$SrWO_4$.

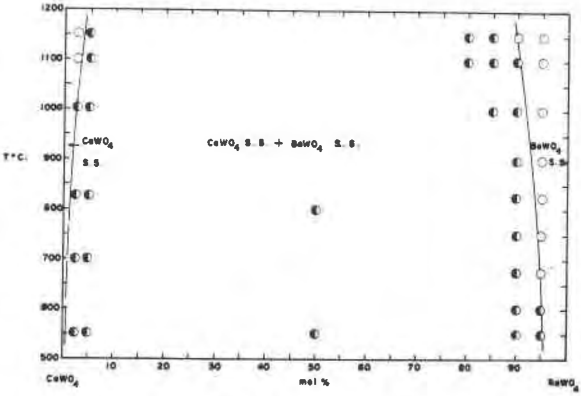

FIG. 5. Phase relations in the system $CaWO_4$-$BaWO_4$.

of several $CaWO_4$ diffraction lines in the X-ray diffraction patterns indicates a small amount of $BaWO_4$ does exist in $CaWO_4$ at this temperature. A run made at higher temperature shows that 2.5 mole percent $BaWO_4$ are soluble in $CaWO_4$ at 1100°C. The solubility of $CaWO_4$ in $BaWO_4$ is represented by the solvus in the Ba-rich side, which is 4.5 mole percent at 550°C and increases to almost 10.0 mole percent at 1150°C.

The System $CaWO_4$-$PbWO_4$. The phase relations in the system $CaWO_4$-$PbWO_4$ are shown in Figure 6. A complete series of solid solutions forms above 815°C. The solvus is also asymmetrical with a maximum near the composition $Ca_{85}Pb_{15}$. This series of solid solutions is not as refractory as that in the system $CaWO_4$-$SrWO_4$ and melting was encountered in the temperature range of this investigation. By direct visual observation on

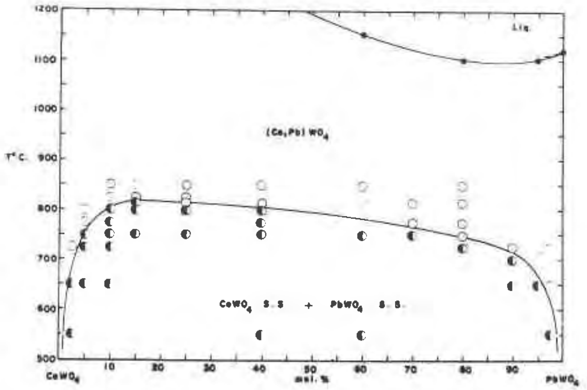

FIG. 6. Phase relations in the system $CaWO_4$-$PbWO_4$.

a resistance strip furnace, the melting points of $PbWO_4$, and solid solutions of compositions Ca_5Pb_{95}, $Ca_{20}Pb_{80}$ and $Ca_{40}Pb_{60}$ were determined and a melting curve based on these observations is plotted in the upper right portion of Figure 6. The melting point of $PbWO_4$ is 1124°C, in excellent agreement with a value previously reported (1123°C, Jaeger and Germs, 1921).

Jaeger and Germs (1921) proposed that $PbWO_4$ has a phase change at 877°C, but they did not characterize the difference in the high- and low-temperature forms. Two minerals of this composition are known in nature, tetragonal stolzite and monoclinic raspite. In the present study, only stolzite was obtained regardless of the temperature at which the $PbWO_4$ was prepared. Differential thermal analysis conducted on $PbWO_4$ was prepared at 650°C gave a single endothermal peak at 1124°C indicating no thermal effect except the melting. The raspite is not expected to be a stable phase in the system under present experimental conditions, since it was reported (Shaw and Claringbull, 1955) that raspite transforms irreversibly to stolzite at about 400°C.

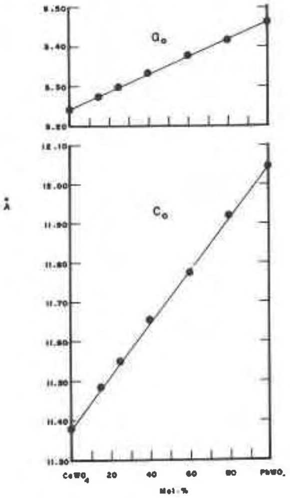

FIG. 7. Variation of lattice parameters in the system $CaWO_4$-$PbWO_4$.

The variation of lattice parameters in the system $CaWO_4$-$PbWO_4$ is shown in Figure 7 as a function of composition. Plots for both a_0 and c_0 follow Vegard's law very closely.

The System $CaWO_4$-$CdWO_4$. The crystal structure of $CdWO_4$ has not been very well established. Sharp (1960) reported that this tungstate belongs to a space group, $C_{2h}^{5}\mathrm{i}P2_1/b$, whereas Coing-Boyat (1961) suggested it relates to a wolframite-type.

The phase relations in the system $CaWO_4$-$CdWO_4$ are shown in Figure 8. Mutual solid solubility was found, but the slopes of the solvus are distinctly different. Below 700°C, an almost identical range of solid solution was found at both sides. As the temperature rises, the solid solubility of $CdWO_4$ in $CaWO_4$ increases to 10 mole percent at 750°C, to 25 mole percent at 900°C, and to 55 mole percent at 1150°C, whereas the maximum solubility of $CaWO_4$ in $CdWO_4$ in the temperature range of this investigation is 10 mole percent at 1150°C.

In a recent study, Demyanets and Tombak (1965) reported 65 mole percent $CdWO_4$ in $CaWO_4$ and $CaWO_4$ insoluble in $CdWO_4$ at 1000°C.

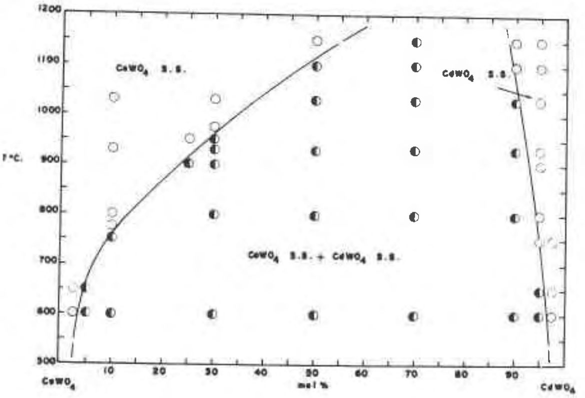

FIG. 8. Phase relations in the system $CaWO_4$-$CdWO_4$.

Since the details of that investigation are not available, a second check on the present data was conducted. A new series of compositions was made with both mixed and coprecipitated $CaWO_4$ and $CdWO_4$, and then subjected to heat treatment at 1000°C along with a sample of the solid solution $(Ca_{0.5}Cd_{0.5})WO_4$ prepared at 1150°C. Both raw materials produced similar results to those previously obtained and the solid solution dissociated into a two-phase asesmblage. This indicates that the limits of solid solubility found in the present study are reproducible and the exsolution curve established is thermodynamically univariant.

Lattice parameters of the solid solution of the scheelite-type structure were calculated and are shown as a function of composition in Figure 9. Measurements were made on samples quenched from 1150°C where maximum solid solubility was observed. Both a_0 and c_0 decrease linearly with the increasing amount of $CdWO_4$.

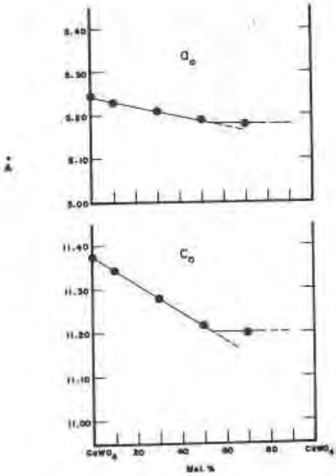

FIG. 9. Variation of lattice parameters of the scheelite-type solid solution in the system $CaWO_4$-$CdWO_4$.

DISCUSSION

It is well known that the formation of solid solution is dependent on the size, the charge, and the polarizability of the ions in the reaction. In this study where only divalent cations are actually involved, the size relationship and the relative polarizing ability become major factors in defining the limits of solid solutions. This fact is well illustrated in tungstate systems.

Where only alkaline earth cations are involved, the effect of the difference in ionic size between calcium and each of barium, magnesium, and strontium is shown by the formation of a fairly extensive range of solid solution in the Ba-rich side of the system $CaWO_4$-$BaWO_4$, very limited solid solution in the Ca-rich side of the system $CaWO_4$-$MgWO_4$, and a complete series of solid solutions above 825°C in the system $CaWO_4$-$SrWO_4$.

Nickel and manganese are two transition elements. Their ionic structures differ from that of calcium, yet the large difference in ionic size still plays the major role in shaping the phase relations in the systems. In the system $CaWO_4$-$NiWO_4$, only very limited solid solution was found, whereas in the system $CaWO_4$-$MnWO_4$, a mutual solid solution exists.

In the system $CaWO_4$-$CdWO_4$, although the divalent cations involved are almost identical in inoic size, unmixing was found up to 1150°C, and it is very likely that no complete solid solution would exist in the system since the melting point of $CdWO_4$ was observed at a slightly higher temperature of 1255°C. The large polarizing ability of the Group IIB cations compared with those of Group IIA aklaline earth cations, permits only cadmium ions to enter easily into both 8-coordinated positions in the scheelite-type structure and 6-coordinated positions in the wolframite-type structure. This fact is shown by the extensive solid solubility of $CdWO_4$ in $CaWO_4$ as compared with the very limited range of solid solution in the Cd-rich side. In the system $CaWO_4$-$ZnWO_4$, although zinc belongs to the same group as that of cadmium, the larger difference in ionic size between zinc and calcium causes relationships similar to those found in the systems with the small cations (magnesium or nickel), to prevail.

In the system $CaWO_4$-$PbWO_4$, a complete series of solid solutions is formed at a lower temperature than is found in the system $CaWO_4$-$SrWO_4$, although the difference in ionic size between calcium and lead is larger than that between calcium and strontium. This can also be attributed to the fact that lead ions are easily polarized.

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