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Solubility Limits in Binary (Ca,Mn) Chalcogenides

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Solid solubilities progressively decrease in the systems CaS-MnS, CaSe-MnSe, and CaTe-MnTe. In CaS-MnS, full solid miscibility extends from 1150° to 1500°C, the liquidus minimum. With CaSe-MnSe, this range is 1070° to 1340°C. The solid miscibility gap between CaTe and cubic MnTe intercepts the liquidus as a eutectic at 1050°C. The solid solutions follow Vegard's law closely.

I. Introduction

THE calcium and manganese chalcogenides offer an opportunity to examine the solubility limits in simple isomorphous systems. The compounds CaS, CaSe, CaTe, MnS, and MnSe possess the NaCl structure at all temperatures; MnTe, which is hexagonal (NiAs structure) at <1040°C, has the NaCl structure at high temperatures. The present work is a report on the solubility limits in the binary systems CaS-MnS, CaSe-MnSe, and CaTe-MnTe, which involve cation substitution within each system.

II. Previous Work

The Group VI-A compounds of iron and manganese have been studied^{1–8} extensively because sulfides, selenides, and tellurides are present as nonmetallic phases in steels. The compounds MnS, MnSe, and the high-temperature form of MnTe possess the NaCl-type structure, leading to easy deformation of the manganese compounds, particularly at high temperatures.⁹ In contrast, the corresponding binary iron compounds (and the low-temperature form of MnTe) are hexagonal and less readily deformed.

Manganese chalcogenides dissolve significant amounts of iron into solid solution by cation substitution.^{3–5} Previous studies of anion substitution reveal complete solubility between MnS and MnSe¹⁰ and between MnSe and the cubic form of MnTe,¹¹ very limited solubility ($\approx 1\%$) between MnS and MnO,¹² and moderate solubility (8%) between MnS and cubic MnTe.¹³

There is interest in the phase relations between manganese and calcium chalcogenides because Chao and Van Vlack¹⁴ reported that

a few percent of CaS in solution hardens MnS. This reaction has technological significance because calcium has been used to obtain "shape control" of MnS phases in rolled steel.¹⁵ Presumably this microstructural effect occurs because of solution hardening. Therefore, the extent of mutual solubility is desirable information.^{7,16–18} The present paper focuses on solubility limits in the systems Ca(VI)-Mn(VI).

Attention to the structural variations of solid solutions dates back more than 50 years, when Vegard^{19–21} studied lattice changes within mixed crystals, i.e. solid-solution compounds. Specific attention was directed to the NaCl-type compounds by Havighurst *et al.*²² They used the differences in lattice parameters and found that, if two salts with the same structure had lattice constants of a_1 and a_2 , and if

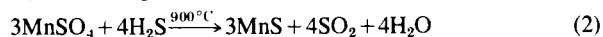
$$\delta = \frac{|(a_1 - a_2)|}{[(a_1 + a_2)/2]} \leq 0.05 \quad (1)$$

solid solutions could form. In the context of the present study, this result indicates that twice the difference in two cation sizes must be <5% of the average lattice constant, since we are considering the NaCl-type structure. However, their studies were limited to alkali halides which have predominantly ionic bonds. Work by Primak *et al.*²³ on MnS-SrS and CaS-MgS showed greater solubility. Kondrashev and Omelchenko,²⁴ who studied the systems ZnS-MgS and ZnS-CaS, concluded that the controlling effect of solid solubility was that of chemical bond type and not of radii of atoms or ions.

III. Experimental Procedures

(1) Materials Preparation

(A) *Manganese Sulfide:* MnS was prepared by reducing MnSO₄ with H₂S gas at 900°C:



According to Chao *et al.*,² it is also possible to reduce MnSO₄ by sulfur vapor.

(B) *Manganese Selenide and Manganese Telluride:* MnSe and MnTe were prepared by reacting appropriate mixtures of the elements in a vacuum-sealed borosilicate glass* tube, following the procedure established by Riewald and Van Vlack.^{25,26}

The MnS, MnSe, and MnTe were further purified by melting in a carbon crucible within a vacuum induction furnace. Microscopic

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examination of the purified compounds revealed no oxide or other extraneous phases.

(C) *Calcium Sulfide*: CaS was obtained by reducing CaO with H₂S at 1000°C:



(D) *Calcium Selenide and Calcium Telluride*: CaSe and CaTe were prepared from the elements; however, extreme care was required since the reaction is sufficiently exothermic to easily become autocatalytic and to build up temporarily high vapor pressures. This problem was avoided by slow heating and by the presence of a temperature gradient within the borosilicate glass tube. Since metallic calcium accumulates an oxidized surface when stored in the laboratory, all calcium used was cut from the interior of bulk material immediately prior to sealing in an evacuated tube with the Se or Te. Under these conditions, the calcium surface remained bright. Furthermore, there was neither microscopic nor diffraction evidence of CaO as a separate phase in the final product. Lattice parameters for CaSe and CaTe are 5.932 and 6.363 Å, respectively. (These parameters compare with 5.924 and 6.356 Å reported in X-ray diffraction tables.²⁷) As with the manganese compounds studied by Chao *et al.*¹² and Riewald and Van Vlack,^{25,26} the soluble oxygen levels in CaS, CaSe, and CaTe are expected to be very low.

Binary mixtures were prepared by grinding the selected compositions under acetone with an agate mortar and pestle. The mixtures were then pressed into 6-mm pellets with a force of ≈ 4500 N (1000 lb), giving a calculated pressure of ≈ 160 MPa (23 000 psi).

(2) Equilibration

Three procedures were used for thermal treatment, depending on the temperature. For equilibration at $< 1150^\circ\text{C}$, the samples were sealed inside evacuated silica tubes. To avoid chemical reaction, the Te samples were isolated from the SiO₂ tube by a graphite insert. The tubes were heated in a wound resistance furnace and, following equilibration, were quenched in ice water.

Since the MnTe-rich phase tends to dissociate to Mn + MnTe₂, manganese powder was also added to the opposite end of the sample tubes which contained that phase. The manganese powder was physically separated from the sample powder to prevent any possible contamination. This procedure satisfactorily avoided MnTe₂ formation, presumably through an increased manganese vapor pressure.

Samples were equilibrated at 1150° to 1400°C in an SiC resistance furnace within an atmosphere of copper-deoxidized, desiccated Ar. The specimens were placed in a 6-cavity graphite container (2.5 cm in diam.) as described by Leung.²⁸

Samples were tested at $> 1400^\circ\text{C}$ by placing the graphite sample holder in an induction furnace, where it served as the susceptor. The purified Ar atmosphere and the quenching procedures were the same as for the samples in the intermediate temperature range.²⁸ In each case, the gas train was isolated from the external atmosphere by the use of a slight positive pressure and the usual ground glass joint seals.

A noble-metal thermocouple, calibrated against a secondary standard thermocouple, was used at $\leq 1400^\circ\text{C}$. Temperatures were measured in the high-temperature range with an optical pyrometer which was calibrated against the melting temperature of MnS (1610°C). The power supply could be held constant to about $\pm 15^\circ$ within a 2-h period.

In the 1150° to 1400°C furnace, rapid cooling was achieved by pulling the sample holder into the cold end of the furnace chamber into an Ar blast. In the induction furnace, the sample temperature decreased as soon as the power was turned off so that it was $< 500^\circ\text{C}$ in ≈ 1 min; however, the specimens were not removed from the furnace until they were at ambient temperatures, to avoid surface oxidation.

(3) Sample Analyses

Phase compositions were determined by microprobe analyses. Calibrations followed the procedure of Mann,²⁹ who obtained accuracies of ± 1 mol%. Lattice constants were determined by an X-ray procedure using a Guinier-type camera with a 100-mm film cylinder. Silicon powder provided an internal standard. A computer

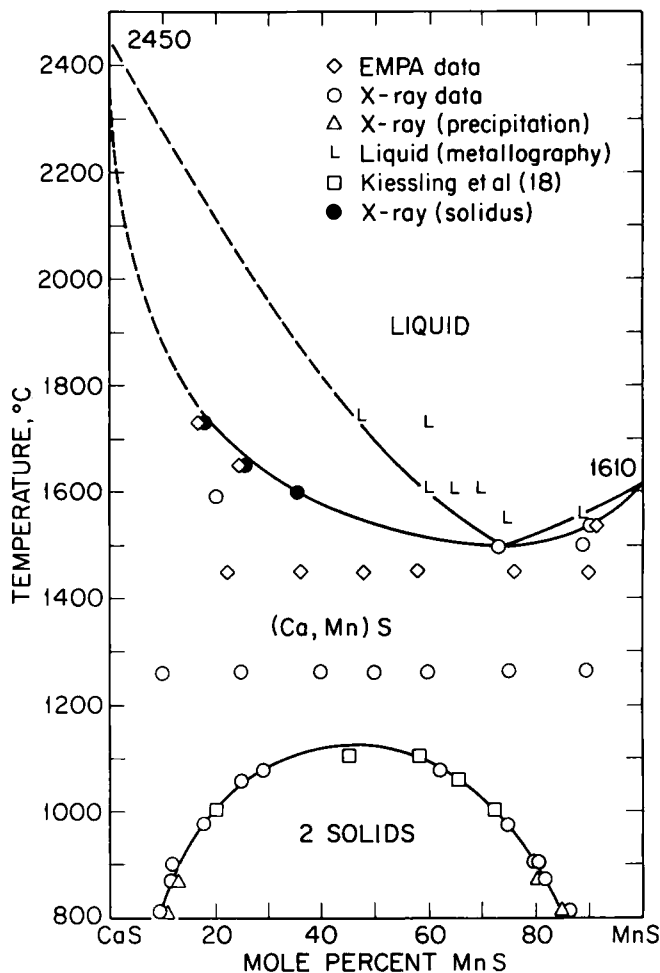


Fig. 1. The system CaS-MnS, drawn from results of this study, showing a miscibility gap and minimum melting point.

program with a LaGrange form of interpolation was used to calculate the lattice constants to ± 0.002 Å.³⁰ This variance corresponds to about ± 0.5 mol% difference in solid solubility for all systems studied. Details of the procedure and calculations involving the silicon internal standard are discussed elsewhere.²⁸

The solvus and solidus boundaries within all three systems were determined by using data obtained from the preceding analyses. Liquid-containing regions of the phase diagrams were identified by microscopic examination.

The quenching procedures were rapid enough to avoid any evidence of subsolidus phase separation. Nor was there microscopic or X-ray evidence that proeutectic solids were altered by the solidifying liquid during quenching from above the solidus.

IV. Results

(1) The System CaS-MnS

The results of this study are shown in Fig. 1. Both CaS and MnS possess the NaCl-type structure. Increased mutual solubility leads to full miscibility at 1150°C. The solvus curve is slightly skewed in the CaS direction. The two points of data from the study by Kiessling and Westman⁷ fall on the more complete solvus of our figure.

Complete miscibility exists between 1150° and 1500°C, where a minimum occurs in the liquidus at 26 CaS and 74 MnS (mol%). Higher-temperature data extend the solidus to 1730°C at 15% MnS and extrapolate the phase diagram to 2450°C, the melting temperature of CaS, according to Vogel and Heumann.³¹

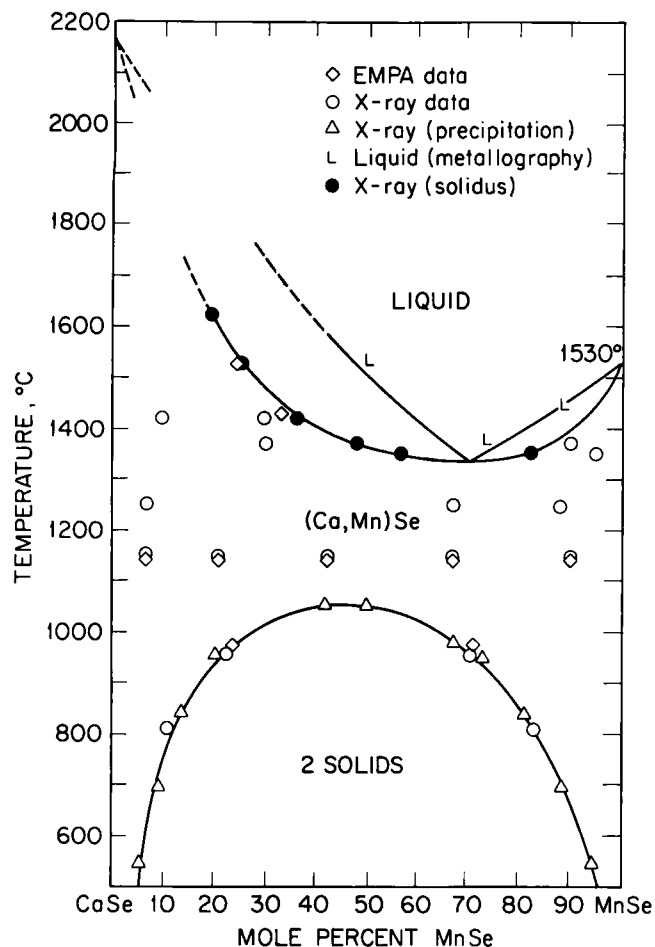


Fig. 2. The system CaSe-MnSe, drawn from results of this study, showing a miscibility gap and minimum melting point.

(2) The System CaSe-MnSe

This system parallels the system CaS-MnS very closely, but at lower temperatures. The maximum of the miscibility gap is at 1070°C, some 80° below that in the sulfide. The liquidus minimum, which is 160° below the minimum in the sulfide system, is at 1340°C and 30CaSe-70MnSe. The melting temperature for CaSe is not known; however, an extrapolation of the solidus curve suggests a value >2000°, but <2450°C, as reported for CaS.³¹

As with the sulfides, a slightly greater solid solubility occurs on the MnSe side of the miscibility gap than on the CaSe side. The phase diagram is shown in Fig. 2.

(3) The System CaTe-MnTe

The downward trend in liquidus temperatures from the sulfides to the selenides is continued to the tellurides (Fig. 3) with the result that the liquidus intercepts the miscibility gap to form a eutectic at 1050° ± 20°C (55CaTe-45MnTe). Again, as with the sulfides and the selenides, the miscibility gap between the isomorphous phases is asymmetrically located nearer the CaTe side.

The system CaTe-MnTe is complicated by the polymorphic transition of MnTe from the NaCl structure (at >1040°C) to the NiAs structure below that temperature. This transition leads to a eutectoid reaction at 800°C and 10CaTe-90MnTe. The maximum solubility of CaTe in the hexagonal polymorph is limited to ≈5 mol%.

(4) Vegard's Law

Figure 4 shows that the cation substitution produces an ideal change in the lattice parameter in the sulfide and telluride systems, since Vegard's law is followed linearly in those samples quenched from high temperature. There is a very slight, but detectable, positive variation from ideality in the selenide system.

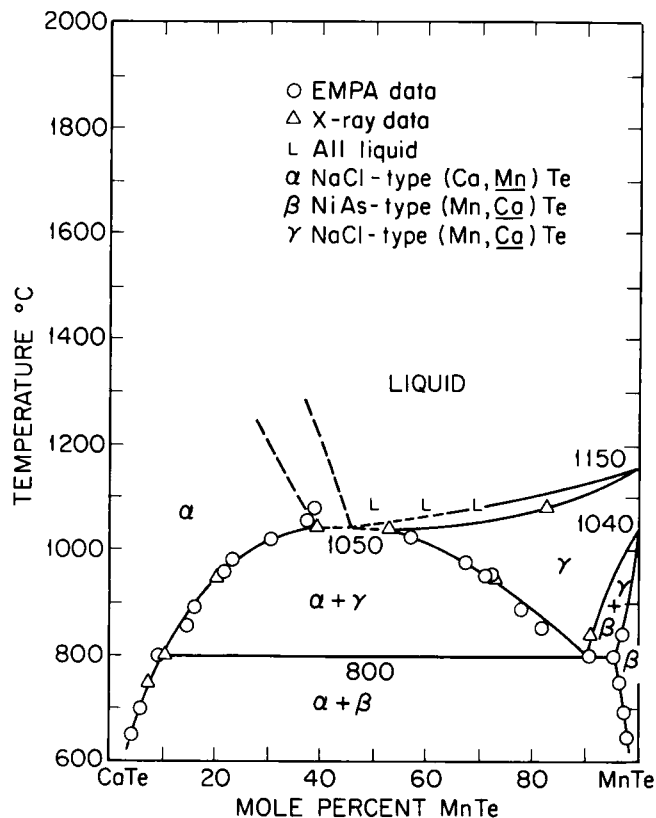


Fig. 3. The system CaTe-MnTe, drawn from results of this study, showing a eutectoid and eutectic point.

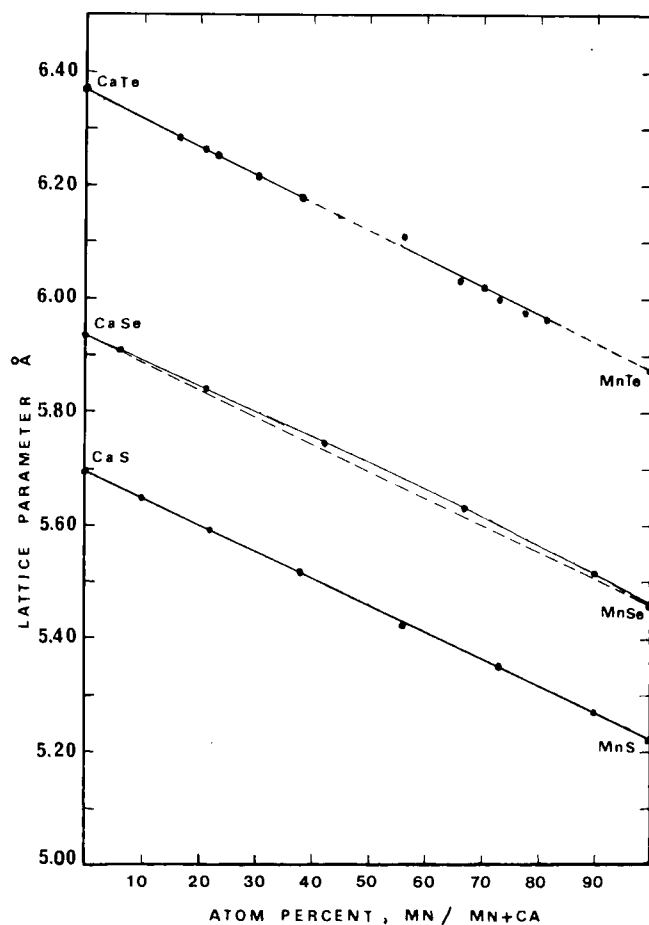


Fig. 4. Lattice parameters for cubic Ca-Mn chalcogenides. CaTe=6.363, CaSe=5.932, CaS=5.694, and MnTe≈5.875. MnSe=5.463, MnS=5.224 Å.

V. Discussion

The three binary chalcogenide systems, CaS-MnS, CaSe-MnSe, and CaTe-MnTe, may be compared directly. Except for the low-temperature form of MnTe, all solid phases are cubic NaCl. Each system possesses a solid miscibility gap; each gap is slightly asymmetric to the Ca(VI) side. Each system has a low-melting liquid with the minimum toward the Mn(VI) side. The melting temperatures drop sequentially from the sulfides to the selenides to the tellurides (and, initially, from the oxides). Likewise, the solvus temperature decreases, but less drastically than the liquidus and solidus temperatures. The solid solutions in all three systems are nearly ideal as measured by Vegard's law.

The higher melting temperatures for the Ca(VI) than for the corresponding Mn(VI) compounds may be attributed to the greater ionicity of the Ca²⁺ ion as compared to that of Mn²⁺. In the presence of nearly ideal solid solutions, this melting differential would lead to the asymmetrical solidus curve which was observed. The progressive decrease in melting temperatures from sulfides to selenides to tellurides is consistent with that of other binary compounds, such as the alkali halides in downward sequences through the periodic table. Although this decrease may also be attributed to changes in ionicity from S to Se to Te, it is probably simpler to assign this temperature trend to the increase in the atom size and, therefore, reduced coulombic attractions.

In each of the S, Se, and Te series, the lattice constant for the Ca(VI) exceeds that of Mn(VI) by $\approx 0.475 \text{ \AA}$, indicating that the radius of Ca²⁺ is consistently 0.24 \AA greater than that of Mn²⁺, independent of the anion when the anions are S, Se, and Te. This difference varies from 4.3% of the average sulfide lattice constant to 4.0% of that for the cubic telluride. This consistency probably accounts for the similarity of the solvus curves for the NaCl-type phases in each of the three systems.*

The very slight departure from Vegard's law for the selenides has no apparent explanation. Rather, it is surprising that subsolidus miscibility develops, in view of the near ideality found in all three systems. This reaction suggests that the miscibility gap arises solely from the difference in the cation size and not from Ca-Mn interactions.

VI. Conclusions

Solid solutions within the three chalcogenide Ca-Mn systems are nearly ideal with respect to Vegard's law. The miscibility gaps in the three systems permit less substitution to Mn²⁺ for Ca²⁺ than vice versa.

There is a systematic decrease in the liquidus temperatures from the sulfide to the selenide to the telluride systems. The solid misci-

bility gap also decreases, but less drastically; therefore, the liquidus and solvus intercept in the telluride system to produce a eutectic.

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*This consistency also suggests a possible miscibility gap in the system CaO-MnO. This system was not included in the present study of the Ca-Mn chalcogenides. Glasser (Ref. 32) said, "No evidence was obtained that a miscibility gap exists." It should be noted, however, that comparable systems once considered to be fully soluble have subsequently been shown to have a miscibility gap, e.g. NiO-CoO (Ref. 33) and NiO-MgO (Ref. 34).