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Phase Relations in the Alkaline Earth Fluoride-Yttria Systems

(In Three Parts)

3. The SrF_2-Y_2O_3 Phase Diagram and Information on the SrF_2-SrO System

UNITED STATES DEPARTMENT OF THE INTERIOR

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(In Three Parts)

3. The SrF_2-Y_2O_3 Phase Diagram and Information on the SrF_2-SrO System

by

Laurance L. Oden,[1] Herbert R. Babitzke,[2] and Philip E. Sanker[3]

ABSTRACT

The Bureau of Mines is developing melting data for binary combinations of the alkaline earth fluorides and yttria to facilitate the formulation of slag compositions. The present report deals with the SrF_2-Y_2O_3 system for which liquidus and solidus temperatures and solid solubilities were determined. The information is presented as the phase diagram.

The phase diagram was constructed from information obtained by ceramography, X-ray diffraction, thermal analysis, and electron probe microanalysis of small specimens encapsulated in platinum-20 percent rhodium or molybdenum ampoules. The data indicate a simple eutectic system with limited terminal solid solubilities. The eutectic temperature is 1,457°±5° C, and the eutectic composition is 4±1 mole-pct Y_2O_3.

Strontium fluoride containing up to 2 wt-pct O_2 was studied to determine the effects of oxygen contamination. Oxygen levels in excess of 0.2 wt-pct resulted in eutectic formation between SrF_2 and SrO. The eutectic composition is between 0.2 and 0.7 wt-pct O_2, and the eutectic temperature is 1,447°±5° C. No intermediate oxyfluoride phases were detected.

INTRODUCTION

This is the third and final report dealing with phase relations in the alkaline earth fluoride-yttria systems. The CaF_2-Y_2O_3 and BaF_2-Y_2O_3 phase diagrams were reported in prior publications (2-3).[4] The investigation, which is believed to be the first to deal with the SrF_2-Y_2O_3 system, was sponsored by the Bureau of Mines and conducted at the Bureau's Albany Metallurgy Research Center for the purpose of determining melting data for binary salt systems that have potential utility in electroslag melting.

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[1] Research chemist.
[2] Physical scientist.
[3] Physical science technician.
[4] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

Phase relations were determined using optical-quality, single-crystal SrF_2 and high-purity Y_2O_3. The SrF_2-SrO system was also studied to aid in determining the effects of contamination of the SrF_2 by O_2.

MATERIALS AND SAMPLE PREPARATION

Specimens were prepared by blending freshly powdered single-crystal optical-quality SrF_2 obtained from Alpha Inorganics, Inc.,[5] and a minus 100-mesh fraction of high-purity Y_2O_3 obtained from the General Electric Co. Metallic impurities in the SrF_2 were below the limits of detection by optical emission spectroscopy, and the total impurity content of the Y_2O_3 did not exceed 0.05 wt-pct. The preceding values do not include the rare-earth elements for which no analyses were performed. The oxygen level of the SrF_2 was 0.027 wt-pct,[6] which is equivalent to 0.2 mole-pct SrO. The influence of oxygen impurity is discussed later in the text. The lattice parameters of SrF_2 and Y_2O_3 were 5.7981±0.0002 A and 10.6023±0.0003 A, respectively. No extraneous substances were detected roentgenographically.

Specimen components, weighed to 0.1 mg and intimately mixed by hand grinding in an agate mortar for 15 min, were encapsulated in either platinum-20 percent rhodium or molybdenum ampoules by the method described previously (2).

DETERMINING PHASE RELATIONS

The liquidus line (fig. 1) was determined by the method of quenching. The line to 1,650° C was resolved with an estimated accuracy of ±20° C using specimens encapsulated in platinum-20 percent rhodium. Above that temperature molybdenum ampoules were used, and the data are less reliable. The specimens interacted with the molybdenum ampoules to form $SrMoO_4$, which was identified by X-ray diffraction. The quantity of $SrMoO_4$ formed was small but sufficient to require a tentative (dotted) liquidus line above 1,650° C.

It was observed that Y_2O_3 dissolved slowly in liquid SrF_2 but exsolved very rapidly on cooling. Therefore, to assure equilibrium at the temperature of interest, specimens were preheated to a higher temperature to exceed the solubility at the lower temperature and then cooled for final equilibration. The heat-treated specimens were quenched in diffusion pump oil, sectioned by diamond sawing, and mounted in Buehler 20-8130AB plastic epoxide resin under a pressure of 80 psi. Fractures and voids within the specimens were usually completely filled by the mounting resin. Polishing of mounted specimens was accomplished by abrading on successively finer SiC papers through 600 grit followed by polishing on diamond-impregnated laps through the particle size range 16 to 1/4 μm.

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[5] Reference to specific products is made to facilitate understanding and does not imply endorsement by the Bureau of Mines.

[6] Oxygen analyses, by the method of inert gas fusion, were conducted at the Reno Metallurgy Research Center of the Bureau of Mines, Reno, Nev.

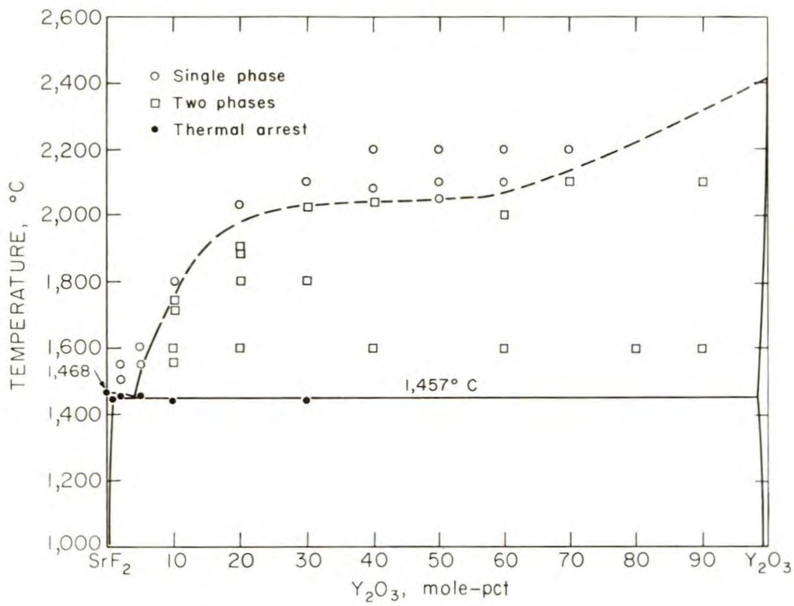

FIGURE 1. - The SrF_2-Y_2O_3 phase diagram.

The quenching procedure, although affording a very rapid cooling rate, was not sufficient to retain the phases present at temperature. On quenching, the Y_2O_3 solid solution precipitated from solution in a fine dendritic array that was easily distinguished from the solid material in equilibrium with the liquid at temperature. Figure 2 illustrates the microstructure typically observed in quenched specimens that comprised liquid plus Y_2O_3 solid solution at temperature. Note that the more dense Y_2O_3 solid solution physically separated from the liquid, an event also contributing to delayed equilibration.

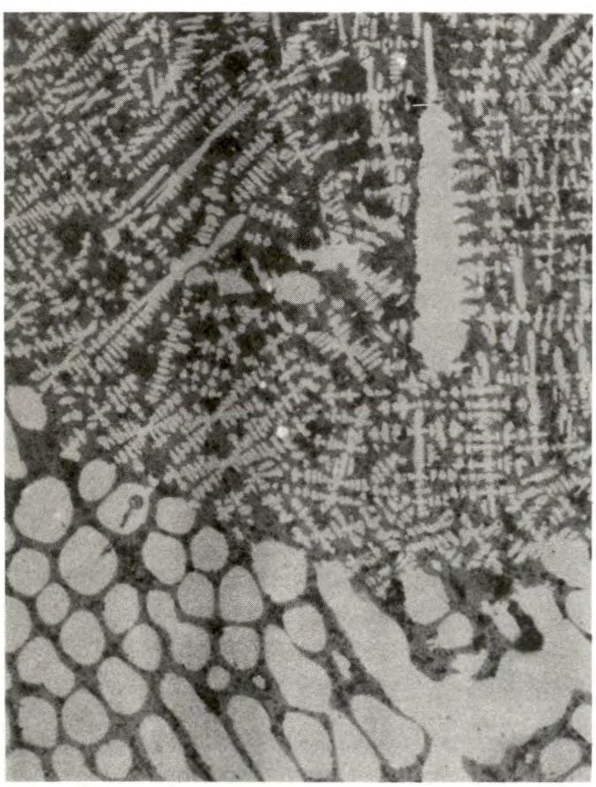

FIGURE 2. - Microstructure of specimen quenched from the liquid plus Y_2O_3 solid solution region: SrF_2-60 mole-pct Y_2O_3, heat-treated ¼ hour at 2,200° C, held ½ hour at 2,000° C, quenched in oil. Magnification X 125.

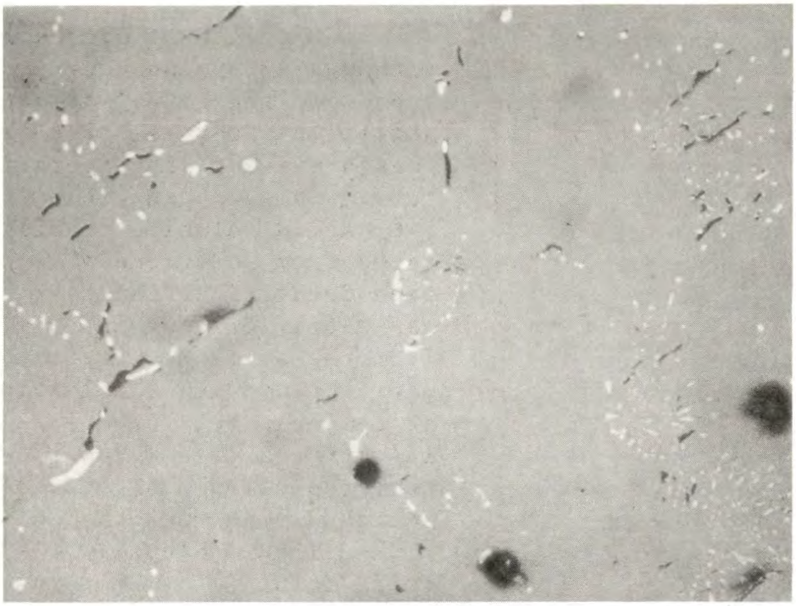

FIGURE 3. - Primary SrF_2 and eutectic structure in hypoeutectic SrF_2-1 mole-pct Y_2O_3. Magnification X 100.

Specimens rich in SrF_2 when cooled from the liquid region exhibited the eutectic structure shown in figure 3.

Eutectic structure was not always observed in hypereutectic compositions because of the tendency of Y_2O_3 to nucleate on crystallites of primary Y_2O_3 solid solution. The eutectic composition was placed at 4±1 mole-pct Y_2O_3 by observing numerous heat-treated specimens.

Differential thermal analysis (DTA) of specimens encapsulated in platinum-20 percent rhodium, as described in a previous report (1), was used to establish the eutectic isotherm at 1,457°±5° C, where the temperature is based on the IPTS of 1968. The possible error in the temperature was estimated considering thermal gradients in the furnace, interpretation of the thermograms, and possible thermocouple inaccuracy. The latter contribution to the total error was very small, as shown by thermal analysis of high-purity nickel (total metallic impurities less than 10 ppm). The observed melting point was 1,453° C, which is the accepted value. Table 1 lists the observed thermal arrests for compositions to 5 mole-pct Y_2O_3. Compositions in the range 10 to 30 mole-pct Y_2O_3 encapsulated in molybdenum were also analyzed by DTA. The eutectic isotherm, as detected at 1,436° C, was presumably decreased by $SrMoO_4$, which was observed in all specimens encapsulated in molybdenum.

The optical-quality SrF_2 was observed to freeze with considerable supercooling if rapidly cooled. However, at slower rates of cooling the tendency was less pronounced, and at 2° C/min a value of 1,468° C was recorded for the freezing point. This value compares with 1,463°±5° C reported by Porter and Brown (5) and Petit and Delbove (4), and 1,463°±1° C reported by Kojima, Whiteway, and Masson (1) before treatment of the material with HF. Hydrofluorination of SrF_2 by Kojima increased the melting point to 1,473°±1° C.

TABLE 1. - Differential thermal analysis of SrF_2-Y_2O_3

Specimen,[1] mole-pct Y_2O_3	Cooling arrest,[2] ° C	Cooling rate, ° C/min	Remarks
0	1,468	2	Isothermal arrest.
0	1,466	4	Supercooled 11° C.
0	1,470	8	Supercooled 14° C.
0	1,467	4	Pt-13Rh thermocouples, supercooled 5° C.
1	1,453	4	Isothermal arrest.
2	1,456	2	Do.
5	1,457	2	Do.

[1]All specimens were prepared from optical-grade, single-crystal SrF_2, encapsulated in platinum-20 percent rhodium and outgassed in vacuo at red heat overnight prior to sealing.

[2]Temperatures were measured with premium-grade W5Re-W26Re thermocouple wire 0.010 inch in diameter obtained from Engelhard Industries, Inc.

The terminal solid solubilities at 1,325° C were determined by electron probe microanalysis of a specimen encapsulated in platinum-20 percent rhodium containing 10 mole-pct Y_2O_3 that had been solution heat-treated at 1,550° C for 6 hr, aged 72 hr at 1,325° C, and quenched in diffusion pump oil. The Y_2O_3 and SrF_2 solid solutions contained 0.47±0.03 wt-pct Sr and 0.15±0.05 wt-pct Y, respectively. These values convert to 1.2±0.08 mole-pct SrF_2 in the Y_2O_3 and 0.11±0.04 mole-pct Y_2O_3 in the SrF_2.

EFFECTS OF OXYGEN CONTAMINATION IN SrF_2

Strontium fluoride of reagent grade or powdered optical grade was observed by thermal analysis to freeze at temperatures considerably below the value recorded for the single-crystal optical grade. X-ray diffraction analysis of the less pure materials indicated the presence of foreign material, but the pattern was insufficient for identification. Oxygen was surmised to be the source of the freezing point lowering, therefore the less pure materials were analyzed for oxygen. The results are compared with the oxygen content of single crystal SrF_2 in table 2.

The powdered SrF_2 contained appreciable adsorbed water and/or oxygen that was desorbed on heating to 600° C. Very little conversion of SrF_2 to SrO in air occurred at that temperature, but limited conversion occurred at higher temperature, as shown in the table. Specimen 8 in table 2 was analyzed by X-ray and the presence of SrO was verified.

The results of differential thermal analysis of the powdered SrF_2 materials encapsulated in platinum-20 percent rhodium ampoules are shown in table 3.

TABLE 2. - Oxygen content of SrF_2

Material	Weight loss on heating, pct	O_2,[1] pct	SrO equivalent to O_2	
			Wt-pct	Mole-pct
1. Optical-grade, single crystal[2]	As-received	0.027	0.175	0.212
2. Optical grade powder[3]	...do......	1.6	-	-
3. Reagent grade[4]	...do......	8.3	-	-
4. No. 2 heated 1 hr, 600° C in air	1.7	.85	5.5	6.3
5. No. 2 heated 7 hr, 600° C in air	1.5	.69	4.5	5.2
6. No. 2 heated 1 hr, 1,300° C in air	2.4	[5]1.3	8.4	9.4
7. No. 2 heated 1/2 hr, 1,400° C in air	2.6	[5]1.4	9.1	10.1
8. No. 2 heated 1/2 hr, 1,475° C in air	3.4	[5]2.0	13.0	13.8

[1]Analysis by method of inert gas fusion conducted at the Reno Metallurgy Research Center, Reno, Nev.

[2]Purchased from Alpha Inorganics, Inc.

[3]Purchased from Alpha Inorganics, Inc.; the oxygen content is due primarily to adsorbed water.

[4]Purchased from Mallinckrodt Chemical Co.; the oxygen content is due primarily to adsorbed water.

[5]Calculated from weight loss assuming that the optical-grade powder contained 0.7 pct O_2 as adsorbed water that was desorbed on heating.

TABLE 3. - Differential thermal analysis of SrF_2-SrO

Specimen condition[1]	SrO,[2] mole-pct	Cooling arrest, ° C	Cooling rate, ° C/min	Remarks
1. As-received	<5	1,440	4	Eutectic, supercooled 8° C.
2. Rerun	<5	1,440	2	Do.
3. Heated 1 hr, 600° C in air.	<6.3	1,472	4	Liquidus.
		1,438	4	Eutectic, supercooled 32° C.
4. Rerun	<6.3	1,475	2.5	Liquidus.
		1,439	2.5	Eutectic, supercooled 29° C.
5. Heated 7 hr, 600° C in air.	5.2	1,484	5	Liquidus.
		1,445	5	Eutectic, supercooled 32° C.
6. Rerun	5.2	1,484	4	Liquidus.
		1,441	4	Eutectic, supercooled 36° C.
7. Do	5.2	1,447	<1	Eutectic, isothermal freezing.

[1]All specimens prepared from optical-grade powder, encapsulated in platinum-20 percent rhodium, and outgassed in vacuo at red heat overnight prior to sealing.

[2]Computed from oxygen analysis.

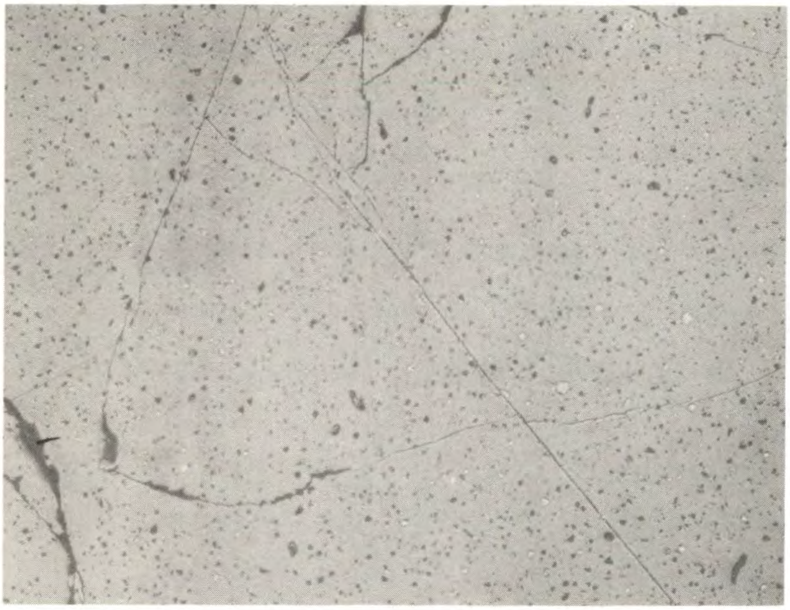

FIGURE 4. - The SrF_2-SrO eutectic structure, SrF_2-1.4 wt-pct O. Magnification X 100.

The liquidus and a thermal arrest attributed to a eutectic reaction were detected in specimens that had previously been heated to 600° C in air. Supercooling prevented accurate determination of the eutectic temperature in specimens 1 through 6 in table 3; but the problem was overcome for specimen 7 by exploiting the finite kinetics of freezing and melting of the eutectic. By alternately heating and cooling within a narrow temperature interval on either side of the eutectic temperature, a state of quasiequilibrium was obtained in which solid nuclei existed. The nuclei prevented supercooling, and isothermal freezing of the eutectic was observed.

Specimen 7 in table 2 was encapsulated as previously described, heated to 1,550° C, cooled at 20° C/min to 1,400° C, and then cooled at about 100° C/min to room temperature. The eutectic microstructure of the specimen is shown in figure 4. The composition of the specimen is apparently slightly hypereutectic. The SrF_2 matrix contained less than 0.2 wt-pct O_2, as determined by microprobe analysis.

The limited evidence presented is adequate to construct a simple eutectic phase diagram for the SrF_2-SrO system. The eutectic composition occurs within the range 0.2 to 0.7 wt-pct O_2 and 1,447°±5° C.

SUMMARY AND CONCLUSIONS

Specimens of SrF_2-Y_2O_3 were encapsulated prior to heat treatment to preclude vaporization and hydrolysis of the fluoride. Terminal solid solubilities, the eutectic point, and the liquidus to 1,650° C were determined from specimens encapsulated in platinum-20 percent rhodium ampoules. The liquidus from 1,650° to 2,200° C, which is considered tentative, was determined from specimens encapsulated in molybdenum. Interaction between specimens and the molybdenum occurred at high temperatures to produce $SrMoO_4$.

No amorphous phases were observed in specimens quenched from the single-phase liquid region. In hypereutectic specimens fine dendrites of Y_2O_3 solid solution formed, and eutectic structure was not observed due to a pronounced tendency of Y_2O_3 to nucleate on primary dendrites. Such behavior, indicative of highly mobile cations in the liquid phase, was not expected in view of the high ratio of charge to radius for the trivalent yttrium ion (r = 0.98 A; Z/r = 3.06).

Oxygen contamination of SrF_2 results in formation of a eutectic at 1,447°±5° C in the composition range 0.2 to 0.7 wt-pct O_2. The liquidus temperature increases rapidly with oxygen content in excess of the eutectic composition. In SrF_2 of purity likely to be encountered in the laboratory the oxygen content exceeds the eutectic composition, and eutectic melting could be misinterpreted as fusion of the SrF_2. One lot of reagent-grade material contained 8.3 wt-pct O_2 of which over 90 pct was evolved on heating to 600° C. The fluoride is very resistant to hydrolysis in air at temperatures to 600° C.

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