RI 7437

Bureau of Mines Report of Investigations/October 1970

Phase Relations in the Alkaline Earth Fluoride-Yttria Systems

(In Three Parts)

1. The CaF_2-Y_2O_3 Phase Diagram

UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 7437

Phase Relations in the Alkaline Earth Fluoride-Yttria Systems

(In Three Parts)

1. The CaF_2-Y_2O_3 Phase Diagram

By Laurance L. Oden, Philip E. Sanker,
Herbert R. Babitzke, and Donald H. Sumner

MARCH 3, 1849

UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

This publication has been cataloged as follows:

Oden, Laurance L

Phase relations in the alkaline earth fluoride-yttria systems (in three parts). 1. The CaF_2-Y_2O_3 phase diagram, by Laurance L. Oden [and others. Washington] U.S. Dept. of the Interior, Bureau of Mines [1970]

10 p. illus., table. (U.S. Bureau of Mines. Report of investigations 7437)

Includes bibliography.

1. Calcium fluoride. 2. Yttrium oxide. 3. Slag. 4. Phase diagrams. I. Title. (Series)

TN23.U7 no. 7437 622.06173

U.S. Dept. of the Int. Library

CONTENTS

ILLUSTRATIONS

TABLE

PHASE RELATIONS IN THE ALKALINE EARTH FLUORIDE-YTTRIA SYSTEMS

(In Three Parts)

1. The CaF_2-Y_2O_3 Phase Diagram

by

Laurance L. Oden,[1] Philip E. Sanker,[2] Herbert R. Babitzke,[1] and Donald H. Sumner[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 CaF_2-Y_2O_3 system for which solidus and liquidus temperatures and solid solubilities were determined. The information is presented as the phase diagram.

All specimen compositions were blended from high-purity materials and encapsulated in Mo or Pt20Rh prior to heat treatment. Liquidus temperatures were determined by ceramographic examination of heat-treated and quenched specimens. Solidus temperatures were determined by differential thermal analysis and by electron microprobe analysis of quenched specimens. Terminal solid solubilities were derived by parametric methods.

The peritectic system was found to be pseudobinary due to the formation of yttrium oxyfluoride at temperatures near the liquidus. The peritectic point occurs at 7 mole pct Y_2O_3 and 1,438°±5° C. The terminal solid solubility of Y_2O_3 in CaF_2 decreases from 7 mole pct at 1,438° C to 1 mole pct at 1,100° C, and the solubility of CaF_2 in Y_2O_3 decreases from 9.5 to 7 mole pct over the same temperature interval.

INTRODUCTION

Combinations of the alkaline earth fluorides and yttria contain potentially useful compositions for slag melting metals by both conventional and electroslag techniques. However, basic information on melting points and electrical properties needed to predict performance of the slags is generally not available. The present investigation was undertaken to develop melting data for the alkaline earth fluoride-yttria systems, and this report deals with CaF_2-Y_2O_3. The data are presented as the equilibrium diagram shown in

---

[1] Research chemist.

[2] Physical science technician.

[3] Chemist.

Authors are with the Albany Metallurgy Research Center, Bureau of Mines, Albany, Oreg.

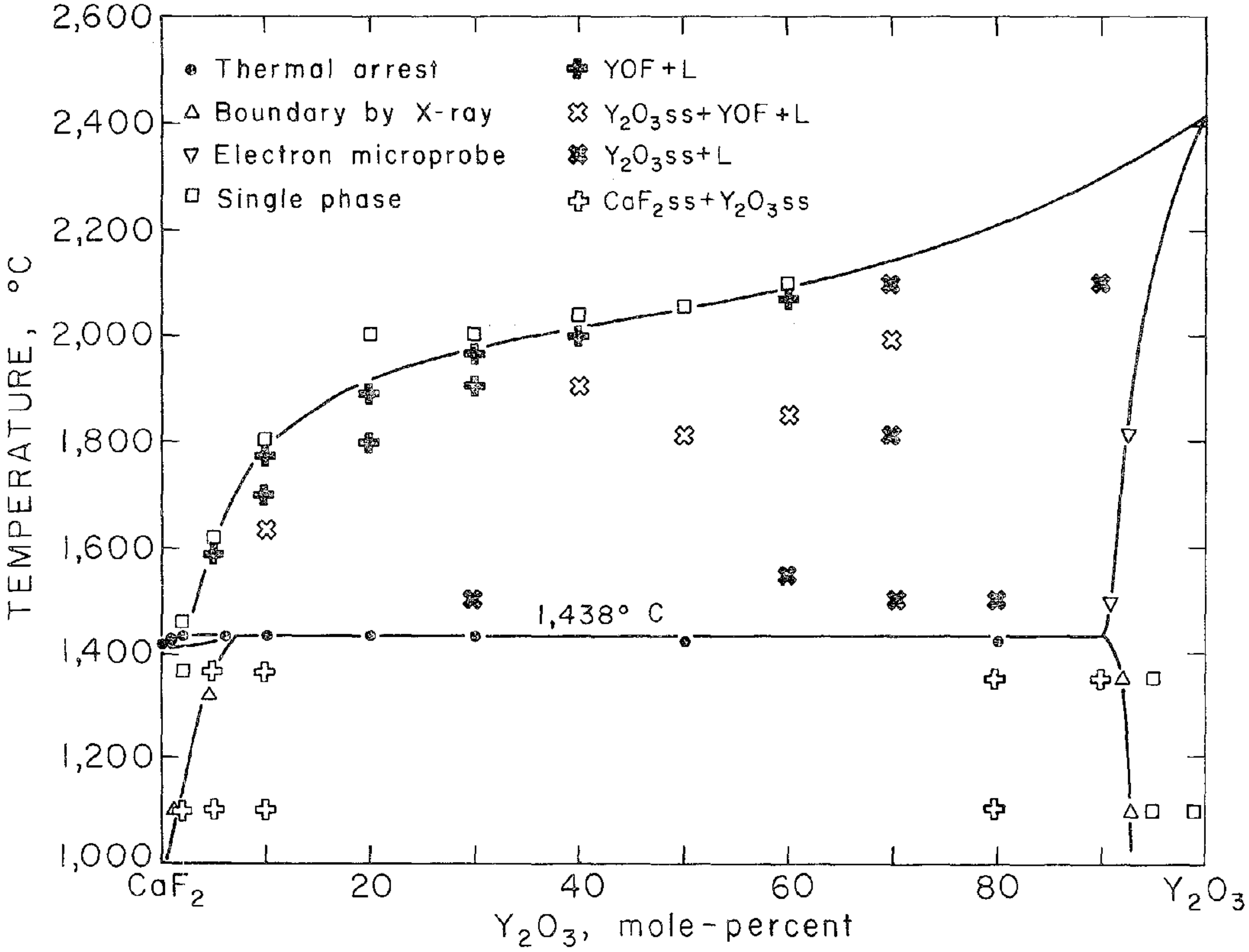

FIGURE 1. - The CaF_2-Y_2O_3 Phase Diagram.

figure 1. Phase relations, determined using optical quality CaF_2, were reinvestigated with reagent-grade CaF_2 as a first step toward approximating the impurity levels encountered in slag melting applications.

This investigation, sponsored by the Bureau of Mines and conducted at the Bureau's Albany Metallurgy Research Center, is believed to be the first to deal with phase relations in the CaF_2-Y_2O_3 system. Reports to follow will deal with BaF_2-Y_2O_3 and SrF_2-Y_2O_3.

MATERIALS

Specimen compositions were prepared from the minus 100-mesh fraction of high-purity yttria obtained from the General Electric Co.[4] and optical-quality CaF_2 from the Harshaw Chemical Co. No metallic impurity in the Y_2O_3, as determined by optical emission spectroscopy, exceeded 100 ppm. The principal metallic impurities in the CaF_2, determined by the same method, were 1,000 ppm Y,

---

[4] Reference to specific brands or producers is made to facilitate understanding and does not imply endorsement by the Bureau of Mines.

500 ppm Al, 50 ppm Fe, 50 ppm Ti, and 20 ppm Si. The above analyses did not include the rare earths for which no analyses were performed. X-ray diffraction analysis of the starting materials revealed no extraneous substances.

The oxygen level of the CaF_2 was determined directly to be 0.024 wt pct by the method of inert gas fusion.[5] This value is nearly stoichiometrically equivalent to the yttrium level. The combined yttrium and oxygen contents, although seemingly high, correspond to less than 0.05 mole pct Y_2O_3. This value is within the experimental weighing uncertainty for the 1 mole pct Y_2O_3 specimen.

The reagent-grade CaF_2, obtained from the J. T. Baker Chemical Co., contained 500 ppm Al, 10 ppm each of Fe and Si, and 0.85 wt pct oxygen. This oxygen level converts to 3.9 mole pct CaO after subtracting the oxygen equivalent to the metallic impurities present.

EXPERIMENTAL PROCEDURES AND RESULTS

Specimen compositions were prepared by hand mixing the pure materials, weighed to 0.1 mg, in an agate mortar for about 15 minutes. The materials were alternately ground and scraped from the sides of the mortar to achieve mixing.

Encapsulation

To preclude hydrolysis or evaporation at high temperatures, all specimens were encapsulated in either Mo or Pt20Rh alloy prior to heat treatment.

Encapsulation in Mo was accomplished by tamping the premixed powders into small Mo cylinders, adding a Mo plug, and sealing the capsules by arc welding under He gas at 20 inches absolute pressure. The Mo cylinders were drilled from 1/4-inch-OD rod stock. Wall and bottom thicknesses were 0.030 inch and 0.125 inch, respectively. Depth was about 0.375 inch, and the plug or lid was about 0.125 inch long. The capsules were cleaned prior to use by heating them to 1,850° C in a vacuum of 10^{-6} torr, and the capsules and their contents were outgassed in vacuo for 12 hours at 400° C prior to sealing. The capsules held about 250 mg of samples, depending on the density of the composition and the degree of compaction.

The premixed powders were also sealed within Pt20Rh alloy tubing. Encapsulation was accomplished by placing the sample in a tube having one end closed, crimping the tube above the sample, and cutting the tube with an oxyhydrogen flame. The powders were carefully outgassed in situ prior to sealing by heating them to about 600° C in vacuo at about 10^{-6} torr. The vacuum was maintained during the cutting operation and contributed to the success of the method.

---

[5] Oxygen analyses were done at the Reno Metallurgy Research Center of the Bureau of Mines, Reno, Nev.

The possibility of contamination of the specimens by the Mo capsules was investigated by measuring the lattice parameter of the optical quality CaF_2 before and after exposure to Mo at 2,000° C. The lattice parameter was 5.4637A±0.0005 before exposure and 5.4635A±0.0002 after exposure, evidence that interaction between the specimens and capsules can be ignored.

The Solidus

The solidus was determined by differential thermal analysis (DTA) and by electron microprobe analysis of heat-treated specimens. Selected compositions listed in table 1 were encapsulated in Mo or Pt20Rh alloy, heattreated to achieve equilibrium above the solidus temperature, and subjected to DTA. Heating and cooling rates of 2° to 8° C per minute were obtained in a model 300 Brew furnace having a split-tube tantalum heating element. The furnace was powered by a programable saturable core reactor, and temperatures to about 2,000° C could be attained.

All thermal analyses were conducted in vacuo using either W3Re-W25Re[6] or Pt-Pt13Rh thermocouples. A reference body of Mo (required in DTA) and the encapsulated specimen were spot-welded to the thermocouple wires and suspended side-by-side within a larger Mo cylinder which occupied the hot zone of the furnace. The cylinder, 5 inches long with 0.125-inch walls, served to minimize thermal gradients. Longitudinal thermal gradients were further reduced by placing two heat shields immediately above and below the sample and reference bodies.

Thermal arrests for any given specimen composition were reproducible within the limits of interpretation of the DTA curves. The solidus temperatures listed in table 1 are the temperatures taken from the cooling curves at which ΔT first departed from constancy. These temperatures were the most reproducible points on the DTA curves. The freezing point of optical-quality CaF_2 could not be measured by DTA because of pronounced supercooling (up to 39° C at a cooling rate of 4° C per minute). Therefore, the temperature listed in table 1 is the observed melting point. This temperature compares with values from 1,392° to 1,423° C reported in the literature (<u>3</u>-<u>4</u>).[7]

The accuracy of the W3Re-W25Re thermocouple wire was determined by analyzing high-purity nickel in the DTA furnace. The nickel, containing 10 ppm total metallic impurities, melted at 1,450° C, indicated temperature, in triplicate analyses as compared to the accepted value of 1,453° C. The correction was added to all temperatures reported in table 1. The possible error of the reported temperatures is estimated to be less than ±5° C. This value was derived considering thermal gradients in the DTA furnace, interpretation of the thermograms, and possible thermocouple inaccuracy.

---

[6] Premium-grade W3Re-W25Re thermocouple wire 0.010 inch in diameter obtained from Engelhard Industries, Inc.

[7] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

TABLE 1. - Results of differential thermal analysis

Composition, mole pct Y_2O_3	Capsule	Cooling rate, ° C per minute	Cooling arrest, ° C
CaF_2	Pt20Rh	4	[1]1,418
CaF_2[2]	-	-	1,423
CaF_2	Mo	2	[1]1,417
1	Mo	8	1,421
2	Mo	4	1,438
5	Pt20Rh	8	1,438
5	Mo	8	1,440
10	Mo	8	1,437
20	Mo	8	1,433
30	Mo	8	1,437
50	Mo	8	1,433
80	Mo	8	1,421

[1] Melting point.

[2] Datum from Mitchell (3).

Thermograms of specimens containing 1 and 2 mole pct Y_2O_3 did not indicate isothermal melting (or freezing), whereas a definite isotherm was observed for the specimens containing 5 to 80 mole pct Y_2O_3. No indications of the liquidus temperature beyond the peritectic point were observed by DTA, and this was attributed to the steeply rising liquidus curve. The results of thermal analysis definitely indicate an increase in the melting point of CaF_2 with Y_2O_3 addition and suggest a peritectic system.

Two additional points on the solidus curve were obtained by electron microprobe analysis of specimens containing 30 and 70 mole pct Y_2O_3 that had been equilibrated at 1,505° C and 1,815° C, respectively. The Y_2O_3 solid solution phase was found to be homogeneous in both specimens and contained 9.2 mole pct CaF_2 at 1,505° C and 7.2 mole pct at 1,815° C, where the uncertainty of the compositions is less than 10 percent of the amount present. The analytical values obtained for calcium and fluorine were consistent with a simple solution of CaF_2 in Y_2O_3.

The Liquidus

The liquidus between 2 and 70 mole pct Y_2O_3 was determined by ceramographic examination of specimens which were heattreated and then quenched in diffusion pump oil. Representative data points defining the liquidus are entered on figure 1.

All samples after heat treatment were porous or fractured to some degree; therefore, specimens for ceramographic examination were mounted in Buehler 20-8130AB plastic epoxide resin under a pressure of 80 psi. Nearly complete filling of all voids was achieved at that pressure. The mounting resin could be distinguished by its continuous character from the phase rich in CaF_2. Polishing of mounted specimens was accomplished by abrading on successively finer SiC papers through size 600 grit followed by polishing on successively finer diamond-impregnated laps through the particle size range 16 to 1/4 micron.

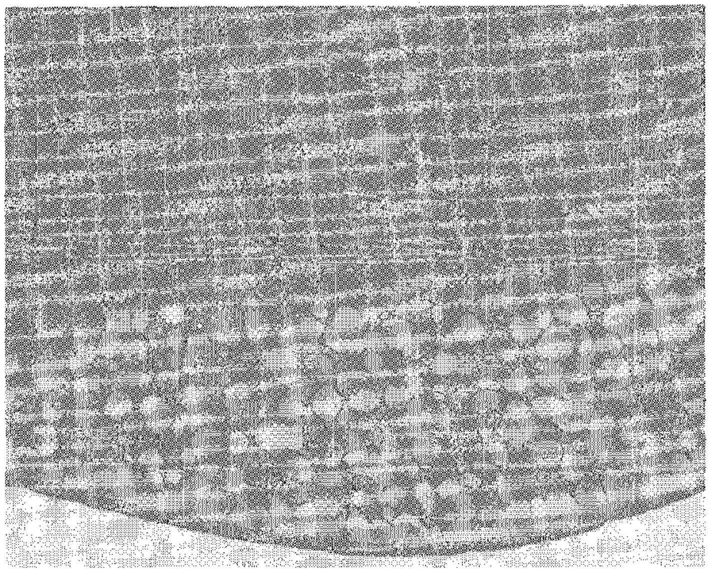

FIGURE 2. - Separation of Phases Due to Difference in Densities: CaF_2-20 Mole Pct Y_2O_3 Heat-treated 2½ Hours at 1,880° C, Quenched in Oil, X 50.

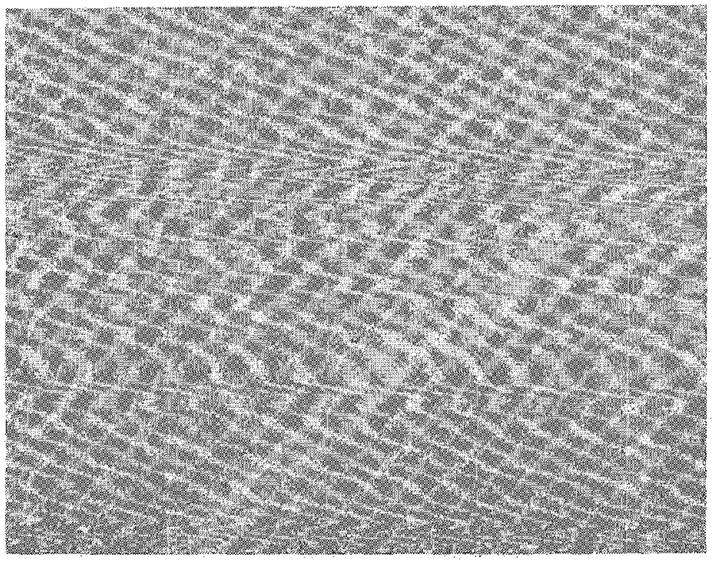

FIGURE 3. - Microstructure of Specimen Quenched From the Liquid Region: CaF_2-10 Mole Pct Y_2O_3 Heattreated 1¼ Hours at 1,870° C, Quenched in Oil, X 150.

It was observed that Y_2O_3 dissolved slowly in both solid and liquid CaF_2 but precipitated from solution rapidly. Therefore, heat treatments were preceded by a short treatment at higher temperatures to assure an excess of Y_2O_3 in solution at the lower temperature. Within the region between isotherm and liquidus, the solid phases were more dense than the liquid and settled to the bottom of the capsule during heat treatment. This separation of phases inhibited dissolution of the Y_2O_3, an additional reason for preheating specimens above the final soaking temperature. Figure 2 shows the separation of phases typically observed at temperatures between the isotherm and liquidus. The gray continuous phase distributed near the center of the photograph is mounting resin.

Figure 3 illustrates the microstructure observed in specimens which were quenched from the liquid region. It is apparent that the Y_2O_3 solid solution (SS) precipitated as fine dendrites during cooling of the specimen.

Specimens between 5 and 60 mole pct Y_2O_3 that were equilibrated at temperatures near but below the liquidus line contained a phase which appeared as the cores of larger particles shown in figure 4. The cored particles were concentrated in the bottoms of the Mo crucibles, an indication that, at temperature, they were solid, more dense than the liquid. The cores were analyzed by the electron microprobe and found to contain 5.2 wt pct Ca, 12.5 wt pct F, and about 68 wt pct Y; the remainder was assumed to be oxygen. The observed weight ratio of

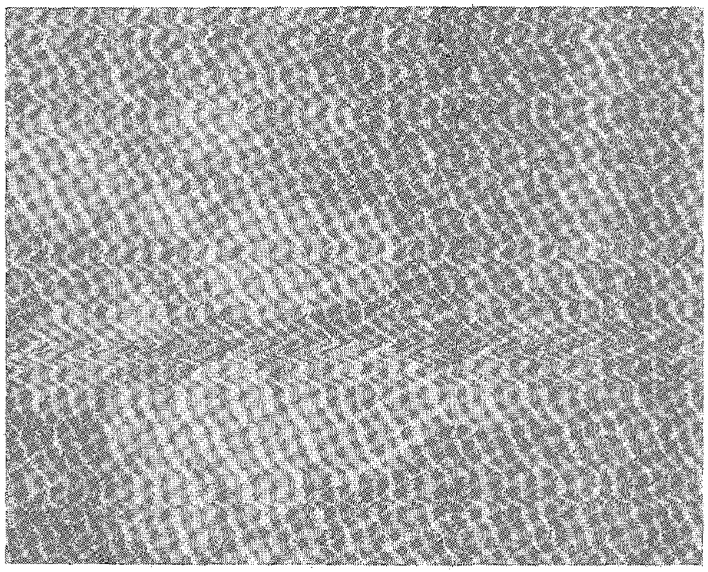

FIGURE 4. - Cored Particles Observed Below the Liquidus Temperature: CaF_2-30 Mole Pct Y_2O_3 Heattreated 2½ Hours at 1,905° C, Quenched in Oil, X 150.

Ca to F is 0.416, whereas the ratio in CaF_2 is 1.05. This indicates that the cores are not composed of a linear combination of CaF_2 and Y_2O_3 but contain more fluorine than provided by CaF_2. The fringe of the cored particles and the small dendrites were also analyzed by the microprobe and contained 2.7 wt pct Ca, 1.9 wt pct F, and 77 wt pct Y. The observed ratio of Ca to F is 1.42, which is larger than the ratio for CaF_2. Therefore, it is likely that CaF_2 reacted with Y_2O_3 at high temperature in an exchange reaction to produce CaO and YF_3. The CaO solidified with the Y_2O_3 on cooling, and the YF_3 reacted with either or both CaF_2 and Y_2O_3 to form a separate phase. Both YF_3-CaF_2 (5-6) and YF_3-Y_2O_3 (1, 7) compounds have been reported in the literature. The YF_3-CaF_2 compounds have melting points much too low to be the cores observed here, but the YF_3-Y_2O_3 compounds ($3YF_3 \cdot 2Y_2O_3$ and $YF_3 \cdot Y_2O_3$) are distinct possibilities.

On the basis of the microprobe results, the composition of the cores was calculated to be 10.1 wt pct CaF_2, 19.3 wt pct YF_3, and 70.5 wt pct Y_2O_3. On a molar basis this is 22.6 mole pct CaF_2, 23.1 mole pct YF_3, and 54.3 mole pct Y_2O_3. The molar ratio is approximately 1:1:2, respectively. The observed stoichiometry of the cores agrees with the compound $YF_3 \cdot Y_2O_3$ if CaF_2 is substituted for one-half of the YF_3 in the formula; that is, $1/2CaF_2 \cdot 1/2YF_3 \cdot Y_2O_3$. Substitution may occur as the result of solid solubility, or the composition may represent a ternary compound.

The compound $YF_3 \cdot Y_2O_3$ has two allotropic forms: at temperatures to 571° C it is rhombohedral, and above that temperature to the melting point at 2,020° C, it is cubic (1). This information is consistent with the observation of a transformed structure in the cores of the particles. Evidence of a transformation is visible in figure 4, but a better illustration of the transformed structure was obtained at higher magnification. Figure 5 is an electron micrograph at 2,700 magnification of a specimen of CaF_2-10 mole pct Y_2O_3 which was cooled slowly to room temperature. Note the Y_2O_3SS, which displays the scratches incurred during polishing; the ternary phase, which is transformed in a eutectoidlike structure; and the CaF_2SS, which has a wavy appearance.

One component of the eutectoidlike structure is definitely known to be CaF_2. It was surmised that CaF_2 substituted for YF_3 in the cubic modification

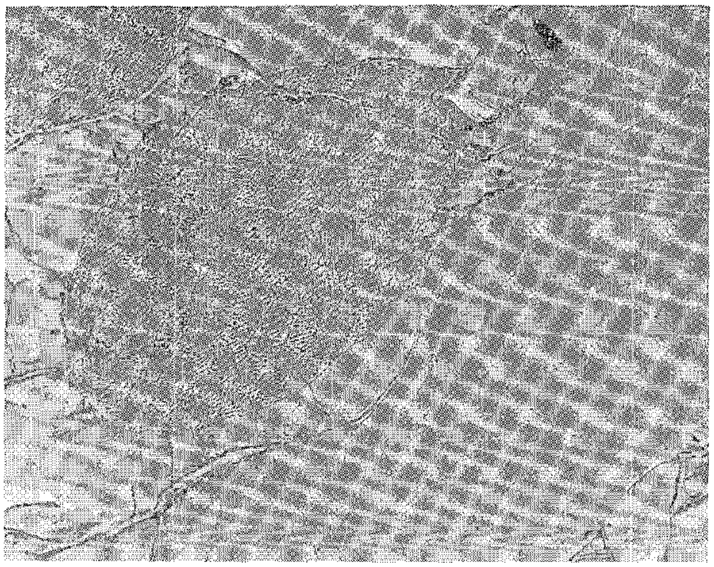

FIGURE 5. - Transformed Structure of the Ternary Phase: CaF_2-10 Mole Pct Y_2O_3 Heat-treated 1 Hour at 1,820° C, 1 Hour at 1,460° C, and Cooled Slowly, X 2,700.

of $YF_3 \cdot Y_2O_3$ but was rejected from the rhombohedral structure at lower temperatures in what appears to be an eutectoid reaction. This supposition is in harmony with the observation that the transformation temperature of $YF_3 \cdot Y_2O_3$ was increased from 571° C for the stoichiometric compound to 790° C with the addition of 20 mole pct CaF_2. The phase region in which the ternary compound and liquid coexist consists of a thin band immediately below the liquidus, and this band is separated from the Y_2O_3SS + liquid region by a three-phase region in which the ternary compound, Y_2O_3SS, and liquid coexist. The boundaries have not been drawn on figure 1 because they were not sufficiently defined, but the data indicate the approximate positions of the boundaries. Note that the appearance of the ternary compound renders the CaF_2-Y_2O_3 system pseudobinary.

The position of the liquidus was unchanged, within the experimental uncertainty, by the substitution of reagent-grade CaF_2 for the optical-quality material. The uncertainty of the W3Re-W25Re thermocouple and the temperature variation of the furnace during heat treatment contributed to a possible error of ±25° C in the liquidus boundary.

Solid Solubilities

Terminal solid solubilities at 1,100° and 1,350° C were determined by the parametric method. Samples containing progressively increasing proportions of the minor component were heattreated at 1,800° C for 2 hours to exceed the solubility at lower temperature and then quenched to 1,100° or 1,350° C and held for at least 20 hours. Following the heat treatment, the specimens were quenched to room temperature and analyzed by X-ray diffraction using CuKα radiation (45KV, 35 ma, Ni filter). The diffraction data were reduced to a_0 values by standard techniques (2), and the a_0 values were plotted versus composition of the specimen for each temperature. The point on each curve at which the slope changed to zero was interpreted as the limit of solid solubility, and these values are plotted in figure 1. The smooth solubility curves from 1,000° C to the peritectic temperature were calculated by assuming that the log of the solubility, expressed in mole percent, was proportional to the reciprocal of the absolute temperature.

The terminal solid solubility of Y_2O_3 in reagent-grade CaF_2 was also determined to assess the effect of oxygen in the reagent-grade material. The results were identical within the experimental uncertainty (±0.5 mole pct).

DISCUSSION

The CaF_2-Y_2O_3 system was found to be pseudobinary due to the formation of a ternary phase which was observed over a wide range of CaF_2-Y_2O_3 compositions. The phase was found in equilibrium with the liquid at temperatures near the liquidus, and it decomposed on cooling into an eutectoidlike structure. The ternary phase was tentatively identified as $CaF_2 \cdot YF_3 \cdot 2Y_2O_3$ on the basis of its thermal behavior and by electron microprobe analysis.

The phase diagram was constructed as a peritectic, although a typical peritectic microstructure was never observed. The peritectic reaction seems most probable in view of the fact that Y_2O_3 increases the melting point of CaF_2 and is more soluble in solid than in liquid CaF_2 at temperatures near the isotherm. The phase relations as determined using optical-quality CaF_2 were unchanged, within the experimental uncertainty, by the impurities present in reagent-grade CaF_2.

The absence of Y_2O_3 dendrites in regions surrounding primary or undissolved Y_2O_3 particles in specimens quenched rapidly from temperatures above the isotherm is indicative of highly mobile Y(+3) and O(-2) ions. This observation is opposite to that predicted from the ratios of charge to radius for the two ions, which values are higher than the corresponding ratios for Ca(+2) and F(-1) ions.

The terminal solid solubilities are probably enchanced by the similarity of crystal ionic radii:

Y(+3) = 0.92A compared with Ca(+2) = 0.99A,

and O(-2) = 1.32A compared with F(-1) = 1.33A.

Parametric measurements showed that Y_2O_3 contracted the CaF_2 lattice, thereby indicating a substitutional solid solution wherein Y(+3) replaced Ca(+2) on the cation lattice sites. Electroneutrality then requires vacancies in the anion lattice. The addition of CaF_2 expanded the lattice of Y_2O_3, suggesting the substitution of Ca(+2) on Y(+3) lattice sites and requiring occupation of interstitial positions by one-fourth of the F(-1) ions.

REFERENCES[8]

1. Banks, C. V., O. N. Carlson, A. H. Daane, V. A. Fassel, R. W. Fisher, E. H. Olson, J. E. Powell, and F. H. Spedding. Studies on the Preparation, Properties, and Analysis of High Purity Yttrium Oxide and Yttrium Metal at the Ames Laboratory. USAEC Res. and Devel. Rept. IS-1, July 1959, pp. 43-44.

2. Cullity, B. D. Elements of X-Ray Diffraction. Addison-Wesley, Reading, Mass., 1959, pp. 324-344.

3. Mitchell, A. The CaF_2-CaC_2 System, and Its Relation to Electroslag Remelting Practice. Trans. AIME, v. 242, 1968, pp. 2507-2511.

4. Porter, Bernard, and E. A. Brown. Melting Points of Inorganic Fluorides. J. Am. Ceram. Soc., v. 45, No. 1, January 1962, p. 49.

5. Short, J. M., and R. Roy. Confirmation of the Defect Character in Calcium-Fluoride-Yttrium Fluoride Crystalline Solutions. J. Phys. Chem., v. 67, 1963, pp. 1860-1861.

6. Sobolev, B. P., E. G. Ippolitov, B. M. Zhigarnovskii, and L. S. Garashina. (Phase Composition of Systems CaF_2-YF_3, SrF_2-YF_3, and BaF_2-YF_3.) Izv. Akad. Nauk SSSR, Neorgan. Materialy (Russian), v. 1(3), 1965, pp. 363-368.

7. Zachariasen, W. H. Crystal Chemical Studies of the 5f Series of Elements. XIV. Oxyfluorides, XOF. Acta. Cryst., v. 4, 1951, p. 231.

---

[8] Title enclosed in parentheses is translation from the language in which the item was published.

INT.-BU.OF MINES,PGH.,PA. 15320