

as a high-level dosimeter is in progress at this Laboratory.<sup>21</sup>

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## CONFIRMATION OF DEFECT CHARACTER IN CALCIUM FLUORIDE-YTTRIUM FLUORIDE CRYSTALLINE SOLUTIONS<sup>1</sup>

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Interstitial  $F^-$  is the predominant defect in crystalline solutions of  $YF_3$  in  $CaF_2$ , according to a comparison of measured pycnometric densities with calculated X-ray densities over the range 0–40 mole %  $YF_3$ . The phase diagram of the system  $CaF_2$ – $YF_3$  has been determined tentatively, and the influence of the defects is evident in the unusual maximum in the liquidus and a sharp drop in thermal stability near the solubility limit of 55 mole %  $YF_3$ . A new hexagonal phase with composition near  $CaF_2 \cdot 4YF_3$  is described, with  $a = 6.77 \text{ \AA}$ . and  $c = 6.98 \text{ \AA}$ .

### Introduction

Vogt<sup>2</sup> investigated the mineral yttrifluorite and found it to consist of a crystalline solution of 0–50 mole %  $YF_3$  in  $CaF_2$ . Goldschmidt<sup>3</sup> hypothesized that this ionic solution attained charge balance by containing interstitial  $F^-$ . Such a high concentration of point-defects in an ionic solid solution is quite extraordinary, but a density determination by Zintl and Udgard<sup>4</sup> on an artificial preparation apparently supported this hypothesis. However, in view of the relative lack of precision of their single observation (see Fig. 1) on a preparation heavily contaminated (over 10%) with rare earths and which was heated under oxidizing conditions, it seemed desirable to re-examine the nature of this unusual defect crystalline solution and to determine its saturation limit. Also, the current interest in doped  $CaF_2$  as laser host materials makes the determination of absolute defect configurations essential.

### Experimental

**Materials.**—Yttrium fluoride, 99.9% pure (m.p. determined as  $1142^\circ$ ), from Research Chemicals Co., Burbank, California, was pre-dried under purified nitrogen at  $800^\circ$ . Calcium fluoride, reagent grade (m.p. determined as  $1394^\circ$ ), from J. T. Baker Co., was similarly pre-dried at  $1000^\circ$ . Single crystals of  $CaF_2$ – $YF_3$  crystalline solutions were prepared by melting mixtures at  $1450^\circ$  in sealed platinum tubes, cooling slowly, and annealing at  $800^\circ$ . Other samples were allowed to react as powder mixtures in sealed platinum tubes at  $1050^\circ$  for 2–3 days. Special care was taken to exclude oxygen during all high-temperature stages of preparation of the solutions.

**Density Measurements.**—The densities of the single crystals were measured by the sink-float technique of adjusting the specific gravity of aqueous heavy liquid solutions, made after the method of Sullivan<sup>5</sup> from thallium malonate and thallium formate, until the crystals would remain suspended upon centrifugation and then determining the specific gravity of the liquid with a pycnometer. The crystalline solutions which had the highest  $YF_3$  content had densities too high for these liquids; in those very high in  $CaF_2$  the viscous melt tended to entrap air bubbles.

X-Ray powder measurements were made by standard proced-

ures on a Norelco diffractometer, using Si as an internal standard for lattice parameter measurements. All samples were pre-treated in sealed platinum or gold tubes. Calibrated platinum–rhodium thermocouples were used for temperature measurement.

**Phase Diagram.**—The solubility limit and the compound composition were established with X-ray and liquidus measurements. Liquidus temperatures were determined visually to  $\pm 10^\circ$  with a platinum-resistance strip-furnace which was equipped with an optical pyrometer and microscope. The strip-furnace was calibrated relative to the melting points of  $CaF_2$  and  $YF_3$  which were redetermined precisely in sealed platinum tubes by quenching from a tube-furnace in a series of successively higher temperature runs.

### Results and Discussion

**Density Measurements.**—In order to determine the predominant type of defect present, the measured pycnometric densities of single crystals of the crystalline solutions were compared with hypothetical densities, which were calculated on the basis of the measured lattice parameters and two structure models. One assumes the creation of one normal cation vacancy for each two  $Ca^{++}$  ions replaced by  $Y^{3+}$ ; the other assumes that one  $F^-$  enters the  $CaF_2$  lattice interstitially for each  $Y^{3+}$  that substitutes. The X-ray powder measurements of the quenched crystalline solutions showed only  $CaF_2$ -structure lines up to 55 mole %  $YF_3$ ; at 60% lines of a second phase appeared. The lattice parameter changes linearly with addition of  $YF_3$ , from 5.462 for  $CaF_2$  to 5.500 for 20 mole %  $YF_3$ , and 5.537 for 40%  $YF_3$ . From these data the densities that would result based on the pure interstitial  $F^-$  model and the pure cation vacancy model have been calculated and plotted as the straight lines in Fig. 1. Shown also are the experimentally determined densities of the crystals. These data confirm Goldschmidt's<sup>3</sup> hypothesis and establish unequivocally that interstitial  $F^-$  ions are by far the predominant defect up to 40% mole %  $YF_3$  and presumably to the solubility limit, 55 mole %  $YF_3$ .

The interstitial sites that are the most "open" and thus probably of minimum potential energy are four per unit cell:  $(\frac{1}{2}00)$ ,  $(0\frac{1}{2}0)$ ,  $(00\frac{1}{2})$ ,  $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ . They are, like  $Ca^{++}$ , in eightfold coordination with respect to  $F^-$ , but are in sixfold coordination with respect to the next-nearest neighbor  $Ca^{++}$ . It is highly likely that the extra  $F^-$  from the  $YF_3$  enters these interstitial positions. Further indirect evidence for this was found in the sharp increase with increasing  $YF_3$  content in the relative X-ray intensities of the (200), (222), and (420)

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(2) T. Vogt, *Neues Jahrb. Mineral.*, VII, 9 (1914).

(3) V. M. Goldschmidt, *Skrifter Norske Videnskaps-Akad. Oslo, I: Mat.-naturv. Kl.*, No. 2, 88 (1926).

(4) E. Zintl and A. Udgard, *Z. anorg. allgem. Chem.*, **240**, 150 (1939).

(5) J. O. Sullivan, U. S. Bur. Mines, Tech. Paper No. 381, (1926).

lines which are suppressed in f.c.c.  $\text{CaF}_2$ . The powder X-ray data do not indicate whether or not  $\text{Y}^{3+}$  and interstitial  $\text{F}^-$  are associated, and a complete refined structure analysis is in progress to answer this question.

**Phase Equilibria.**—Investigation of phase equilibria in the system  $\text{CaF}_2\text{-YF}_3$  (Fig. 2) has shown some unusual features which may be connected with the defect character of the crystalline solution. A definite maximum in the liquidus occurs at about 33 mole %  $\text{YF}_3$ , thus confirming the early study by Vogt.<sup>2</sup> Such a temperature-composition maximum is a quite unusual occurrence in inorganic systems. A possible thermodynamic explanation may lie in a smaller than normal entropy of fusion, because of the additional disorder introduced into the crystal by the defects. This increases the melting temperature, which is thermodynamically defined as the ratio of the heat of fusion to the entropy of fusion.

TABLE I

POWDER X-RAY PATTERN FOR  $\text{CaF}_2\cdot 4\text{YF}_3$ 

$d$ , Å.	$I/I_0$	$hkl$
3.785	70	002
3.401	25	110
3.058	100	111
1.961	55	300
1.918	60	113
1.740	15	004
1.710	35	302
1.650	10	221
1.549	3	114
1.528	3	222
1.372	10	223
1.302	10	304
1.288	5	115
1.264	5	411
1.162	3	006
1.124	5	330

Crystalline solution extends up to about 55 mole %  $\text{YF}_3$ , and apparently persists at room temperature, even upon cooling slowly from  $1050^\circ$  for several hours. The liquidus drops very sharply ( $320^\circ$ ) near the solubility limit in going from 55 to 60%  $\text{YF}_3$ . These two phenomena probably have a structural cause; when more than two of the four possible interstitial sites in the unit cell are occupied, the  $\text{F}^-$  repulsion (and also  $\text{Y}^{3+}\text{-Y}^{3+}$  repulsion) results in thermal instability, and the limit of solid solution is reached. A tendency for a weak 1:1 compound formation could also cause these effects, but no structural evidence for this was obtained.

Beyond 55%  $\text{YF}_3$  a new phase was found. This new phase exhibits a powder pattern analogous to hexagonal  $\text{LaF}_3$ , but not to  $\text{CaF}_2$  or  $\text{YF}_3$ . In Table I the pattern has been tentatively indexed. The calculated hexagonal lattice parameters are:  $a = 6.77$  Å.;  $c = 6.98$  Å. The phase is uniaxial negative, with a mean index of refraction of 1.537 and a m.p. of  $1159 \pm 10^\circ$ . This may be a hitherto unreported compound of composition  $\text{CaF}_2\cdot 4\text{YF}_3$ , showing some nonstoichiometry, or it could represent the limit of  $\text{CaF}_2$  solubility in a

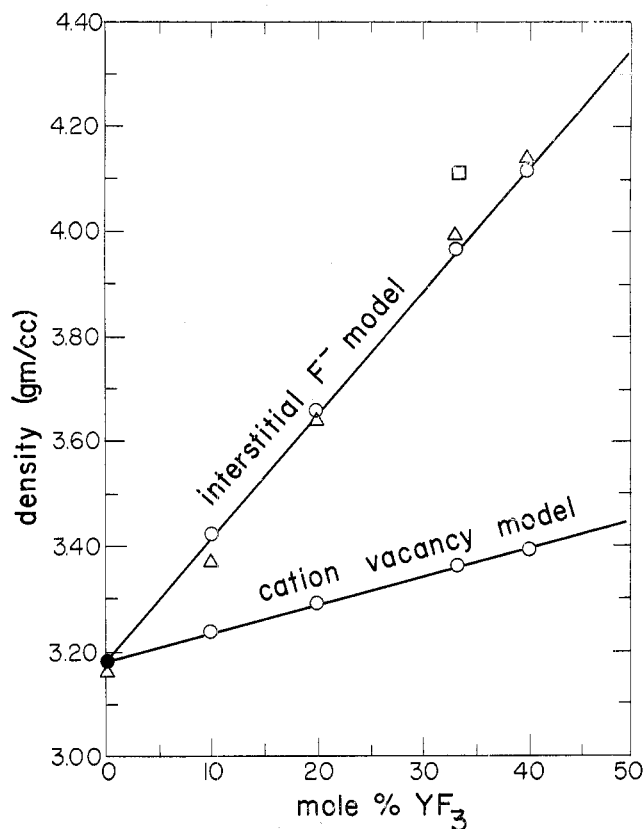


Fig. 1.—Measured pycnometer densities ( $\Delta$ ) and theoretical X-ray densities ( $\circ$ ) of  $\text{CaF}_2\text{-YF}_3$  crystalline solutions as a function of  $\text{YF}_3$  content;  $\square$ , measurement of Zintl and Udgard<sup>4</sup>;  $\bullet$ , pycnometer density of Harshaw single crystals.

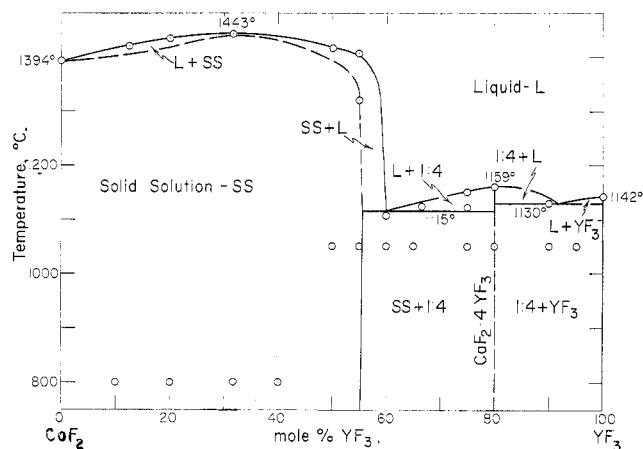


Fig. 2.—Tentative phase diagram of the system  $\text{CaF}_2\text{-YF}_3$ .

hitherto unreported hexagonal form of  $\text{YF}_3$ . Phase boundaries in this area of the diagram are still unclear and are complicated by uncertainty as to the effect of the first-order transition in  $\text{YF}_3$  at approximately  $1050^\circ$ . Nevertheless, distinct two-phase regions were easily seen in the diffractometer patterns of quenched mixtures from 60–75% and from 85 up to 100 mole %  $\text{YF}_3$ . The best interpretations of the data are combined to give Fig. 2.