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Crystal Growth and Fluorescent Properties of Rare Earth-Doped Calcium Fluorovanadate

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$Ca_5(VO_4)_3F$, crystallizing in the $P6_3/m$ space group of the hexagonal apatite structure, has been grown into large single crystals by the Czochralski technique. The compound was used as a host for the rare earths Sm, Eu, Tb and Dy; fluorescent emission properties of these were measured.

Introduction

Although the first crystal host used for a laser was the simple binary oxide Al_2O_3 (*1*), ternary compositions such as $CaWO_4$ (*2*) soon found use, especially when the active species to be incorporated was from among the rare earth ions. The compound CaF_2 (*3*) was the first pure fluoride studied as a laser host, and very recently, a mixed fluoro-oxide, $Ca_5(PO_4)_3F$ with apatite structure, has been used as a host for Nd^{3+} (*4*).

In a paper on the blue luminescence in calcium chlorovanadates, Aia (*5*) mentioned the preparation of polycrystalline $Ca_5(VO_4)_3F$. He found that the undoped composition does not exhibit visible fluorescence and suggested that it may have a slightly different structure from that of apatite. Neither crystal growth nor substitutional studies in $Ca_5(VO_4)_3F$ were described. It was decided therefore to attempt melt growth of this fluorovanadate and to determine its suitability as a host matrix for rare earth substitution on the calcium site. For the substitutional studies, the need for valence compensation is obvious. One possible mechanism for such compensation would be the simultaneous substitution of Ti^{4+} for V^{5+} and Ca^{2+} for Ln^{3+}; however, in this study, replacement of two Ca^{2+} ions by the pair Na^{1+}/Ln^{3+} was employed. In crystal growth experiments, the substitution of some O^{2-} for F^{1-} can also act as a compensation scheme when rare earths are incorporated into the Ca^{2+} sites.

Experimental

The polycrystalline samples used for most fluorescent emission studies were prepared from the best commercially available chemicals. In a typical example, the preparation of

$$Na_{0.1}Sm_{0.1}Ca_{4.8}(VO_4)_3F,$$

the constituent components Na_2CO_3 (Baker & Adamson), Sm_2O_3 (Lindsay Chemical Divison), CaF_2 (Baker & Adamson), $CaCO_3$ (Baker & Adamson) and V_2O_5 (Vanadium Corporation of America) were carefully weighed and mixed according to the following stoichiometry:

$$0.1\ Na_2CO_3 + 0.1\ Sm_2O_3 + CaF_2 + 8.6\ CaCO_3 + V_2O_5 \rightarrow 2\ Na_{0.1}Sm_{0.1}Ca_{4.8}(VO_4)_3F + 8.7\ CO_3$$

This mixture was fired under argon in a platinum dish at 700° for about 10 hr. The primary reaction product was then ball milled under acetone (using an agate mill) for complete homogenization and finally fired at 1200° for about 2 hr. All samples were examined by X-ray diffraction and all diffraction lines were indexable on the basis of the well-established apatite structure.

Single Crystal Growth. For the Czochralski growth of $Ca_5(VO_4)_3F$, high purity $Ca_3(VO_4)_2$ was prepared as previously described (*6*). This compound was then mixed with the stoichiometric amount of CaF_2 and melted in an iridium crucible using a 25 kW–450 kc/sec. Westinghouse rf generator as a source of power. The visually observed melting point using an uncorrected pyrometer reading was $1420 \pm 20°$. Original growth was initiated on a pure Ir wire. Subsequent crystals were grown on seeds cut from this first crystal. The cross-sections of all grown crystals were circular (*c*-axis). Pulling speeds between 0.5 and 1 in. per hr produced crystals $\frac{1}{2}$–$\frac{3}{4}$ in. in diameter.

Results. As in the case of $Ca_3(VO_4)_2$, the $Ca_5(VO_4)_3F$ crystals showed a very light yellow color. Semiquantitative spectroscopic analysis did not reveal the presence of any detectable impurities, and presumably, the color is intrinsic because of absorption in the blue end of the sprectum. Precession X-ray photographs of a thin, single-crystal wafer showed that growth occurred along the 6-fold *c*-axis of the apatite structure. This is demonstrated in Fig. 1, which shows both the growth lines of the actual crystal and the 0-level X-ray pattern. Cell edges derived from these patterns were $a_h = 9.64$ Å; $c_h = 7.00$ Å. This is in good agreement with Aia's (l.c.) values of 9.67 Å and 7.01 Å obtained on powders. Aia stated that $Ca_5(VO_4)_3F$ may have a structure slightly different from that of apatite, but our single crystal data now establishes that $Ca_5(VO_4)_3F$ crystallizes in an undistorted apatite structure, space group $P6_3/m$. With two molecules per unit cell, an X-ray density of 3.32_6 g·ml^{-1} can be calculated. The measured density of a massive single crystal is 3.31 g·ml^{-1}. The refractive index is 1.95.

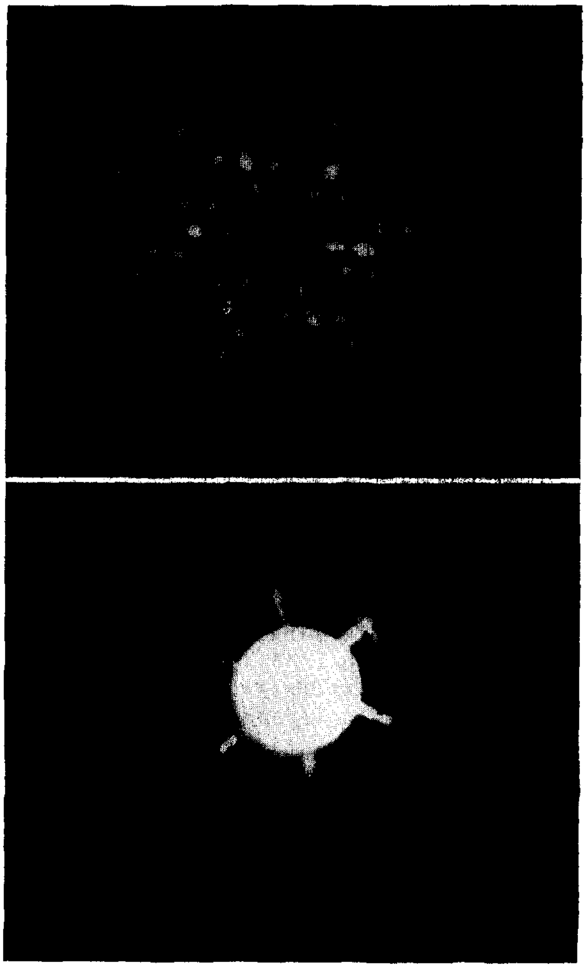

FIG. 1. 0-level X-ray pattern (top), and view down *c*-axis (bottom) of $Ca_5(VO_4)_3F$ crystal.

For the growth of a Nd^{3+}-doped crystal, previously grown $Ca_5(VO_4)_3F$ was used as "feed" material and the replacement of part of the F^{-1} ions by O^{2-} to restore electroneutrality for the Nd^{+3}/Ca^{2+} substitution was relied upon to provide "self-compensation." In one of these experiments, the protective argon atmosphere was inadvertently lost and a 3-in. long crystal was grown in air. Such a crystal did contain the "feathery imperfection" observed by Mazelsky (l.c.) for $Ca_5(PO_4)_3F$ crystals. It was first assumed that this second phase was due to exsolved CaO resulting from a partial hydrolysis of the fluorine. However, X-ray fluorescence analysis established no detectable difference in the F concentration between top and bottom of the crystal.

Found (Top):	36.3% Ca;	27.4% V;	3.4% F
(Bottom):	36.8% Ca;	27.7% V;	3.4% F
Calculated:	35.52% Ca;	27.09% V;	3.37% F.

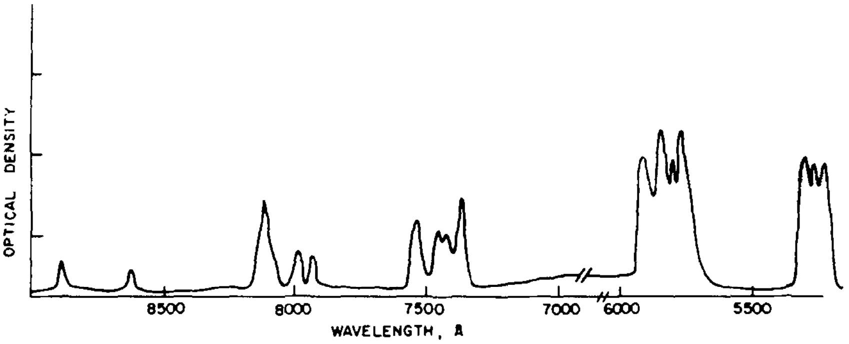

FIG. 2. Absorption spectrum of $Ca_5(VO_4)_3F$: Nd crystal.

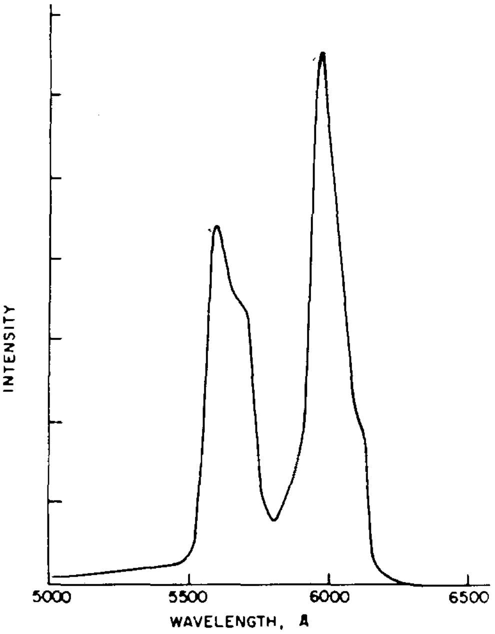

FIG. 3. Fluorescent emission spectrum of $Ca_{4.8}Sm_{0.1}Na_{0.1}(VO_4)_3F$.

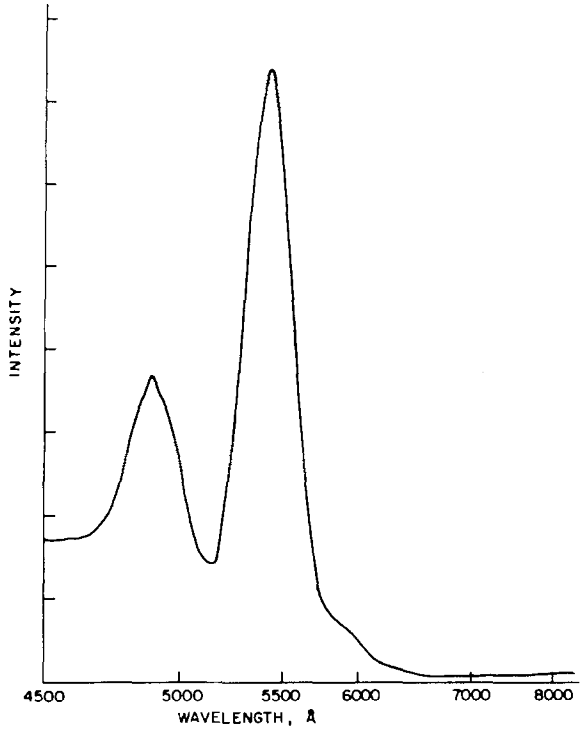

FIG. 5. Fluorescent emission spectrum of $Tb_{0.3}Na_{0.3}Ca_{4.4}(VO_4)_3F$.

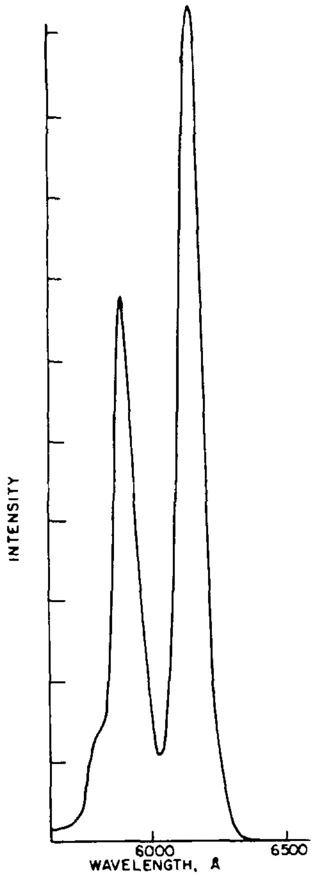

FIG. 4. Fluorescent emission spectrum of $Eu_{0.2}Na_{0.2}Ca_{4.6}(VO_4)_3F$.

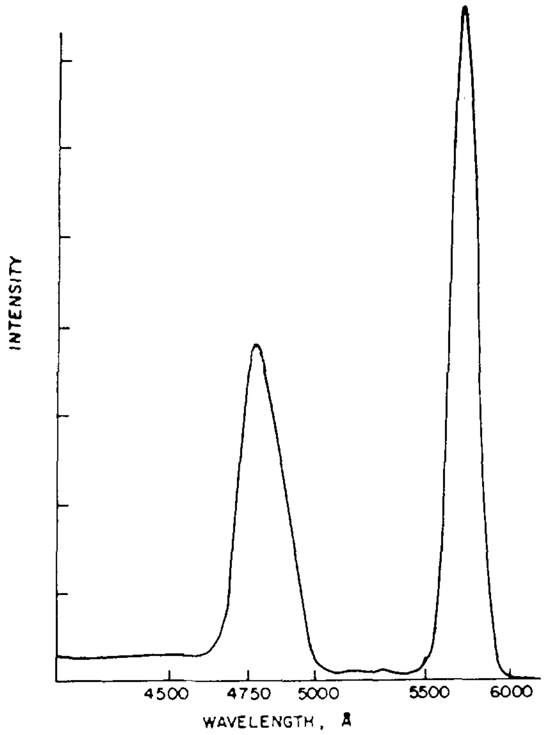

FIG. 6. Fluorescent emission spectrum of $Dy_{0.3}Na_{0.3}Ca_{4.4}(VO_4)_3F$.

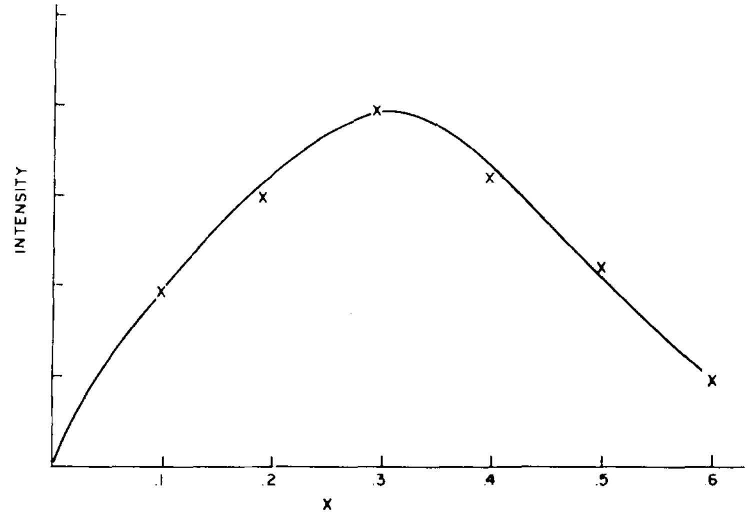

FIG. 7. Intensity of fluorescent emission as a function of composition for the $Ca_{5-2x}Na_xSm_x(VO_4)_3F$ system.

An electron microprobe analysis of a cross-sectional cut of such a crystal also did not reveal any change in the relative Ca concentration. This would, however, not be a significant finding if the second phase exsolved on such a small scale that it would be below the resolution of the beam (~ 0.5–1 μ). The possibility of twinning as a source of the optical imperfections was also eliminated by complete Laue back-reflection studies of the surface of a single crystalline slice.

In order to determine the segregation coefficient of Nd_2O_3 in $Ca_5(VO_4)_3F$, an Nd-doped crystal was grown with a nominal charge of 1 wt % Nd_2O_3, relying on self-compensation of the type

$$Ca_{5-x}Nd_x(VO_4)_3F_{1-x}O_x.$$

The analytically determined molar concentration, x, of Nd varied from 0.12, on the top, to 0.14 on the bottom. Based on this information and the analytically determined concentrations of the remaining constituents (Ca, V, F), the segregation coefficient $K = C_s/C_l$ was calculated by Pfann's (7) method as 0.69. This compares with 1.1 for Nd_2O_3 in $Ca_3(VO_4)_2$ or 0.52 for Nd_2O_3 in $Ca_5(PO_4)_3F$. Figure 2 shows the absorption spectrum of Nd^{3+} in $Ca_5(VO_4)_3F$. While the relative location of the absorption peaks is only very slightly shifted, the spectrum in general is simpler than those for Nd^{3+} in most other host lattices.

Fluorescence Studies. All optical studies with the rare earths Sm, Eu, Tb and Dy incorporated in the fluorovanadate host were done on powder samples. Coarse fluorescent scans were obtained with a Beckman DK2 recording spectrophotometer, while more refined spectral data came from measurements with a Cary Model 14 spectrometer. All samples were valence compensated with Na^{1+} according to the general formula $Ln_xNa_xCa_{5-2x}(VO_4)_3F$. Typical spectra for the four rare earths emitting in the visible are given in Figs. 3, 4, 5 and 6. Figure 7 represents the intensity of fluorescent emission vs. activator concentration plot for the sample containing samarium. The same basic type of curve was obtained for the other three rare earths. Optimum activator concentrations are summarized in Table I.

TABLE I

CONCENTRATIONS IN $Ln_xNa_xCa_{5-2x}(VO_4)_3F$ COMPOSITIONS

Ln	x for maximum emission	Peaks at Å	Relative peak intensity
Sm	0.2	5992, 5630	66, 45
Eu	0.2	6160, 5900	77, 41
Tb	0.3	5452, 4778	74, 37
Dy	0.3	5752, 4755	76, 38

Discussion

Although no specific laser experiments were conducted, one can state that the fluoroapatite of vanadium $Ca_5(VO_4)_3F$ is another potentially useful host for stimulated Nd^{3+} emission. This statement is based on the fact that Mazelsky (l.c.) has recently established excellent spectral quantum efficiency for Nd in the structurally identical host $Ca_5(PO_4)_3F$. Since, furthermore, energy exchange between the VO_4^{-3} group and rare earths has been established for such other vanadates as YVO_4 (*8*) or $Ca_3(VO_4)_2$ (*6*), it can be assumed that such will also be the case for the fluorovanadate host. The fact that pure $Ca_5(VO_4)_3F$ by itself does not fluoresce under either 3660 or 2537 Å excitation, while the corresponding chloro-compound is an efficient self-activated emitter (*5*), suggests that the halide ion plays an important role in the excitation mechanism. It is interesting to note that the Eu^{3+}-doped sample can readily be excited with 3660, 2537 Å radiation, as well as with electrons. As a potential red television phosphor, $Ca_5(VO_4)_3$:Eu would have to compete with YVO_4:Eu. While the optimum Eu concentration at $x = 0.3$ of 5.21% would compare favorably with the 6.8% optimum in YVO_4, the peak emission at 616 nm would definitely be disadvantageous compared with the 619 nm emission for YVO_4:Eu.

Acknowledgment

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