

## Method for producing large, stable concentrations of $\text{Sc}^{2+}$ in optically clear $\text{CaF}_2$ crystals

C. L. Marquardt, J. F. Pinto, R. E. Allen, and L. Esterowitz  
*Naval Research Laboratory, Washington, DC 20375*

A. Yu Dergachev, S. Ke, and S. B. Mirov  
*University of Alabama at Birmingham, Birmingham, Alabama 35294*

(Received 9 May 1997; accepted 16 July 1997)

This communication describes a new method for producing stable, high concentrations of  $\text{Sc}^{2+}$  in optically clear  $\text{CaF}_2$  crystals. We have achieved  $\text{Sc}^{2+}$  concentrations as high as  $3 \times 10^{18} \text{ cm}^{-3}$  without degradation of optical quality. We have converted as much as 5% of the scandium dopant to the divalent state. The concentration of divalent scandium is stable during room temperature storage for periods of at least one year.

Divalent scandium ( $\text{Sc}^{2+}$ ) in crystals such as  $\text{CaF}_2$  has recently generated interest as a potential solid state laser material with broad tunability in the near ultraviolet spectral region.<sup>1,2</sup> This expectation is based primarily on the analogy with  $\text{Ti}^{3+}$  which has the same electronic configuration ( $3d^1$ ) as  $\text{Sc}^{2+}$ .  $\text{Ti}:\text{sapphire}$  is the most important new solid state laser material since  $\text{Nd}:\text{YAG}$ . It is broadly tunable in the near infrared. Spectral features of divalent scandium are expected to be similar to those of  $\text{Ti}:\text{sapphire}$ , but substantially blue shifted. This should permit tunable laser operation in the 350–450 nm spectral region. Various optical properties have been attributed to  $\text{Sc}^{2+}:\text{CaF}_2$  in previous reports.<sup>3–5</sup> However, many of those properties have subsequently been shown<sup>1,2</sup> to arise from species other than  $\text{Sc}^{2+}$ . At the present time, unambiguous identification of  $\text{Sc}^{2+}$  in  $\text{CaF}_2$  can be obtained only from cryogenic Electron Paramagnetic Resonance (EPR) measurements. Three previous studies have used EPR to confirm the presence of  $\text{Sc}^{2+}$  in  $\text{CaF}_2$  crystals which had been doped with scandium and then exposed to ionizing radiation.<sup>6–9</sup> In the early work<sup>7–9</sup> the scandium doping was accomplished by evaporating a film of scandium metal onto a pure  $\text{CaF}_2$  crystal surface, and then diffusing it into the bulk at an elevated temperature prior to irradiation. This process is not suitable for production of laser-quality optical material. It severely limits the ultimate concentration of  $\text{Sc}^{2+}$  and introduces permanent metal colloids which degrade the optical transmission throughout the spectrum. Recent investigators<sup>1,2,6</sup> have doped the pure  $\text{CaF}_2$  starting material with  $\text{ScF}_3$  prior to crystal growth. Trivalent doping levels of 1–2% have been achieved without degrading the optical quality of the crystals. After a subsequent gamma irradiation of  $2 \times 10^5$  rad,  $\text{Sc}^{2+}$  concentrations as high as  $8 \times 10^{16} \text{ cm}^{-3}$  have been detected using EPR, and the crystals have still retained their high optical quality. Nonetheless, all

methods which employ irradiation suffer from unavoidable drawbacks which make them less than optimal for production of laser material. The fraction of the  $\text{Sc}^{3+}$  which can be reduced to  $\text{Sc}^{2+}$  by irradiation is limited to about  $10^{-3}$ , and the initial radiation-induced  $\text{Sc}^{2+}$  concentration decays significantly during dark storage at room temperature. In addition, because of their relatively high cost and limited availability, the use of high-flux gamma sources does not provide a practical basis for the development of a commercial materials production process. In the present communication we describe a new method which has succeeded in producing stable, high concentrations of  $\text{Sc}^{2+}$  in optically clear  $\text{CaF}_2$  crystals. This method does not employ ionizing radiation. To date we have achieved *actual*  $\text{Sc}^{2+}$  concentrations (determined by EPR) exceeding  $3 \times 10^{18} \text{ cm}^{-3}$ . We have converted as much as 5% of the scandium dopant to the divalent state, and the  $\text{Sc}^{2+}$  concentration is stable during room temperature storage for periods of at least one year.

Our method utilizes a procedure which we refer to as “Thermo-Chemical Reduction” (TCR) to produce  $\text{Sc}^{2+}$  in  $\text{CaF}_2$  crystals grown with  $\text{ScF}_3$  in the melt. Our TCR method is similar to a technique previously employed in the preparation of “photochromic calcium fluoride.”<sup>10</sup> It should be noted that although the authors of Ref. 10 refer to their technique as “additive coloration” (AC), there is a fundamental difference between our TCR method and AC techniques used to produce color centers in alkali halides.<sup>11</sup> The latter are based on the interaction between the alkali halide crystal and the corresponding alkali metal *vapor*; typical processing temperatures for AC are governed by proximity to the melting point and boiling point of the crystal and the metal, respectively. TCR is based on the interaction between the  $\text{CaF}_2$  crystal and a film of metallic calcium evaporated onto the crystal surface. The reaction is performed at a much lower temperature, where the vapor pressure of the calcium metal

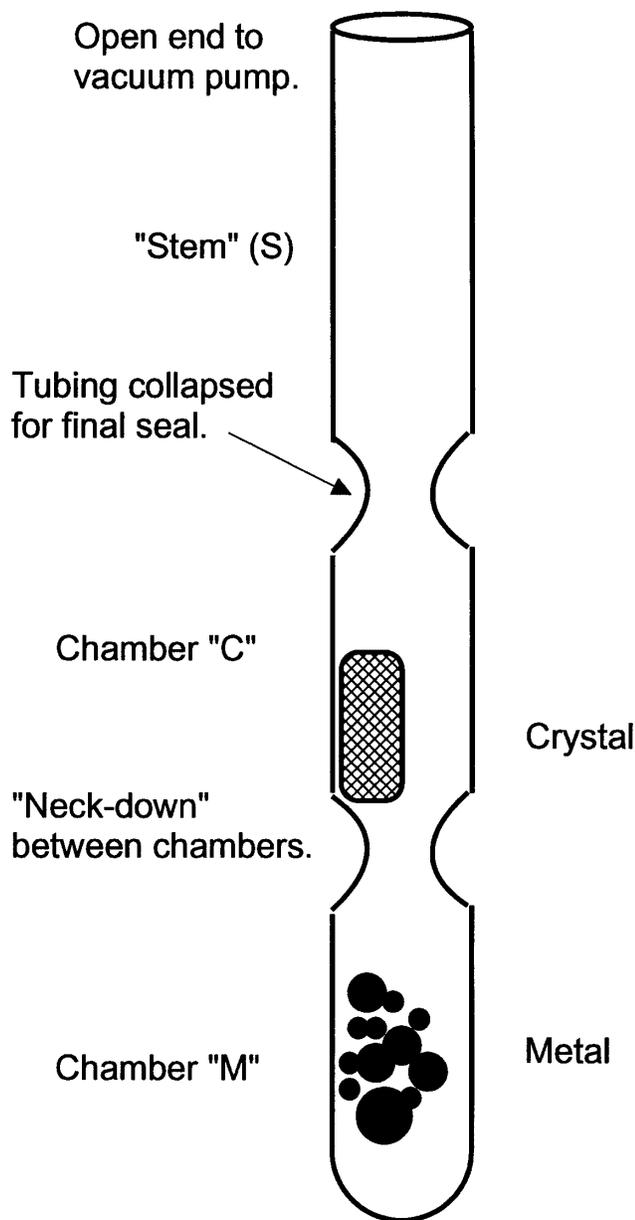


FIG. 1. Schematic diagram of ampoule used in the "thermochemical reduction" (TCR) of scandium in  $\text{CaF}_2$  crystals doped with  $\text{ScF}_3$ .

is negligible. This critical feature of the TCR process has enabled us to achieve high efficiency in conversion of  $\text{Sc}^{3+}$  to  $\text{Sc}^{2+}$ , without degrading the optical quality of the crystal by formation of metal colloids.

We begin with  $\text{CaF}_2$  crystals which have been intentionally doped with trivalent scandium by adding 0.1–1.0 wt. % to  $\text{ScF}_3$  to the high purity  $\text{CaF}_2$  starting material prior to crystal growth. All the crystals were grown at OPTOVAC Inc., North Brookfield, MA, using a Bridgman–Stockbarger technique. For approximately commensurate substitution of lattice cations (e.g.,  $\text{Sc}^{3+}$ , 0.81 Å for  $\text{Ca}^{2+}$ , 0.99 Å), the dopant concentration in

the crystal deviates from that in the melt by less than 10%. Thus we did not make explicit determinations of the  $\text{Sc}^{3+}$  concentrations in the crystals; we assume that they are equal to the concentrations in their respective melts. Samples 2–3 mm thick are cleaved from the 10 mm diameter crystal boules. The cross sections of the samples range from circular to ellipsoidal depending on the orientation of the cleavage planes in relation to the crystal growth direction. These crystal samples are then subjected to a three-step TCR process in order to reduce as much of the scandium as possible to the divalent state, while avoiding deterioration of the optical quality of the crystal due to colloid formation. The three steps of our TCR process are: (1) purification of encapsulation, (2) evaporation of the metal film and (3) diffusion and reaction at elevated temperature.

In Step (1) the cleaved crystal sample (approximately 10 mm diameter 2–3 mm thick) and the calcium metal (approximately 1.5 g of redistilled shot, 99.5% purity) are placed in a two-chamber fused silica ampoule (14 mm i.d.). Each chamber of the ampoule is approximately 3 in. long, and the chambers are connected by a constricted section of the tubing ("neck-down") having an i.d. of approximately 5 mm (see Fig. 1). The overall length of the finished ampoule is approximately 6 in. The calcium metal is confined to the chamber labeled "M", and the crystal is confined to the chamber labeled "C". Once the materials are loaded into the ampoule as shown in Fig. 1, the open end of the tube is connected to a vacuum system and evacuated to approximately  $10^{-7}$  Torr. All parts of the tube, the crystal, and the metal are heated gently with a torch in order to drive off adsorbed moisture and other atmospheric impurities. Next, the calcium metal (chamber M) is heated with the torch to a temperature sufficiently high to drive off volatile impurities. This is detected by a transient pressure rise. When the transient pressure rise has ceased and the system has returned to its base pressure (around  $10^{-7}$  Torr), the heating is discontinued, and the ampoule is sealed off under vacuum by collapsing the tubing at the open end of chamber C, at a position approximately 3 in. from the neck down. Rather than being "pulled off," the sealed ampoule is left mechanically connected to the tubing "stem" (S), typically about 18 in. long. This enables us to support the ampoule in the processing furnace [Step (3)] without any contact with the furnace walls.

In Step (2) the sealed ampoule containing the crystal in chamber C and the purified calcium metal in chamber M is held horizontal. The crystal is manipulated into a position adjacent to the neck-down, where it lies with a cleaved surface facing upward. Chamber M is heated (with a torch) to a high enough temperature to melt the calcium and evaporate a bright metallic film throughout chamber C. The crystal surface is coated with calcium metal by this process.

In Step (3) the ampoule is transferred to an unheated 12 in. tube furnace. The crystal is located in the center of the furnace, near the position of zero temperature gradient, and chamber M extends into the cooler region near the end of the furnace tube. The furnace temperature control is set to 725 °C, and the furnace is turned on. After approximately 20 min, the furnace reaches its equilibrium temperature. The crystal temperature is approximately 725 °C at equilibrium. The temperature at the sealed end of chamber M is approximately 600 °C. The furnace is held at this equilibrium temperature for approximately 1 h, in order to permit diffusion of the calcium metal and the consequent reduction reaction which forms the divalent scandium. The furnace is then turned off, and allowed to cool to room temperature over a period of approximately 4 h. The crystal is removed from the ampoule and visually inspected. In some cases there is a thin black layer on the surface of the crystal. The origin and composition of this layer may be associated with impurities in the quartz tubing. The black layer (if present) is removed by polishing, and the interior of the crystal is found to be optically clear. Test pieces are cut from the crystal for evaluation by means of optical and EPR measurements.

After the TCR processing, the concentration of  $\text{Sc}^{2+}$  in each sample is determined by measuring its X-band EPR spectrum at 15 K. Typical EPR data are shown in Fig. 2. At 15 K the EPR spectrum of  $\text{Sc}^{2+}$  is isotropic,<sup>8</sup> consisting of eight hyperfine lines ( $^{45}\text{Sc}$ , 100% abundance,  $I = 7/2$ ) with a  $g$  value of  $g = 1.968$  and a hyperfine coupling constant of  $A = 65.5 \times 10^{-4} \text{ cm}^{-1}$ . In contrast to previous attempts to infer the presence of  $\text{Sc}^{2+}$  from optical spectra alone, the EPR measurement gives a clear and unambiguous identification of the species, as well as an accurate means of determining its concentration. Using the “spin counting” method (double integration of the EPR spectrum and comparison

with a standard sample such as dpph), together with measured values of sample weight and density, absolute values of  $\text{Sc}^{2+}$  concentration were obtained with an estimated accuracy of  $\pm 20\%$ . We applied this method to a series of seven optically clear TCR  $\text{Sc}:\text{CaF}_2$  samples having initial doping concentrations of 0.1, 0.3, and 1.0%  $\text{ScF}_3$ . The values obtained for  $\text{Sc}^{2+}$  concentration ranged from about  $6 \times 10^{15} \text{ cm}^{-3}$  to  $3 \times 10^{18} \text{ cm}^{-3}$ . Corresponding conversion efficiencies inferred for the TCR process vary between 0.1% and 5%, depending on details of the processing conditions. This represents a fiftyfold improvement over the best results reported for the irradiation method.

We also made EPR measurements on untreated  $\text{Sc}:\text{CaF}_2$  samples, on undoped  $\text{CaF}_2$  samples which had been subjected to the TCR process, and on a 0.1% doped  $\text{Sc}:\text{CaF}_2$  sample which had been processed under conditions more closely approximating conventional AC. In the latter case we omitted Step (2) (evaporation of the metal film), and we increased the furnace temperature (900–950 °C) and processing time (12–15 h). This process was indeed effective for production of  $\text{Sc}^{2+}$  (about 10% conversion efficiency), but the sample was totally opaque, presumably due to the presence of colloids. All attempts to “clear” crystals prepared in this manner by subsequent heat treatments (dissolving the colloids) were unsuccessful. No  $\text{Sc}^{2+}$  EPR signal was detected in any of the undoped or untreated crystals.

Determination of  $\text{Sc}^{2+}$  concentration from cryogenic EPR measurements, albeit straightforward and highly effective, is too tedious and inconvenient to be used as a routine monitor of the TCR process. We would prefer a measurement which is “direct reading” and performed at room temperature using a technique which is readily available in most optical laboratories. An optical absorption band peaking around 295 nm has been observed in *all* optically clear  $\text{CaF}_2$  samples known to contain  $\text{Sc}^{2+}$ , including those prepared by the irradiation method.<sup>1,2,6</sup> Figure 3 shows the optical absorption spectrum in a  $\text{CaF}_2:\text{Sc}$  (1%) crystal which has been subjected to the TCR process; the 295 nm band is clearly the predominant feature. We have used a group of five such TCR crystals, with  $\text{Sc}^{2+}$  varying over a factor of thirty, to investigate the possible correlation between the absorption coefficient at 295 nm ( $\alpha_{295}$ ) and the concentration of  $\text{Sc}^{2+}$ . In earlier work<sup>3-5</sup> the 295 nm band had been assumed to be a transition of  $\text{Sc}^{2+}$ ; a more recent interpretation<sup>1,2</sup> suggests that it is due to a color center ( $V_k$ , hole center) stabilized by the  $\text{Sc}^{2+}$ . Regardless of the specific identification of its origin, this band can be used as a concentration monitor as long as it is generated in some fixed proportion to the  $\text{Sc}^{2+}$ . In Fig. 4 the  $\text{Sc}^{2+}$  concentration in each of the five TCR crystals is plotted as a function of the corresponding  $\alpha_{295}$ . The data were taken on two separate occasions, one sample

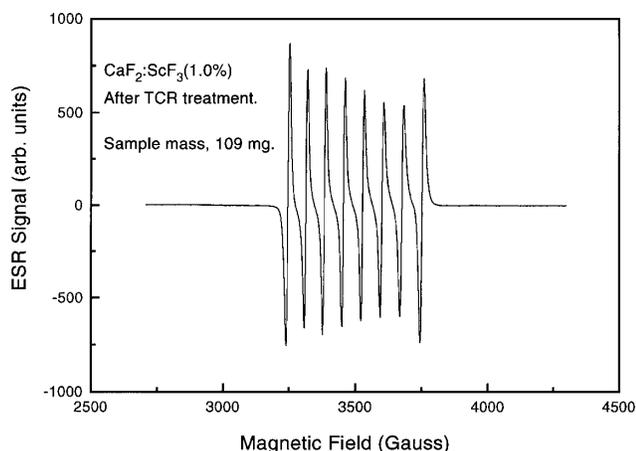


FIG. 2. The X-band EPR spectrum of  $\text{Sc}^{2+}$  observed at 15 K in a  $\text{CaF}_2:\text{ScF}_3$  (1%) crystal which had been subjected to TCR treatment.

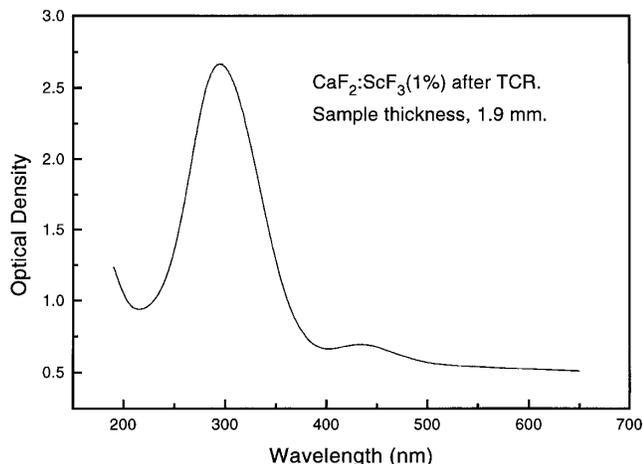


FIG. 3. The room temperature optical absorption spectrum observed in a  $\text{CaF}_2:\text{ScF}_3$  (1%) crystal which had been subjected to TCR treatment.

(A80AC4E1) being measured in both data sessions. The degree of agreement between the two concentrations found for A80AC4E1 demonstrates that the repeatability of the EPR measurement is within the claimed 20% margin of error. Assuming a linear relationship between the concentration and the absorption, the expression

$$\text{Sc}^{2+} = (7 \times 10^{16} \text{ cm}^{-2})\alpha_{295}$$

adequately describes all the data within the known accuracy of the measurements. The inferred corresponding cross section ( $1.4 \times 10^{-17} \text{ cm}^2$ ) is consistent with a 1:1 generation ratio between the  $\text{Sc}^{2+}$  and the absorbing species. These data suggest that, barring the emergence of counterexamples, it may be reasonable to use the absorption peak at 295 nm as a convenient monitor of the  $\text{Sc}^{2+}$  concentration produced by the TCR process.

In summary, we have presented a new method (TCR) for producing stable, high concentrations of  $\text{Sc}^{2+}$  in optically clear  $\text{CaF}_2$  crystals, without the use of ionizing radiation. To date we have achieved actual  $\text{Sc}^{2+}$  concentrations as high as  $3 \times 10^{18} \text{ cm}^{-3}$  in samples of optical quality. We have converted as much as 5% of the scandium dopant to the divalent state, and the material is stable during room temperature storage for periods of at least one year. We have demonstrated that the 295 nm absorption peak may provide a convenient

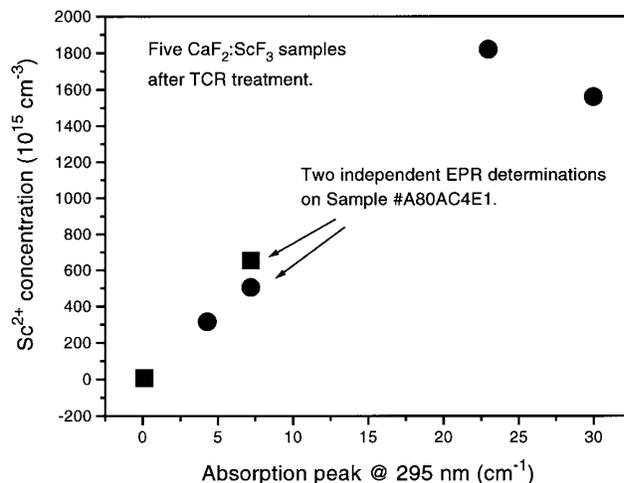


FIG. 4. Correlation between the optical absorption coefficient at the peak of the 295 nm band and the  $\text{Sc}^{2+}$  concentration determined from the EPR measurements. Data are shown for five different  $\text{CaF}_2:\text{ScF}_3$  crystals which had been subjected to TCR treatment; two independent concentration determinations (EPR) are shown for crystal A80AC4E1.

means of monitoring the  $\text{Sc}^{2+}$  concentration produced by the TCR process.

## REFERENCES

1. A. Yu. Dergachev, S. B. Mirov, W. A. Sibley, L. Esterowitz, V. B. Sigachev and A. G. Papashvili, *OSA TOPS: Advanced Solid State Lasers*, edited by S. A. Payne and C. Pollock (Optical Society of America, Washington, DC, 1996), Vol. 1, pp. 482–487.
2. S. B. Mirov, A. Yu. Dergachev, W. A. Sibley, L. Esterowitz, T. T. Basiev, V. B. Sigachev, and A. G. Papashvili, *J. Lumin.* **69**, 35 (1996).
3. G. Kotitz, H. Mothes, G. Persch, R. Rauch, and G. Schwortzer, *Phys. Status Solidi (a)* **31**, 371 (1975).
4. L. V. Krotova, R. G. Mikaelyan, and V. V. Osiko, translated from *Izv. Akad. Nauk SSSR: Neorgan. Mater.* **3**, 1123 (1967).
5. J. R. O'Connor and J. H. Chen, *J. Phys. Chem. Solids* **24**, 1382 (1963).
6. A. Yu. Dergachev, S. Ke, and S. B. Mirov, private communication (Nov. 19, 1996).
7. J. R. Herrington, L. A. Boatner, T. J. Aton, and T. L. Estle, *Phys. Rev. B* **10**, 833 (1974).
8. U. T. Hochli, *Phys. Rev.* **162**, 262 (1967).
9. U. T. Hochli and T. L. Estle, *Phys. Rev. Lett.* **18**, 128 (1967).
10. W. Phillips and R. C. Duncan, Jr., *Metall.* **2**, 769 (1971).
11. See, for example, J–H. Shulman and W. D. Compton, *Color Centers in Solids* (Pergamon Press, New York, 1963), and references cited therein.