

F AND PHOTOCHROMIC CENTERS IN LiYF₄:Nd CRYSTALS†

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Samples of Nd doped LiYF₄ single crystals (scheelite structure) were X-irradiated at room temperature and valence changes plus defect production by radiation damage were studied by optical spectroscopy techniques. The band centered at 3.70 eV showed a temperature dependent gaussian shape indicating a strong electron phonon coupling suggestive of an F type center defect. Reversible valence changes of Nd³⁺→Nd²⁺ after irradiation were observed throughout luminescence studies when (Nd³⁺)^{*}→Nd³⁺ transitions were identified. A new band centered at 4.57 eV was found. This band showed an optical switching mechanism and a correlation to the 4D_{3/2} transition of the Nd³⁺ ion. This band was assigned as being due to a photochromic (F-Nd³⁺) center.

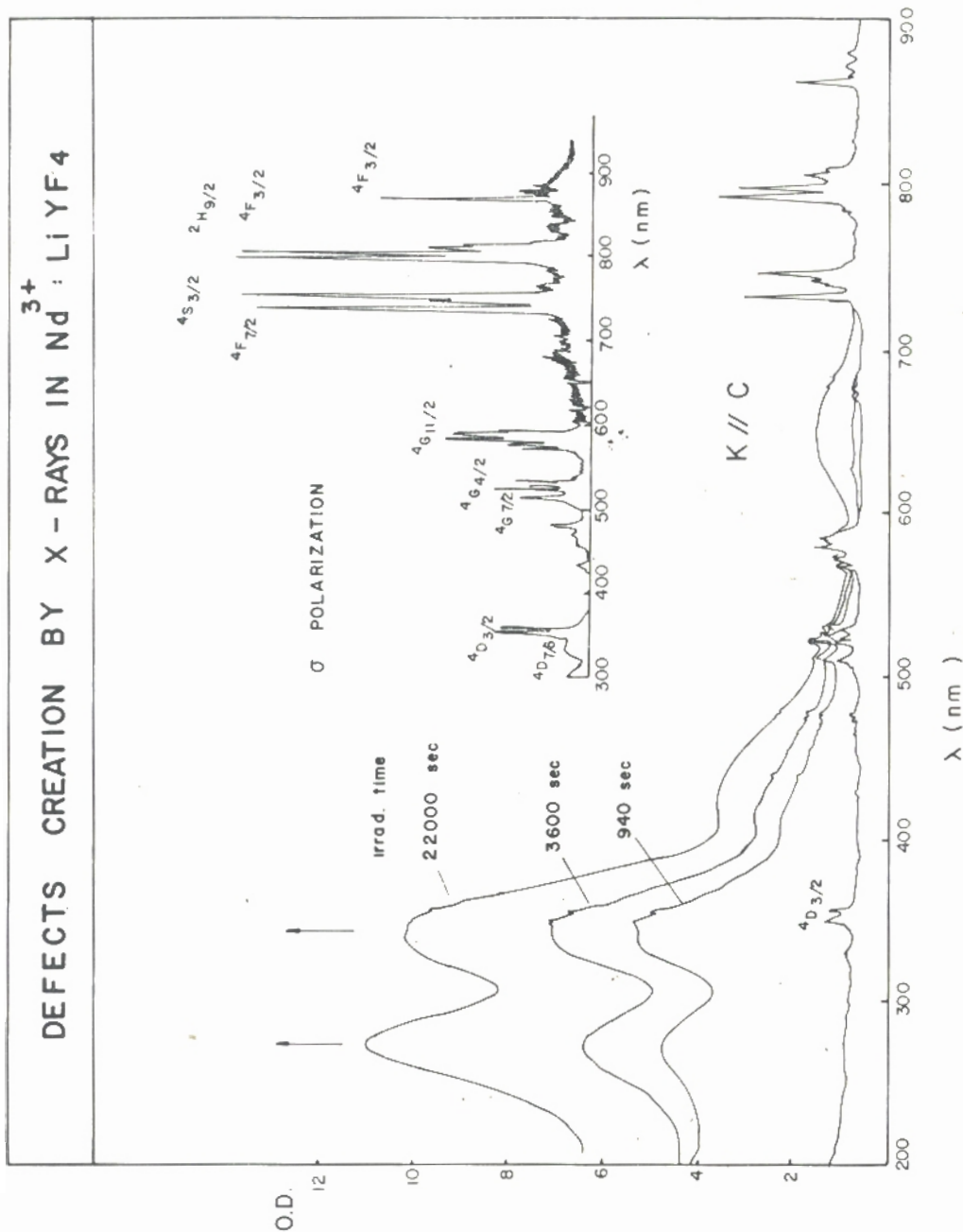
INTRODUCTION

Crystals of LiYF₄ doped with Nd³⁺ (commercially designated by Nd:YLF) have steadily gained importance since they are good substitutes for Nd:YAG crystals in the development of IR lasers.^{1,2} Several studies have been done in the past to understand energy transfer properties between impurity ions and point defects induced by radiation in unirradiated and irradiated YLF. A recent study on radiation effects on YLF was done by Renfro *et al.*,³ who propose the band centered at 3.70 eV as due to the F center. Another band centered at 3.99 eV was identified as the F₂⁻ center (hole center, also an intrinsic defect). This band was shown to decay above 77 K, indicating the annihilation of the F₂⁻ center. Measurements done by these authors were only at low temperatures so primary radiation damage defects could be observed and identified, such as F and hole centers. It was found that every center produced at low temperature decays³ above 300 K. The purpose of the present work was to investigate the effect of radiation on the optical properties of Nd:YLF samples at room temperature—where YLF and YAG lasers operate—and to study the role played by the Nd³⁺ ion in the radiation effects.

EXPERIMENTAL

The crystal boule used in this work was grown by a zone refining technique in a platinum system under an HF atmosphere. Its single crystal character was determined by Laue diffraction method. Typical 10×5×1.5 mm³ samples were cut from the boule using a diamond saw. These samples were oriented with the aid of a

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polarizing microscope such that the optical axis was parallel or perpendicular to c . These samples were X-irradiated at room temperature with a Rigaku-Denki source with a W target and Be windows. Samples were involved in Al foil to prevent the effect of soft X-rays. Irradiation conditions were kept constant at 50 kV/50 mA with irradiation times ranging from 20 to 2×10^4 sec. Samples were hand polished using appropriate abrasives and mounted in a Janis 8DT cryostat for optical measurements and light irradiation. Temperature was controlled with Cu-constantan thermocouples referred to a zero degree source. Optical absorption was measured with a Cary 17D spectrophotometer and emission was measured with the aid of a 25 cm Jarrel-Ash monochromator. Optical bleaching was done with a xenon lamp conveniently dispersed by a monochromator or by interference filters.

RESULTS AND DISCUSSION

A typical absorption measurement of an unirradiated Nd:YLF sample showed the Nd^{3+} transitions that were easily identified. The $E||c$ polarized transitions are shown in Figure 1. After the X-irradiation, the absorption spectra showed a drastic change with the appearance of 4 wide bands at 650, 450, 335 and 270 nm (see Figure 1). This 4-band spectrum is similar in its character to the spectra obtained by irradiating CaF_2 crystals doped with rare earths.⁴⁻⁶ Similarly to $\text{CaF}_2:\text{Gd}^{3+}$ where a reduction was found in the $6I$ transition of Gd^{3+} , we also found a decrease in the $4D_{3/2}$ transition of the Nd ion with the increase of the 4.57 eV band (270 nm).

At a first approximation these wide bands indicate strong electron-phonon coupling interactions and are characteristic of electronic centers (like the F center) produced during the radiation damage process. The coloration curves plotted against irradiation time showed a typical two-stage coloration, a common process that in general occurs in irradiated ionic crystals.

The 335 nm (3.70 eV) band showed similar growth for both polarizations without changes in its λ_{max} when measured in σ and π polarizations. The maximum optical absorption of this band was measured as a function of the polarization angle and it was found, similarly to Renfro *et al.*,³ that the absorption for $E_{\perp}c$ was about 24% of the value for $E||c$ (Figure 2), corroborating their proposition that σ and π bands at 3.70 eV represent the same defect. This band was also adjusted to a gaussian for several temperatures, and at 52 K, for example, $E = (3.66 \pm 0.12)$ eV and $\text{FWHM} = (0.38 \pm 0.02)$ eV for a band of $K_{\text{max}} = (16.9 \pm 1.2)$ cm^{-1} were obtained.

By lowering the temperature from 343 to 52 K a shift to higher energies of $\lambda_{\text{max}} = 10.5$ nm was obtained. All these results, besides the fact that λ_{max} , FWHM and polarization of this band are independent on the RE dopant, strongly favor the assignment of the 3.7 eV to an F center.

The new band centered at 270 nm (4.57) eV and measured with $E_{\perp}c$ (see Figure 2) presented a coloration curve similar to the 376 nm band in CaF_2 assigned to a photochromic center.⁵ This band, as well as the other two at 650 and 450 nm showed a change in λ_{max} for σ and π polarizations (Figure 2). After one hour of X-irradiation at room temperature the Nd:YLF samples were observed to emit a green afterglow that had a lifetime of about 40 min. This emission was measured and identified

FIGURE 1 Four-band absorption spectra after X-irradiation at room temperature for 940, 3600 and 22,000 sec. Inset: Nd^{3+} transitions for polarization σ .

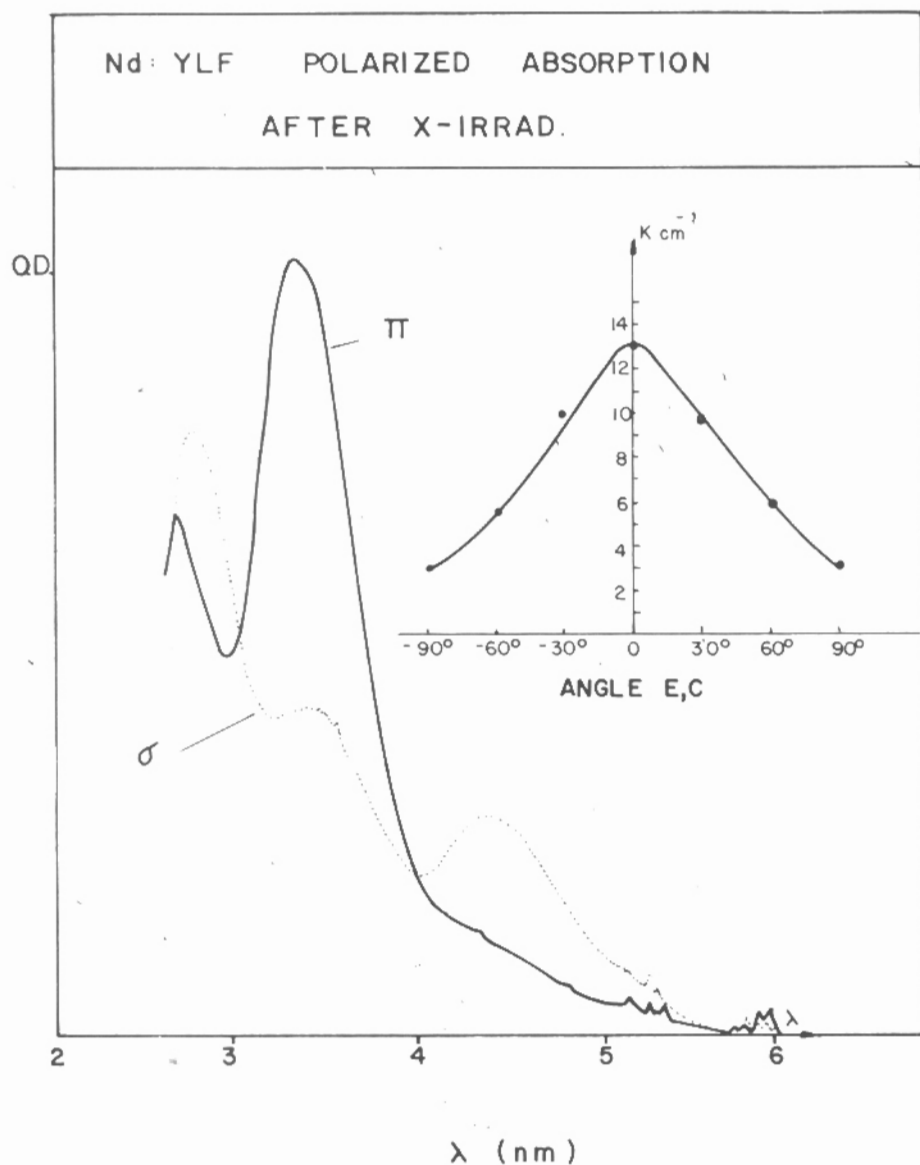


FIGURE 2 Polarized absorption for Nd:YLF crystal after X-irradiation for σ and π polarizations. Inset: maximum optical absorption for the 3.70 eV band as a function of the polarization angle.

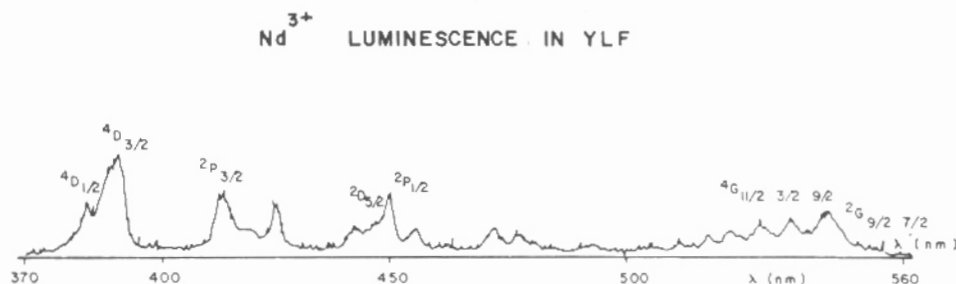


FIGURE 3 Nd³⁺ emission at room temperature after X-irradiation.

according to Diecke⁷ as composed by several transitions due to the de-excitation of Nd³⁺ ions (Figure 3). This effect shows the fast valence oxidation of the Nd²⁺ ion back to Nd³⁺ in the excited state. Renfro *et al.* also observed afterglows in YLF irradiated samples (green in Er³⁺ and pink in Pr³⁺ doped YLF) although they did not measure the spectral characteristic of these phosphorescent emissions. Besides, they observed an increase in the UV region absorption suggestive of valence reduction of Pr³⁺ into Pr²⁺ in the sample doped with this RE ion but they did only identify a band at 3.99 eV as being due to F₂⁻ centers that was unstable above 120 K. Our 4.57 eV band, produced at RT was, instead, completely stable at this temperature besides occurring at a higher energy than the F₂⁻ band thus suggesting a different kind of center. In the present work, similarly to Staebler and Schnatterly,⁶ we did RT irradiations and observed a similar spectrum which led us to assign the band at 4.57 eV to a photochromic center. However, whereas in CaF₂ a RE trivalent ion replacing the Ca²⁺ ion needs charge compensation, it does not happen in YLF since Nd³⁺ replaces Y³⁺ ion.

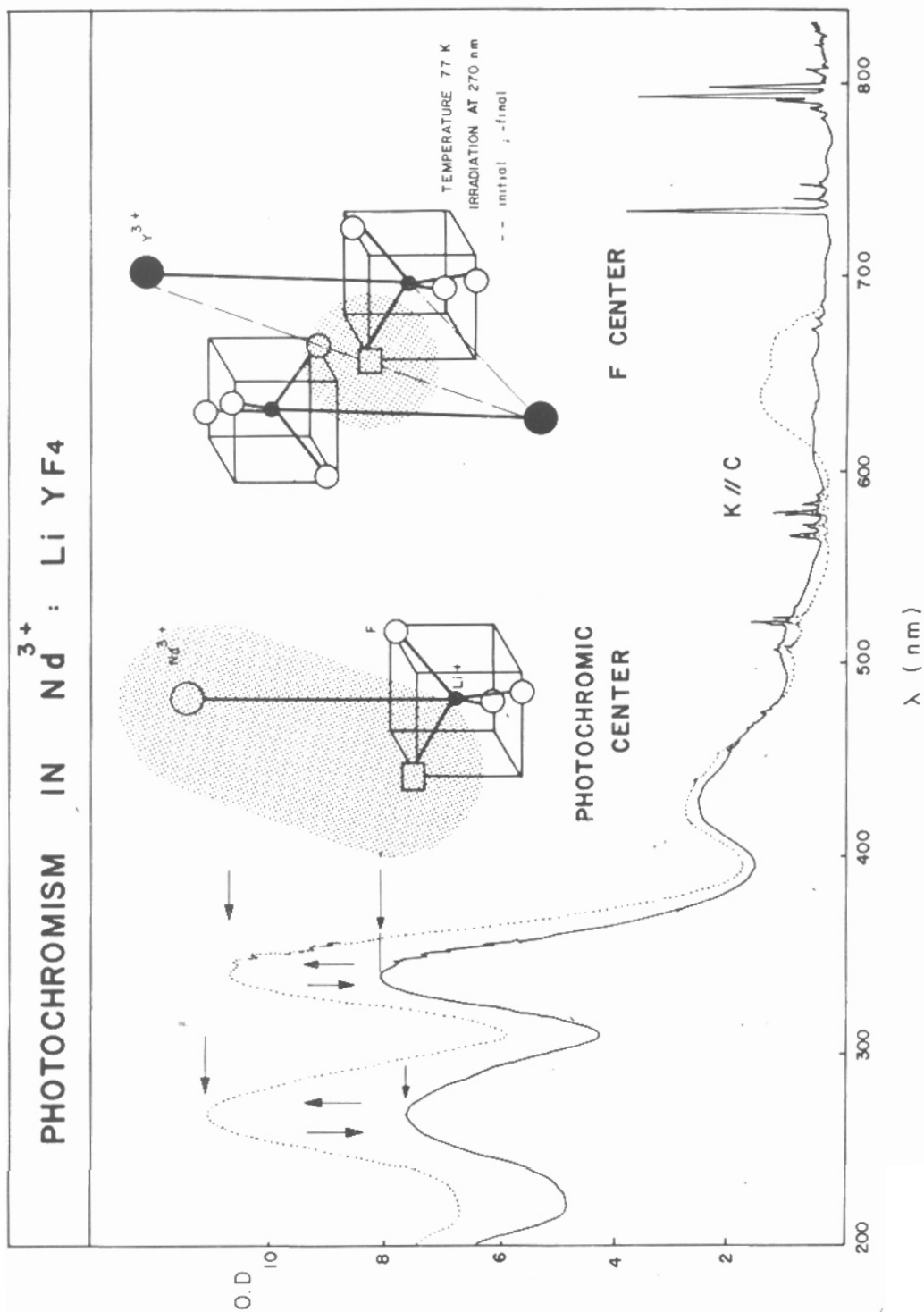
By illuminating in the 4.57 eV band a reduction of this band accompanied by a reduction of the 3.70 eV band at a different rate was qualitatively observed—which discards the possibility of the 4.57 eV band as being due to a distinct transition of the same center. The decrease of the 4.57 eV band was now accompanied by the increase of the 4D_{3/2} transition of the Nd³⁺. This process was thermally reversed by leaving the sample in the dark at room temperature.

Photochromic centers have a similar behavior but in crystals where charge compensation is necessary they are also stable in the ionized form (PC⁺ center) as shown previously.⁶ The formation of a PC center occurs during the irradiation process by releasing from its vacancy (in the YLF crystal) a fluorine ion that lies close to a RE³⁺ ion.



the complex RE³⁺ + □ traps two photoelectrons thus forming the PC center. The switching into the ionized state follows:





CONCLUSIONS

From the above results it is concluded that:

(a) the band centered at 3.70 eV (335 nm) is due to an F center. The structural model of the F center is proposed in Figure 4 where the electron is trapped by a fluorine vacancy lying close to the inversion center of the YLF primitive cell. This configuration is in agreement with the assignment done by Renfro *et al.* Although the positive identification of the F centers cannot be made with optical data alone, our results strongly support the assignment of band at 3.70 eV to an F center.

b) The band centered at 4.57 eV (270 nm) is assigned to a photochromic center (PC). Its structural model is also proposed in Figure 4 where a Nd^{3+} replacing a Y^{3+} ion close to an F center is shown. This system Nd^{3+} -F center traps a photoelectron resulting in a single charged electronic cloud involving the vacancy $-\text{Nd}^{3+}$ configuration. Light irradiation ionizes the electron that will get metastably trapped in another isolated Nd^{3+} ion, reducing its valence and producing the PC^+ center. A thermally reversed mechanism releases the electron from the Nd^{2+} trap bringing it back to the PC configuration.

The remaining bands at 450 and 650 nm were not investigated in this work but are probably due to higher aggregates of the F center.

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REFERENCES

1. E. J. Sharp *et al.*, *J. Appl. Phys.* **44**, 5399 (1973).
2. D. Le Goff *et al.*, *Opt. Comm.* **26**, 108 (1978).
3. G. M. Renfro *et al.*, *J. Phys.* **C13**, 1941 (1980).
4. A. Smakula, *Phys. Rev.* **77**, 408 (1950).
5. L. Prado and S. P. Morato, to be published.
6. D. L. Staebler and S. E. Schatterly, *Phys. Rev.* **B3**, 516 (1971).
7. G. H. Diecke, in *Spectra and Energy Levels of Rare Earth Ions in Crystals* (Wiley, New York, 1968).

FIGURE 4 F and PC centers in YLF. Photochromism after irradiation on the 270 nm band at 77 K.