F_A centers in additively colored KI:Li crystals

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Optical properties are reported for F_A centers produced in KI:Li additively colored under nitrogen-free conditions. Contrary to previous studies for KI:Li, these centers exhibit two distinct absorption bands centered at 0.673 and 0.733 μm. Furthermore, their optical properties are consistent with type-I F_A centers. The elimination of nitrogen at each stage of crystal preparation was essential to the optimum production of these centers in KI:Li.

The most widely investigated extrinsic defect in alkali halide crystals is the F_A center, consisting of an F center next to an alkali ion impurity in a substitutional site, e.g., Li^+ or Na^+ in the KCl lattice.[1] The impurity ion introduces a perturbation in the ⟨100⟩ direction which lowers the symmetry of the defect from O_h to C_{4v}. This splits the $2p$-like state of the F center into two levels so that the F_A center gives rise to two distinct absorptions: the F_{A1} band located on the low-energy side of the F band, with a dipole moment along the vacancy-impurity axis, and the F_{A2} band, peaking near the F-band maximum, with a dipole moment in the plane perpendicular to this axis. Previous reports on lithium-F_A centers in KI, however, indicate that these centers give rise to only a single broad absorption in the F-band region.[2,3]

In a recent study involving $(F_2^+)_A$ centers in KI:Li,[4] it

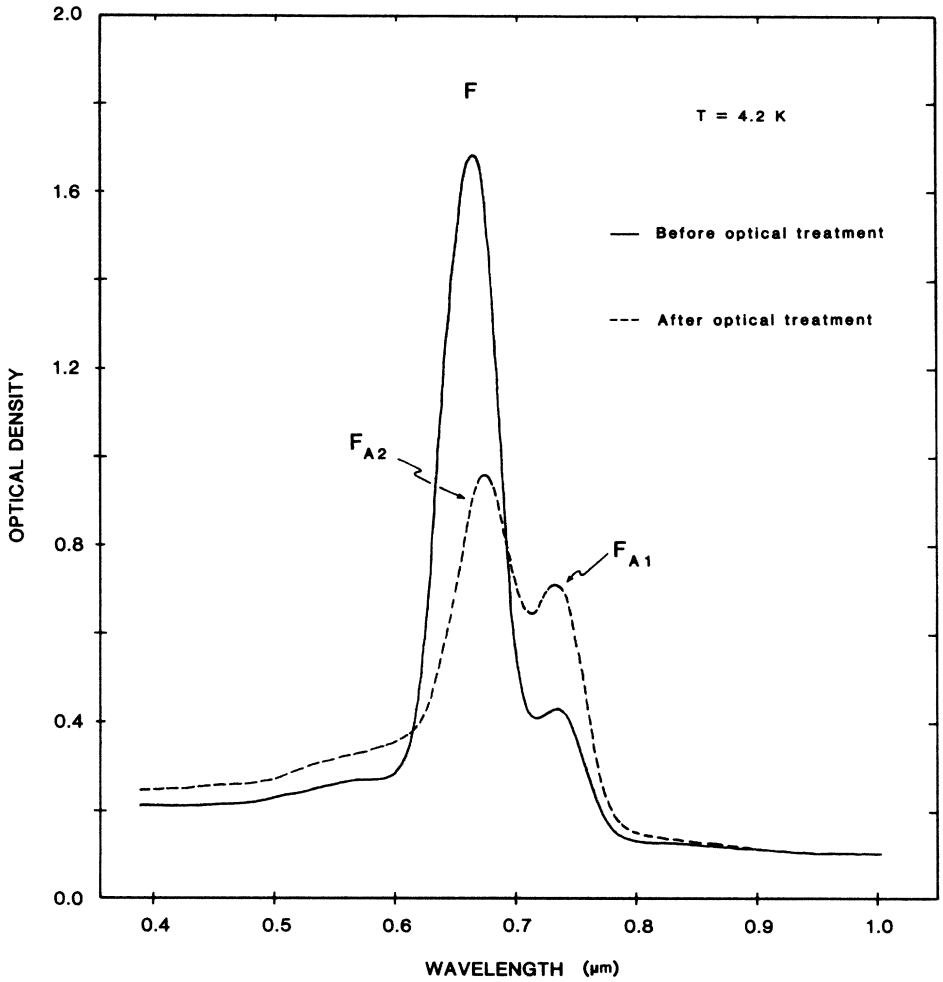

FIG. 1. Absorption spectra measured at 4 K of an additively colored KI:Li crystal, 0.5 mm thick. The solid curve is the initial spectrum of the freshly annealed crystal; the dashed curve was measured after exposure to blue-green light for 20 min at 250 K.

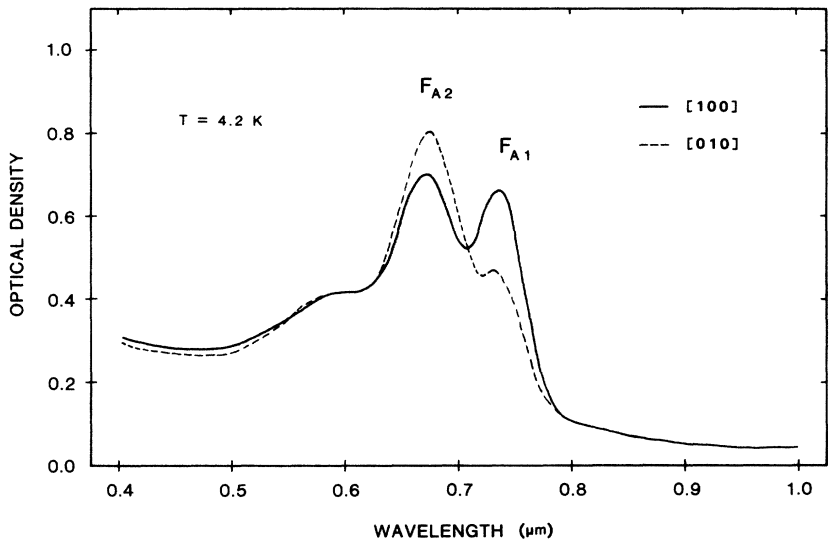

FIG. 2. Absorption spectra obtained on a KI:Li crystal containing F_A centers after exposure for 30 min at 130 K to 0.650 μm light polarized along a [100] direction, and measured with [100]-polarized light (solid curve) and [010]-polarized light (dashed curve).

was discovered that nitrogen diffuses into the lattice during the additive coloration process, and presumably combines with lithium so that $(F_2^+)_A$ centers do not form. Because nitrogen has seldom been viewed as a serious contaminant in alkali halide crystals, it was considered worthwhile to study the lithium-F_A center, whose optical behavior may have been affected by the presence of nitrogen. This note shows that in KI:Li crystals, additively colored in a nitrogen-free atmosphere, F_A centers clearly exhibit two distinct absorptions in the vicinity of the F band, and they can be optically oriented introducing ⟨100⟩ dichroism into their absorptions. As predicted by Lüty[1] and Kung, Lagowski, and Vail,[5] the KI:Li F_A centers display type-I behavior, as indicated from the temperature dependence of their reorientation and the F-center-like properties of their emission.

All crystal boules were grown in an argon atmosphere with 1 mol% LiI added to the melt. Samples were cleaved $2\times5\times5$ mm from the bottom portion of the boule, and contained ~ 0.1 mol% LiI, as determined by atomic absorption analysis. The samples were additively colored using the van Doorn technique in which the coloration density was controlled by varying the argon pressure.[6] Crystals were typically colored at 868 K under 20 mm Hg of argon for 15 min. Just prior to use, each crystal was annealed for 2 min at 848 K in an argon atmosphere and rapidly quenched to room temperature.

Emission spectra were measured using excitation from a tungsten source and monochromator. The emission was viewed perpendicular to the excitation direction and passed through a grating monochromator and silicon filter to a PbS detector. All absorption measurements were made using a Cary Model 14MR spectrophotometer.

F centers were converted to F_A centers by illuminating each KI:Li crystal with blue-green light[7] for 20 min at 250 K. Figure 1 shows absorption spectra measured at 4 K before conversion (solid curve) and afterwards (dashed curve). The crystal initially contains a strong F band peaking at 0.662 μm and a relatively weak absorption centered near 0.733 μm (likely due to some F_A centers originally present). The optical treatment produces a substantial decrease in the F-band intensity and the emergence of distinct F_{A1} and F_{A2} absorptions, peaking at 0.733 and 0.673 μm, respectively.

F_A centers can be aligned through absorption of linearly polarized light in either of their two bands. Figure 2 shows that ⟨100⟩ dichroism is produced in each band (of opposite polarity) by illuminating the crystal for 30 min at 130 K with F_{A2}-band light (i.e., 0.650 μm light) propagating along [001] and polarized along [100]. This dichroism is induced more slowly at 77 K and cannot be produced at all at 4 K.

Figure 3 shows emission spectra measured at 4 K for F centers in pure KI (dashed-dotted curve) and F_A centers in KI:Li (solid curve). The F_A center gives rise to a single emission band centered at 1.78 μm which has a half-width similar to that of the F-center emission peaking at 1.47 μm. The excitation spectrum of the 1.78 μm emission has two

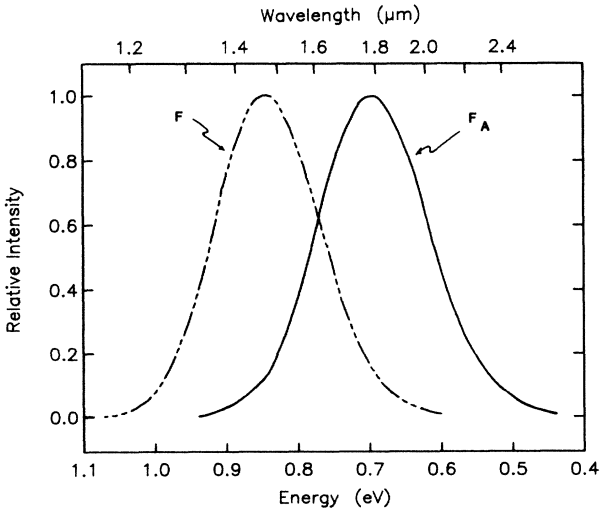

FIG. 3. Normalized emission spectra measured at 4 K for F centers in pure KI (dashed-dotted curve) using 0.660 μm excitation and F_A centers in KI:Li (solid curve) with 0.730 μm excitation.

distinct components with peak positions coinciding approximately with the F_A bands.

In summary, the optical properties of F_A centers in additively colored KI:Li are consistent with those seen in other alkali halide lattices. In contrast to results reported in prior studies, two distinct F_A absorptions are observed and dichroism can be produced in these absorptions through exposure to linearly polarized light. The observations of a temperature-dependent reorientation and a broad F-like emission band with a relatively small Stokes shift indicate type-I behavior, as predicted by Lüty[1] and Kung, Lagowski, and Vail.[5] We conclude that elimination of nitrogen at each stage of crystal preparation is necessary for the optimum production of F_A centers in additively colored KI:Li.

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[1]F. Lüty, in *Physics of Color Centers,* edited by W. B. Fowler (Academic, New York, 1968), Chap. 3.

[2]G. Baldacchini, U. M. Grassano, E. Polito, A. Scacco, and F. Somma, Solid State Commun. **41**, 815 (1982).

[3]A. Scacco, G. Baldacchini, U. M. Grassano, E. Polito, and F. Somma, Radiat. Eff. **72**, 185 (1983).

[4]D. R. Foster and I. Schneider, Opt. Lett. **11**, 213 (1986).

[5]A. Y. S. Kung, L. Lagowski, and J. M. Vail, Phys. Status Solidi B **100**, 621 (1980).

[6]C. Z. van Doorn, Rev. Sci. Instrum. **32**, 755 (1961).

[7]Blue-green light was obtained from a 200 W Hg lamp filtered through a $CuSo_4$ solution and O-52 Corning glass filter.