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Two fully bleachable zero-phonon-line defects in NaF: Possible candidates for highly efficient photochemical hole burning

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In a systematic search for zero-phonon-line (ZPL) defects in ionic solids for photochemical hole-burning applications, we have discovered and studied two defects which can be formed in doped NaF under prolonged electron irradiation at room temperature. The high ratio of the integrated ZPL absorptions (at 889 and 1072 nm) to the integrated phonon sidebands indicates weak electron-phonon coupling ($S \approx 2$) for both defects. Different from all so-far-studied zero-phonon lines of F aggregate centers, both the 889- and 1072-nm lines can be fully and efficiently bleached at lowest temperatures, even with weak spectrophotometer light. In the case of the 889-nm line, this bleaching decreases the $F_2{}^+$-center and increases the F_4-center absorption, indicating its origin to be from a $F_4{}^-$ defect which becomes optically ionized. In crystals with intentionally high-impurity doping, the width of both ZPL could be increased (by a factor of 4) allowing inhomogeneous bleaching even with narrow-band spectrometer light. Thermal recovery of the bleached 889-nm ZPL allows partial reversibility of the process.

I. INTRODUCTION

The optical behavior of typical color centers in alkali halides is in most cases governed by strong electron-phonon coupling, resulting in homogeneously broadened electronic transitions with a sizable Stokes shift between absorption and emission. A prototype defect of this type is the F center, an electron bound to an anion vacancy. Only in more recent stages of work in alkali halides have defect structures with weak electron-lattice coupling been discovered, giving rise to sharp zero-phonon absorption and resolved phonon sideband properties. This behavior is normally observed only in complex defects involving two, three, or four lattice sites, in which the electron occupies "molecular-type" states which are less affected by lattice vibration compared to the "atomic-type" states of single lattice site defects.[1] Defects of this type are the "F aggregate centers," complexes built from $n=2,3,4,\ldots$ F centers, which may be neutral (F_n), positively charged ($F_n{}^+$), or negatively charged ($F_n{}^-$). Zero-phonon lines (ZPL) of these various F aggregate centers have been extensively studied spectroscopically and under applied perturbations, such as electric and magnetic fields and uniaxial stress.[1,2] The anisotropy of the measured Stark, Zeeman, and elasto-optical splitting effects allows one to deduce the symmetry of the defect complex and thus helps to identify microscopic models. The typical width of ZPL's ($1-10$ cm^{-1}) has since been recognized as being produced by an inhomogeneous broadening of the transition due to different values of internal perturbations, like electric field or stress, at different defect sites.[1]

The interest in defect systems of this type has been strongly revived with the advent of the new spectroscopic technique of optical hole burning. If optical bleaching of the ZPL at low temperatures is possible, ultranarrow laser-line irradiation can burn spectral holes into the inhomogeneously broadened ZPL absorption profile. The scientific and application significance of this modern technique is discussed in the following paper.[3] Regarding the ZPL F aggregate centers in alkali halides, the bleaching situation is at present the following:

(a) In the extended earlier "classical" work (reviewed in Refs. 1 and 2), *not a single case of ZPL absorption bleaching with normal spectroscopic techniques at low temperatures has ever been reported.*

(b) Contrary to these spectroscopic results, modern focused laser experiments have achieved in recent years *successful optical hole burning in several F aggregate ZPL absorptions,* (recent short review in Ref. 4).

The apparent contrast between the results (a) and (b) is resolved by the fact that all hole-burning experiments (b) showed only extremely small ($10^{-7}-10^{-6}$) bleaching efficiencies, hardly observable with normal spectrometer techniques (a). Besides the low efficiency, short lifetime and/or small depths of the holes have been abundant in the hole-burning cases.[4]

It was our objective to find, identify, and characterize for the first time with normal spectroscopic techniques *F aggregate centers of highly efficient, 100%, and unlimited lifetime ZPL bleaching properties.* An extended search among a large number of ZPL defects (such as $F_2{}^+$, $F_3{}^+$, $F_2{}^-$, and F_4 centers) in NaF and LiF produced in basically all cases no (or unobservably small) ZPL bleaching effects. However, in contrast to this common behavior, two F aggregate centers in NaF with outstanding bleaching properties (high efficiency, 100% bleaching, and unlimited lifetime at low temperatures) were found in this search and were studied extensively. One of these centers (ZPL at 889 nm) was identified as the very likely and so-far undiscovered "$F_4{}^-$ defect," and was subsequently studied successfully with hole-burning techniques at IBM.[3] The second defect (ZPL at 1072 nm with even higher bleaching efficiency) should be a promising candidate for hole burning, but has not yet been tested with this technique.

II. EXPERIMENTAL RESULTS

All crystals were grown in the Utah Crystal Laboratory from ultrapure material (partially doped with specific impurities) under a pure argon atmosphere by the Kyropolous technique. Electron irradiation was performed with a 1-MeV 1.7-μA/cm^2 electron beam from a Van de Graaf accelerator; the absorption measurements were made with a Cary 17 DX spectrophotometer, using an Air Products closed-cycle refrigerator for sample cooling.

In Fig. 1 we present the low-energy absorption spectra of the two defects of our interest in NaF. The spectrum of Fig. 1(a) consists of a zero-phonon line at 889 nm and a structured phonon sideband around 870 nm. (The existence of a very small ZPL at 889 nm has been observed and reported in an earlier work without any attempt at an interpretation.[5–7]) The spectrum in Fig. 1(b) consists of a ZPL at 1072 nm with a structured phonon sideband around 1030 nm. This spectrum has been observed earlier and attributed to the lowest-energy transition of the F_3^- defect.[8] Figures 2(a) and 2(b) show enlarged views of the two ZPL spectra, measured at three different temperatures. As the temperature is changed, the usual behavior for ZPL's is observed: a shifting to lower energies and a broadening and decrease of integrated absorption strength.

Typical growth curves of the 889- and 1072-nm ZPL absorptions (measured at 10 K), obtained by electron irradiation at room temperature, are presented in Fig. 3. In pure NaF both defects can be produced only in small concentrations, even under high doses of electron irradiation. In both cases, however, the radiation production of the defects can be strongly increased by doping of the crystals with either OH$^-$ or Mn^{2+} impurities. Comparative experiments with x-ray irradiation (50 kV and 20 mA) showed that for equivalent center production corresponding to 1 min of electron irradiation an x-ray exposure of 27 h was needed. Therefore, in order to achieve high optical densities of both ZPL absorptions, *both properly doped crystals and electron irradiation are essential.*

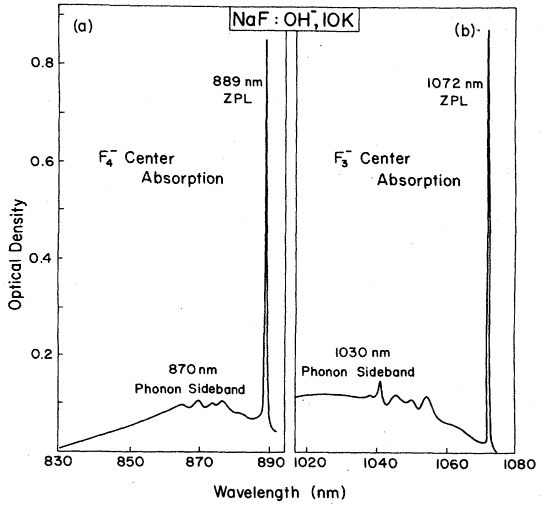

FIG. 1. Low-energy absorption spectra of 10 K of the two defects in NaF investigated in this work.

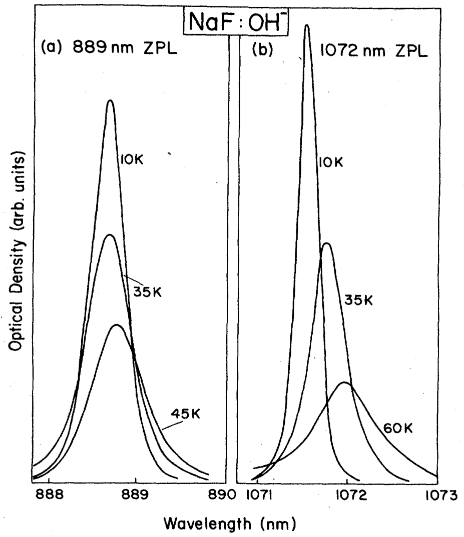

FIG. 2. 889- and 1072-nm zero-phonon line absorptions measured at three different temperatures.

The level of OH$^-$ doping (in the melt) was varied between 0.2 and 2%, and it is known from an earlier work[9] and our present work, that the resulting crystal doping is about one tenth of the melt doping. The best efficiency for the irradiation production of our two defects was found to occur for crystals in the 0.8—1.0% melt doping range. The measurements in Figs. 1, 2, 3, 5, and 8 all refer to a 0.8%-melt doped crystal. Only one level of Mn^{2+}-melt doping (0.15%) was used, producing in the crystal—according to atomic spectroscopy analysis—a Mn^{2+} concentration of 0.02%. The crystal thickness used in all optical measurements reported in the figures was 2±0.1 mm.

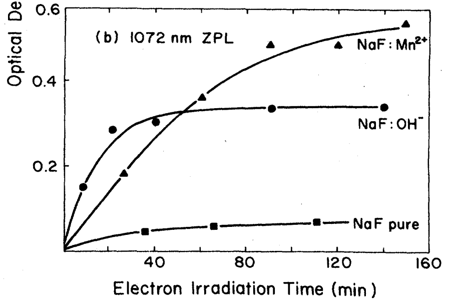

FIG. 3. Growth curves of the 889- and 1072-nm ZPL absorptions (measured at 10 K) produced by electron irradiation at RT for pure, OH$^-$-doped and Mn^{2+}-doped NaF.

A basic difference shows up in the shape of the growth curves (Fig. 3) for the two defects: The 1072-nm ZPL growth has the highest rate at the early stage of irradiation, while the 889-nm ZPL growth starts very gradually and achieves its highest rate only at a later stage. This indicates that the 889-nm ZPL is due to a more complex defect, the production of which is based on the existence of precursory defects formed in the early stage of e^- irradiation.

The important feature, which motivates the detailed study of the two ZPL defects, is summarized in Figs. 4(a) and 4(b). For both defects, optical irradiation at 10 K with narrow-band spectrophotometer light tuned to the ZPL peak position leads to efficient bleaching of the ZPL absorptions. In both defects, under sufficient light illumination, 100% bleaching of the absorption can be achieved. Bleaching with light polarized along a [100] crystallographic direction leads in both centers to isotropic bleaching, i.e., no measurable difference in the reduced absorption when measured with either [100] or [001] polarized light. Using [110] polarized light for irradiation results again in no dichroic bleaching for the 889-nm line. However, for the 1072-nm line preferential bleaching of the [110] absorption compared to the $[1\bar{1}0]$ one is seen. The initial bleaching rate for light polarized along [110] and $[1\bar{1}0]$ has a ratio of about ~ 1.5 in the latter case. An optically anisotropic reading of dichroic holes with frequency-modulation spectroscopy allows a very high sensitivity in hole detection.[10]

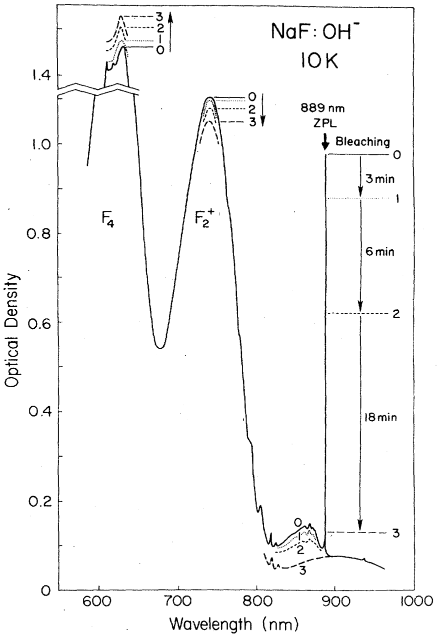

FIG. 5. Optical absorption at 10 K in the 600—1000-nm range of an irradiated crystal before and after optical bleaching with 889-nm light.

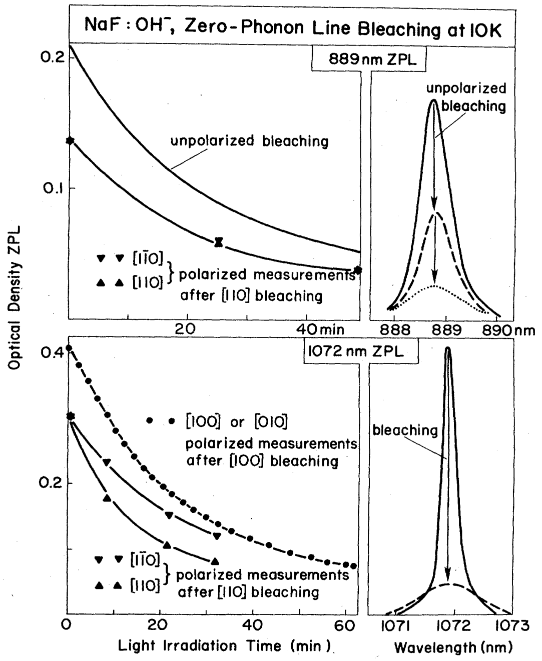

FIG. 4. Bleaching of ZPL at 10 K, measured under variously polarized or unpolarized light as a function of irradiation time (left side), and in its spectral dependence (right side). Upper part, 889-nm ZPL; lower part, 1072-nm ZPL.

Figure 5 displays measurements in which the 889-nm ZPL optical bleaching at 10 K is correlated to optical absorption changes in a wider spectral range. In three successive stages of 889-nm light irradiation, the ZPL and its phonon sideband are bleached to zero absorption. We find that, correlated to this bleaching, the $F_2{}^+$ band (at ~ 740 nm) is reduced, while the F_4 band (at ~ 630 nm) is increased. One probable explanation is that the F_4 center is directly formed by optical ionization of the 889-nm ZPL defect. This leads to an interpretation that the 889-nm ZPL absorption is due to $F_4{}^-$ centers, as will be discussed in more detail in Sec. III. This interpretation is supported by extensive measurements, in which we looked for correlations between the absorption strength of the 889-nm line and the absorption strength of various F aggregate centers in a variety of crystals and at different stages of the e^- irradiation. While the 889-nm ZPL showed little correlation to the F_3 and $F_3{}^+$-center absorption, a good scaling of the 889-nm and F_4-center absorption was detected. Therefore, we use a tentative $F_4{}^-$-center assignment for the 889-nm ZPL and its 870-phonon sideband absorption in the following discussion.

The presence of dopants in the crystal (like OH^- or Mn^{2+}) not only affects the production process of the two defects (Fig. 3), but also affects the spectral properties of the ZPL absorption. Figure 6 shows ZPL absorption spectra for both defects at 10 K obtained in three crystals of different purity (these are selected examples from many systems studied). Narrow linewidths—3.8 and 2.6 cm^{-1} for the 889- and 1072-nm line, respectively—are observed for pure samples. While low concentrations of Mn^{2+} or OH^- dopants cause only modest broadening and no measurable shift of these spectra, high OH^- doping ($\geq 10^{-2}$ in the melt) produces appreciable broadening and a small red shift. More detailed and systematic measure-

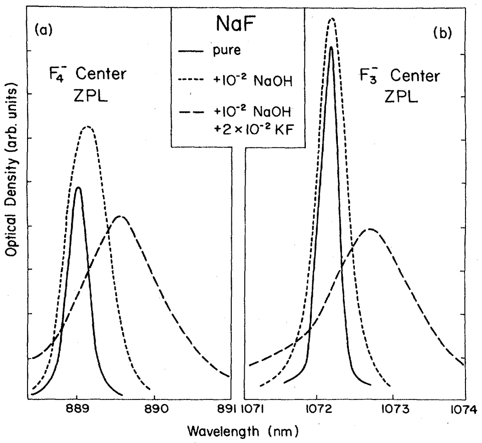

FIG. 6. Spectra of 889- and 1072-nm ZPL absorption at 10 K for pure and doped NaF crystals.

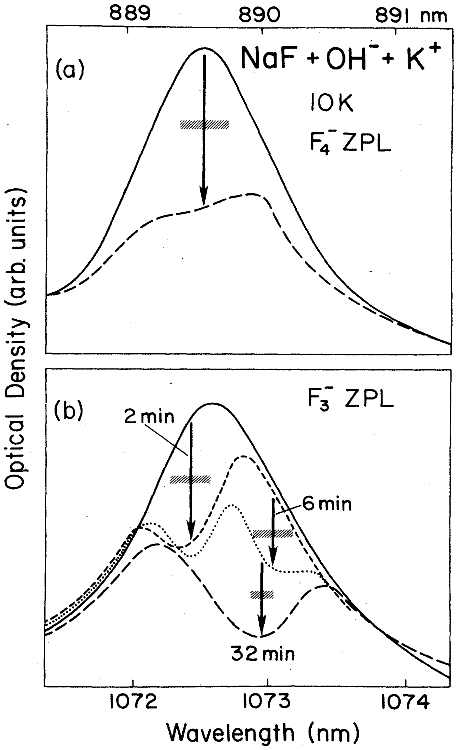

FIG. 7. Effect of bleaching at 10 K with spectrometer light (arrows indicate spectral position, shading indicates spectral width) on the 889- and 1072-nm ZPL absorption for double-doped NaF crystals (shown in Fig. 6).

ments at 1.2 K about the ZPL linewidth dependence on the OH^- doping concentration are reported in the following paper.[3] A crystal doped with high (1%) OH^- concentration and additionally doped with 2% KF (both concentrations in the melt) produced for both defects the largest broadening (about a factor of 4 compared to the pure crystal) and an ~0.5-nm shift to low energies, while turning a major portion of the crystal opaque.

The ZPL absorption in this latter strongly perturbed crystal has a width which is large compared to the spectral slit width of the Cary spectrophotometer used, allowing selective optical irradiation with light through a narrow slit width into different spectral parts of the ZPL absorption. Figure 7 shows the result of such an experiment for the two defect absorptions. In both cases selective optical bleaching could be obtained, particularly for the 1072-nm absorption, where successive optical bleaching at different wavelengths resulted in drastic changes in the absorption profile. This very simple spectrophotometer hole-burning experiment (the first of its type as far as we know) demonstrates, without any sophisticated laser equipment, the inhomogeneously broadened absorption and the principle of photochemical hole burning.

A possible reversal of the photochemical bleaching effect is of the highest importance for studies or applications of optical hole-buring effects. Therefore we studied for both defects the possibilities of recovering the bleached ZPL absorption by optical or thermal treatment. Attempts to recover the bleached 889-nm ZPL absorption by optical irradiation at 10 K in various spectral ranges did not produce any success. Thermal treatment, however, was partially successful as summarized in Fig. 8 for both OH^-- and Mn^{2+}-doped crystals. After nearly total optical bleaching of the 889-nm line at 10 K, pulse annealing in the dark to higher temperatures produced partial recovery of the bleached absorption in the temperature range between 150 and 300 K. About $\frac{2}{3}$ and $\frac{1}{2}$ of the bleached absorption could be recovered in the two crystals by heating to RT. Successive repetitions of this process, i.e., optical bleaching of the recovered absorption at 10 K followed by a new thermal annealing to room temperature, produce in each cycle partial recovery with roughly the ratio seen in the first cycle ($\frac{2}{3}$ and $\frac{1}{2}$). So far we have not yet succeeded in reversing the absorption loss appearing in each (bleaching and annealing) cycle.

The stability of the 889-nm defect at RT was tested in two ways: When freshly electron-irradiated samples (after the 889-nm ZPL absorption was measured at 10 K) were

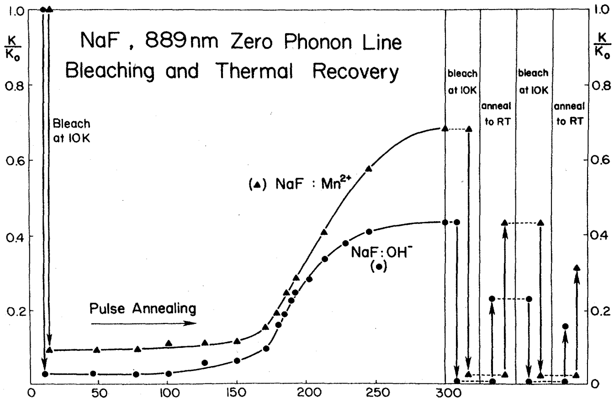

FIG. 8. Normalized strength of 889-nm ZPL absorption after optical bleaching at 10 K and thermal annealing to RT (and four successive repetitions of this cycle) for a Mn^{2+}-doped and OH^--doped NaF crystal.

stored at RT, a decrease of the 889-nm absorption strength by ~30–40 % over a period of about two days was observed. After this initial decrease, however, the remaining 889-nm absorption was found to be stable at RT over extended periods of time. If in freshly electron-irradiated samples, the 889-nm ZPL absorption was totally bleached at 10 K and then partially recovered by pulse annealing to RT (as in Fig. 8), the recovered absorption proved to be extremely stable under RT storage in the dark; no decrease was observed in 35 days.

The recovery and optical stability properties of the 1072-nm ZPL defect were not studied in great detail, but the following main behavior has been established:

(a) After optically bleaching the 1072-nm line at 10 K, no recovery by heating to RT can be produced, as in the case of the 889-nm line (see Fig. 3). This result is in agreement with the results of Chandra[9] in hydroxide-doped crystals.

(b) If sizable amounts of 1072-nm lines but negligible amounts of 889-nm lines are created by short e^- irradiation at RT, optical bleaching of the 1072-nm line at 10 K can, by a major part, be restored by *F*-band irradiation at ~200 K. This optical restoration is not possible after heavy e^- irradiation with sizable 889-nm-line production.

(c) The 1072-nm line, created after e^- irradiation at RT, basically bleaches out thermally to 100% in the dark at RT in about 24 hours (in strong contrast to the 889-nm line).

(d) After thermal or optical bleaching of the 1072-nm line, it can be restored easily by ultra-short x-ray irradiation (1–5 min) or e^- irradiation (~5 sec) in the dark at RT.

III. DISCUSSION

The degree of previous observations and interpretations of the 889- and 1072-nm ZPL in NaF have been very different. The 1072-nm line [easily formed with rather small irradiation doses (see Fig. 3)] had been observed in an early work by Fitchen *et al.*[8] and was interpreted as arising from F_3^- defects. Besides NaF as a host, a similar ZPL was observed in five crystal materials, yielding a reasonable Ivey law for the line positions in different hosts.[1]

In contrast to this, the 889-nm band, appearing only under heavy irradiation in properly doped crystals, has been observed empirically only as a tiny trace in early works,[5–7] without any attempt at a center interpretation. We interpret it to be produced by F_4^- centers due to the following arguments:[11]

(a) The formation curve of the 889-nm line has a "delayed" start with a very small—nearly zero—slope [Fig. 3(a)], in contrast to the nondelayed high initial growth rate of the 1072-nm line [Fig. 3(b)]. Only after the quick buildup of the 1072-nm line does the growth rate of the 889-nm line increase considerably. This clearly shows that the 889-nm line must be due to a more extended aggregate compared to the F_3-type complex. In fact the presence of F_3^- defects may well be the precondition for the formation of an F_4^- defect, as the latter could be formed by an F_3^- defect capturing another irradiation-produced *F* center.

(b) The amount of 889-nm ZPL produced was found in many experiments to be roughly proportional to the F_4 absorption produced, but not related to the F_3-type defect amount.

(c) The photochemical changes, observed under the 889-nm-line bleaching at 10 K, show a decrease of the F_2^+ and an increase of the F_4-center absorption (Fig. 5). This can be easily explained by photoionization of the F_4^- band,

$$F_4^- + h\nu \rightarrow F_4 + e^- , \qquad (1)$$

and an easy capture of the free electron, e.g., by F_2^+ centers,

$$F_2^+ + e^- \rightarrow F_2 . \qquad (2)$$

(d) The observed absence of any bleaching dichroism with ⟨100⟩ or ⟨110⟩ light for the 889-nm line is in agreement with the tetrahedral structure of the F_4 center, which binds an extra electron.

If this interpretation is correct, the 889-nm ZPL defect is the first observed case of an F_4^- center. This allows the extension and discussion of a small table, summarizing the known F_n^- defects ($n=2,3,4$) identified by their ZPL absorptions:

	LiF	NaF	KCl	KBr
F_2^-	1040.4 nm	1292.0	2015.0	?
F_3^-	832.8 nm	1072.1	1629.5	1770.5
F_4^-	?	889.2	?	?

We can attempt to find systematic trends, both in thermal and optical stability among these F_n^- systems, by variation of either the host material (horizontal) or the *n* number (vertical).

(a) Thermal stability is (in all cases measured so far) *enhanced* as one moves from KBR to LiF towards smaller lattice parameters, with vertical variation towards F_n^- defects with a larger *n* number. (This is confirmed by our observation that F_3^- defects in NaF disappear within a day at RT, while they remain stable over a period of many months in LiF.) F_2^- defects have a similar trend, reaching RT stability only in LiF. For vertical variation our work shows that F_4^- defects are much more stable than F_3^- centers at RT in NaF.)

(b) Optical stability appears again to be *enhanced* by horizontal variation in the table to smaller lattice parameters, though only one measured case is experimentally available for testing: Our investigated F_3^- defect in NaF is 100% bleachable with quantum efficiency $\eta \approx 10^{-2}$. F_3^- in LiF, for which hole burning has been done,[12] can be bleached only to a small degree (~10%) with very low ($\eta \approx 10^{-6}$–10^{-7}) quantum efficiency. The vertical (n) variation in our investigated F_3^- and F_4^- defects in NaF indicates 100% bleaching for both centers at lowest temperatures, but a higher quantum efficiency for F_3^- compared to F_4^-. The only opposite trend appears for F_2^- and F_3^- defects in LiF, where F_2^- is stable under the heaviest optical excitation at RT, while F_3^- produces shallow hole-burning effects at lowest temperatures.

Aside from this very last case, it appears that variations towards smaller lattice parameters and higher n numbers increase both the thermal and optical stability of $F_n{}^-$ defects. Within these trends NaF is a rather optimum host for hole burning: The $F_n{}^-$ centers still possess a reasonable thermal stability in NaF at RT, but have a higher optical instability at low temperatures compared to LiF. If one could produce $F_4{}^-$ defects in LiF (expected by an Ivey-type law with a ZPL close to 700 nm), it is questionable whether it would bleach and could be used for hole burning. $F_n{}^-$ centers in the larger lattice parameter hosts (KCl, etc.) are expected to be well bleachable, but due to their observed or expected low thermal stability are harder to produce and to handle.

Of our two investigated defects in NaF, the $F_4{}^-$ (889-nm ZPL) defect has also been studied by hole burning, parallel to this work at the IBM Laboratory, San Jose, as reported in the following paper.[3] Aside from surprising effects found under high-intensity laser-light hole burning,[3] our plain spectrometer bleaching of $F_3{}^-$ and $F_4{}^-$ centers in this work raises some basic unexplained questions and problems.

A ZPL transition at low temperatures leads to an excited bound state in the gap of the band structure, without supplying direct phonon relaxation or phonon-induced changes in the excited state. For the observed bleaching of the ZPL, in principle, only two types of processes can be considered:

(1) Reorientation of the defect complex in the excited state, selected by polarized excitation, creating dichroic absorption. This possibility is clearly excluded—at least for the $F_4{}^-$ defect—by our bleaching experiments with alternatively changing polarization of bleaching- and absorption-measurement light (Fig. 4).

(2) A change of the excited state, reached by ZPL transition, into a new state of the defect, which favors a process destroying the center. As our photochemical experiments (Fig. 5) lead to separation of the electron from the $F_4{}^-$ center (forming F_4), this process could happen only in two ways: (a) By dissociation of the excited electron into the conduction band, where it travels to other defects with strong electron-capture cross sections (like $F_2{}^+$). It is, however, very difficult to see how such an ionization effect could occur at 10 K from a bound excited state, reached with a ZPL transition and therefore not supplying means for phonon relaxation which could raise the bound state into the conduction band. (b) The most reasonable (and very often used) explanation is the fact that in the ZPL excited state the electron could tunnel to another defect lying nearby, where it would become trapped in a stable way.

This last interpretation relies on the distribution and local density of the centers and one would expect different rates of processes depending on how close the neighbors are located. Two of our experimental observations make it hard to accept this picture:

(i) The bleaching effect we found is independent of the dose of e^- irradiation, i.e., the concentration of the formed defects. The bleaching occurs after very small irradiation doses, giving rise to extremely low optical density ZPL absorptions.

(ii) In all cases of high or low center concentration, optical irradiation always leads—with close to exponential decay—to *full bleaching of all the defects.* If the process were to depend on the distance of a neighboring defect, to which the excited electron could tunnel, one would not expect this simple behavior.

Therefore, in spite of the interesting and high-efficiency ZPL bleaching properties, many questions about the responsible physical processes remain open and will be approached with new experimental techniques in the continuing work.

ACKNOWLEDGMENT

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