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Cation impurity effects on $F_2{}^+$:O^{2-} color-center formation in NaCl

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It is experimentally shown that alkali-metal impurities with larger ionic radius than the Na^+ ion (K^+,Rb^+) have no significant effect on the formation of $F_2{}^+$:O^{2-} laser-active centers in additively colored NaCl. However, impurities with smaller ionic radius (Li^+) suppress the formation of these centers.

The $F_2{}^+$:O^{2-} color center in NaCl has been demonstrated to be a powerful laser medium in the near ir,[1] delivering tunable radiation between 1.4 and 1.8 μm. The nearly ideal laser properties of this center have led us to investigate how various ionic impurities (apart from the oxygen impurity that has been shown to be necessary[2]) can affect the formation of the center. In particular, we report some initial experimental results on the effects of alkali ionic impurities on the $F_2{}^+$:O^{2-} center formation in NaCl.

The characteristic absorption and emission bands of the $F_2{}^+$:O^{2-} color center in NaCl peak at 1.09 and 1.55 μm, respectively. Optimum populations of $F_2{}^+$:O^{2-} centers form in NaCl crystals doped with low concentrations (5–50 ppm) of OH^- impurity, following additive coloration and photoaggregation.[2] In previous work it has been shown that a prerequisite for the formation of $F_2{}^+$:O^{2-} centers is the existence of O^{2-}-anion vacancy defects, which are characterized by uv absorption bands peaking at 226 and 288 nm in NaCl. The O^{2-} ions are formed during the coloration process as products of OH^- dissociation.

Single crystals of NaCl, doped with both OH^- and either Li^+, K^+, or Rb^+, were grown using the Kyropoulos technique in a platinum crucible under an inert argon atmosphere. Chlorine-pretreated ultrapure NaCl was used as the starting material. Impurities were added to the NaCl melt in the form of NaOH, LiCl, KCl, and RbCl dopants, respectively. The amount of NaOH dopant in the melt varied from 0.02 to 0.05 mol %, while the concentration of OH^- incorporated in the grown crystals was measured to be in the range of 10–40 ppm. This concentration was determined from the strength of the OH^- uv absorption band (peak at 185 nm in NaCl).[3] The segregation coefficient of OH^- in NaCl, approximately 7% in our crystals, was found not to depend on the amount of alkali codopant. The amount of added alkali cation impurity was varied as will be described below. The results are compared to those obtained from crystals doped with OH^- alone.

Several NaOH-doped crystals were grown with concentrations of 0.01 to 3 mol % KCl codopant, and one crystal with 0.5 mol % RbCl codopant added to the melt. In the case of the Rb^+ impurity we only studied the effects on color center bands lying in the 0.4–1.8-μm region, however the results obtained were similar to the K^+ case described below. In all crystals doped with OH^- and either K^+ or Rb^+, the $F_2{}^+$:O^{2-} absorption bands that formed (following the procedure described in Ref. 2) had optical densities similar to those in crystals doped with OH^- alone. The presence of K^+ impurity did not affect the formation of the uv O^{2-}-related bands. However, in all the K^+-doped crystals, interaction between the K^+ and OH^- ions was evident from the broadening of the characteristic mid-ir OH^- vibrational band (3654 cm^{-1} at liquid-helium temperature), as shown in Fig. 1. The spectra in this figure, taken using a Fourier-transform infrared (FTIR) spectrometer, correspond to two uncolored crystals—one doped with OH^- alone, the other codoped with K^+—with the same concentration of OH^- impurity (as determined by uv spectroscopy). The changes in the ir vibrational stretch due to K^+ imply that association between these ions occurs during crystal growth. However, this did not seem to affect the subsequent formation of oxygen-associated centers.

Previous work has shown that the OH^- ir band in NaCl is particularly sensitive to perturbations such as changes in crystal temperature, OH^- concentration, or electric field.[4] The broadening of this band in NaCl:K can thus be attributed to random elastic strain fields due to the different ionic radii of Na^+ and K^+. Associated with these strains will be electric field gradients,[5] and these will further perturb the OH^- ion through interactions with its electric-dipole moment. The effects of K^+ on the OH^- bands in NaCl—broadening of the ir band but no effect on the uv band—should be compared to those reported in the case of alkaline earth impurities, particularly Ca^{2+}.[6] In that case, cation-oxygen complexes have been shown to form[7] and the OH^- uv band is suppressed, while the ir band is still observed.[6]

As laser media, K^+- or Rb^+-doped NaCl:OH crystals did not exhibit differences in laser output power, tuning range, or peak wavelength, compared with crystals doped with OH^- alone. These results show that the presence of

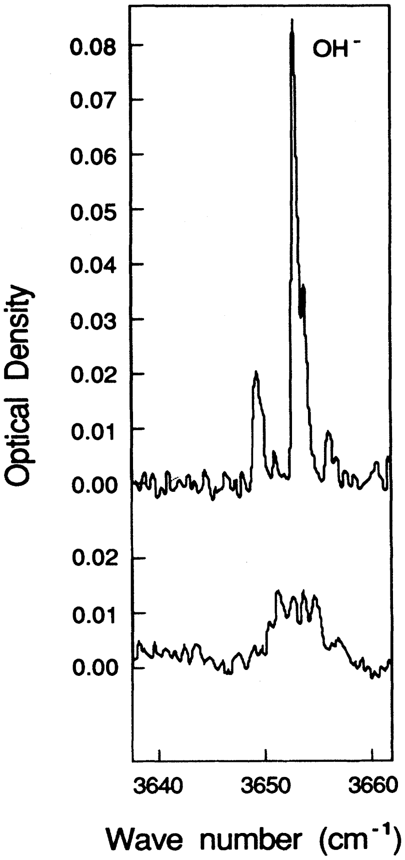

FIG. 1. FTIR absorption spectra at 1.5 K of 1.4-cm-thick uncolored NaCl crystals containing the same concentration of OH^- impurity (17 ppm). The bottom scan corresponds to a crystal codoped with 0.5 mol % KCl added to the melt.

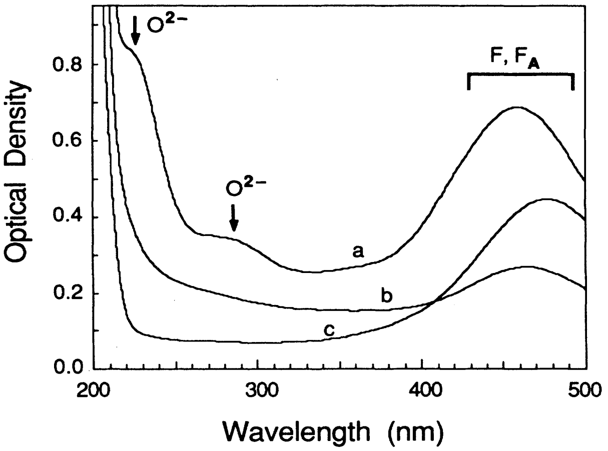

FIG. 2. uv absorption spectra of 3-mm-thick NaCl:OH crystals codoped with Li^+, colored at 20-Torr vapor pressure. Curve *a*, crystal doped with 0.015 mol % LiCl; *b*, crystal doped with 0.1 mol % LiCl; *c*, crystal doped with 1 mol % LiCl. Note the 226- and 288-nm oxygen bands marked with arrows in *a*. Variations in the *F*-band density are due to different OH^- impurity concentrations, while variations in the *F*-band peak wavelength are due to formation of F_A-type centers.

alkali cation impurities with larger ionic radii than Na^+ has no significant effect on the formation of $F_2{}^+$:O^{2-} laser-active centers. Additionally, we have not observed any perturbation of the other color-center bands in the uv and visible spectral regions due to the presence of such impurities.

To study the effects of Li^+ impurity we grew NaCl crystals doped with 1, 0.1, and 0.015 mol % LiCl added to the melt together with 0.03–0.05 mol % NaOH. In the uncolored crystals, again, the OH^- uv absorption band did not appear to be affected, similar to the cases with the K^+ and Rb^+ impurities described above. Following additive coloration at 20-Torr vapor pressure, however, we observed significant effects on the formation of color centers. In the crystals doped with 1 and 0.1 mol % LiCl the formation of O^{2-}-related bands in the uv was completely suppressed (Fig. 2, curves *c* and *b*, respectively) and no detectable $F_2{}^+$:O^{2-} absorption band was formed. These crystals exhibited very slow color-center photoaggregation rates, compared with crystals doped with OH^- alone. In the crystal doped with 0.015 mol % LiCl we observed formation of both the uv O^{2-} bands [Fig. 2(a)], and the near-ir $F_2{}^+$:O^{2-} band (although the absorption of the latter was slightly reduced, compared to similarly processed NaCl:OH crystals with the same OH^- concentration). These results are consistent with the assignment of the 1.09-μm absorption band to an O^{2-}-perturbed $F_2{}^+$-type center.

Remarkable in the spectra of Fig. 2 is also the evident shifting of the *F*-band peak to the red with increasing Li^+ doping. The *F* band peaks at 458 nm (±2 nm) at 300 K in additively colored NaCl crystals doped with OH^- alone. In our Li^+ codoped crystals the *F* band peaked as follows: 459 nm for 0.015 mol % added LiCl, 464 nm for 0.1 mol % added LiCl, and 478 nm for 1 mol % added LiCl. This perturbation indicates the formation of F_A centers in NaCl, analogous to similar cases in other alkali halides doped with cation impurities (e.g., KCl:Li,KCl:Na). To the best of our knowledge this is the first reported observation of F_A centers in NaCl.

This tendency of Li^+ impurity to combine with *F* centers (in contrast with the K^+ or Rb^+ cases) may help to explain the suppression of O^{2-}-vacancy formation. Assuming a simple reaction of the type

$$2F+OH^- \rightarrow O^{2-}+\text{anion vacancy}+H^-$$

for the OH^- dissociation process, it appears that binding of Li^+ to any of the defects involved in the reaction (except for the H^-) could prevent the eventual formation of O^{2-} vacancy-related defects. Binding of Li^+ to *F* centers would also explain the observed slow color-center photoaggregation rates.

The proposed mechanism is supported by the following argument. The segregation coefficient of Li in NaCl during crystal growth is on the order of 10%.[8] From absorption data we calculate that the typical color-center population introduced by additive coloration, at 20-Torr Na vapor pressure, into a NaCl:OH^- crystal containing 20 ppm OH^- is approximately $6\times10^{16}/cm^3$, or 4 ppm.[9] Hence, the effects of Li^+ impurities become apparent when the Li^+ concentration in the crystal becomes significantly larger (on the order of 100 ppm or more) than the corresponding concentrations of color centers and OH^- ions.

In conclusion, there seem to be no significant perturbation effects on the NaCl color-center bands due to the presence of K^+ or Rb^+ impurities. Thus, alkali ionic impurities with larger ionic size than Na^+ do not affect the formation of $F_2{}^+$:O^{2-} centers. Conversely, in the Li^+-doped crystals suppression of the O^{2-}-related bands and formation of a perturbed *F* band are observed.

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