

OPTICAL PROPERTIES AND STABLE, BROADLY TUNABLE cw LASER OPERATION OF NEW F_A -TYPE CENTERS IN Ti^{4+} -DOPED ALKALI HALIDES

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A new group of complex color centers with F_A -type properties, involving simple center production and high thermal and optical stabilities, has been found in six Ti^{4+} -doped alkali halides: NaCl, KCl, RbCl, KBr, RbBr and RbI. In its first tested examples, KCl and KBr, broadly-tunable cw laser operation over the 1.4 to 1.7 μm range has been obtained, with output powers in the 100 mW range. In contrast to already existing F_2^+ and F_2^{2+} -like centers, operating in the same wavelength range, the new $F_A(Ti^{4+})$ lasers are optically stable and do not show any bleaching effects under laser operation.

The color center systems, which so far have been successfully operated as broadly tunable cw ir lasers, can be divided into two characteristic groups with distinctly different physical and performance features:

1) F centers, attached to either Li^+ impurities ($F_A(II)$ centers) or Na^+ pairs ($F_B(II)$ centers), form in certain hosts after optical excitation ionic saddle-point configurations of $\langle 110 \rangle$ symmetry [1], with electronic states highly favorable for laser operation [2,3]. The large Stokes-shift and limited quantum efficiency of the emission produce rather small slope efficiencies. The great virtues of these systems, however, are extremely simple center production, high thermal stability and easy handling procedures at room temperature, as well as complete absence of any fatigue or bleaching even under high power and long time operation. These positive features promoted their wide application, particularly in the first commercial color center laser, covering the 2.2 to 3.3 μm range.

2) F or F_A centers, when attached to empty anion vacancies, form the large group of F_2^+ or $(F_2^+)_A$ centers, the emissions of which cover a wide spectral range (0.8–2.5 μm). In spite of very positive features

for laser operation (low threshold, high slope efficiency, wide tuning range) [4], they have two serious disadvantages:

(a) Rather complicated production procedures, low thermal stability and therefore difficult handling properties at room temperature.

(b) Due to center reorientation, ionization and/or migration effects under optical excitation, the centers bleach under laser operation. Part of these losses (the reversible ones) can be counteracted by various auxiliary UV light irradiation or polarization switching techniques. Irreversible losses, however, allow laser operation of a particular spot in the crystal only for limited times. These difficulties (a) and (b) have prevented a wide routine use of F_2^+ type centers for tunable lasers.

We report here on a new group of complex color centers, which overcomes the difficulties (a) and (b) of the F_2^+ centers, and supplies in its first tested examples tunable and completely stable laser operation over the 1.4–1.7 μm range [5]. This new defect is most likely an F_A center which gives rise to a different type of relaxed excited state, which we call $F_A(III)$. To put it in perspective, we compare it with the two other types of F_A centers, which so far have been realized by

Na^+ or Li^+ impurity partners of the F centers:

1) In $F_A(\text{I})$ centers the distinct $\langle 100 \rangle$ optical anisotropy and 2p state splitting observed in absorption disappears essentially in the relaxation process: The relaxed excited state becomes extended, the 2s state lies lower than the 2p states, so that a nearly depolarized and long life-time emission results, very similar to the pure F center case [1]. These systems are not favorable for and have not been operated in laser emission.

2) In the $F_A(\text{II})$ centers, the large size misfit of the Li^+ impurity produces after optical excitation an ionic relaxation into a new defect structure, the saddle-point configuration [1], with a very low lying $2p_z$ state along the new $\langle 110 \rangle$ defect axis and highly favorable optical properties for laser operation.

3) In the new $F_A(\text{III})$ centers, a $\langle 100 \rangle$ neighboring impurity ion for the F center is chosen with the following properties:

(a) Its size is too large to form the saddle-point stage of type II, so that the center keeps its original $\langle 100 \rangle$ symmetry.

(b) The electron affinity of the impurity ion is larger than that of the Li^+ and Na^+ ions used so far. Firstly this will lead to a larger splitting of the 2p state in absorption, considerably lowering the $2p_z$ state parallel to the center axis. Due to this downward shift of $2p_z$, in the relaxation process the 2s state will no longer cross the $2p_z$ state, so that the latter becomes the relaxed excited state. A fully $\langle 100 \rangle$ polarized emission (parallel to the center axis) with short life-time and emission energies somewhat lower than F centers are expected for these $F_A(\text{III})$ centers.

Candidates of impurity ions with a large electron affinity are for instance Tl^+ , In^+ and Ga^+ . They have ionic radii comparable to K^+ , which makes type II saddle-point behavior highly unlikely. As the Tl^+ defect is most extensively studied and well established in terms of its electron affinity and trapping properties [6], we focused our attention first on this system.

When attempting to additively color Tl^+ doped crystals, one does not obtain any F centers, but instead a very broad absorption, which neither by quenching from high temperature nor by high energy irradiation can be converted into F or F aggregate centers. Therefore the coloration was performed with electron irradiation (1.8 MeV, $1.7 \mu\text{A}/\text{cm}^2$). The most efficient production method starts with prolonged e^- irradiation at LNT. In this process Tl^+ , Tl^{2+} , $(\text{Tl}_2)^+$,

V_K and large amounts of F centers are formed. On the low energy side of the F band (in the range of F-aggregate center absorptions), however, only extremely weak absorptions around 1.04 and 1.76 μm occur (curve a in fig. 1) the latter one attributed to dimer defects $(\text{Tl}_2)^+$ [7]. Under white light irradiation, this weak 1.76 μm band disappears, and under additional heating of the crystal the 1.04 μm band grows drastically in the temperature range above -40°C , as seen in the insert of fig. 1. After this thermal annealing under light irradiation, the spectrum shown as solid line in fig. 1 is obtained, consisting of an extremely strong band at 1.04 μm , and the well known F_2^+ band at 1.36 μm . The latter can be easily thermally removed by heating to about -10°C , while the 1.04 μm band remains completely stable.

By similar production methods, the same type of band could be created in Tl^+ doped NaCl, KBr, RbCl, RbBr and RbI. Fig. 2 summarizes the absorption curves. Light irradiation at LNT into these bands leads to Stokes-shifted strong ir emissions, which are also displayed in fig. 2. Polarized excitation and emission measurements, performed for the KCl: Tl^+ case in various geometries, showed that the emission occurs fully

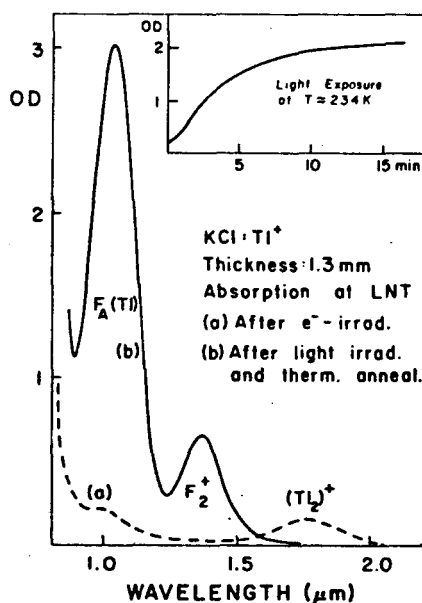


Fig. 1. Absorption spectra of $\text{KCl}:\text{Tl}^+$ at 77 K after e^- irradiation at 77 K (dashed) and subsequent exposure to white light at -40°C (solid curve). Insert shows growth of $F_A(\text{TI})$ band at 234 K during light exposure.

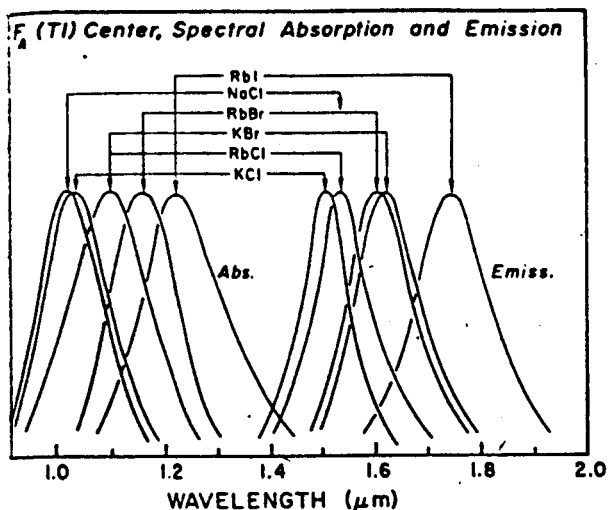


Fig. 2. Absorption and emission bands of the low energy transitions of $F_A(Tl)$ centers in various alkali halides at 77 K.

polarized parallel to a $\langle 100 \rangle$ excitation of the ir absorption band. We therefore assign the ir absorption bands to the lowest energy transition along the center axis of a $\langle 100 \rangle$ oriented defect, which is followed after relaxation by an equally polarized emission from the same type of lowest excited axial state of the defect. This model implies that at higher energies absorptions due to transitions perpendicular to the center axis must be present. We observe, in fact, that together with the appearance of the $1.04 \mu m$ band several absorptions (weaker ones at 830, 720, and 620 nm, and a very strong one at 340 nm) develop. Quantitatively we have already observed that the characteristic ir emission of the defect can indeed be excited in the spectral range on the high energy side of the ir absorption band in fig. 2. A comprehensive study of these higher energy bands and their relation to the $\langle 100 \rangle$ Tl center as well as a study of all details of the formation kinetics is under way and will be published separately.

We interpret the spectra in fig. 2 as the lowest energy absorption and emission transitions along the $\langle 100 \rangle$ center axis of a complex defect formed by an F center and a $\langle 100 \rangle$ neighboring Tl^+ ion. Obviously, the defects have been formed by light-induced F center migration in the same temperature range where F_A , F_B and F_Z centers can be formed [8], and the abundantly present Tl^+ ions are the natural choice for the role as an association partner. Actually, a complex of this type has been postulated to interpret EPR data in irradiated

Tl^+ -doped crystals [9] with indications that the spin density of the ground state electron is shared between the Tl^+ and the anion vacancy site, which is understandable in view of the high electron affinity of the Tl^+ . This strong electron binding effect of the Tl^+ can possibly explain the unusually small and not "Ivey-law type" variation of the transition energies with host materials, as seen in fig. 2.

The thermal stability of the $F_A(Tl)$ center is excellent. Fig. 3 shows (curve a) the absorption strength of the $1.06 \mu m$ band in $KCl:Tl^+$ as a function of storage time at RT. A certain decay occurs during the first five days, which levels off later, indicating that it is not due to an intrinsic thermal instability of the F_A center itself but most likely due to a slow reaction with some partner which becomes exhausted. Storage in a refrigerator (curve b in fig. 4) slows down this first decay dramatically. Modest light exposure of the crystals at RT has not any appreciable effect on the F_A absorption band.

For laser experiments the two $F_A(Tl)$ systems in KCl and KBr hosts were chosen as initial candidates. Both can be effectively pumped with the strong $1.064 \mu m$ line of a Nd^{3+} :YAG laser. As resonator, a folded astigmatically compensated four mirror cavity was used, consisting of two plane, dichroically coated mirrors and two spherical mirrors ($r = 75 \text{ mm}$) which are gold coated and highly reflective for pump laser and crystal fluorescence ranges of interest. The pump beam is coupled collinearly into the resonator through one of the plane end-mirrors and is focussed onto the crystal by one of the folding mirrors. The crystal slab is clamped under Brewster's angle onto an adjustable 77

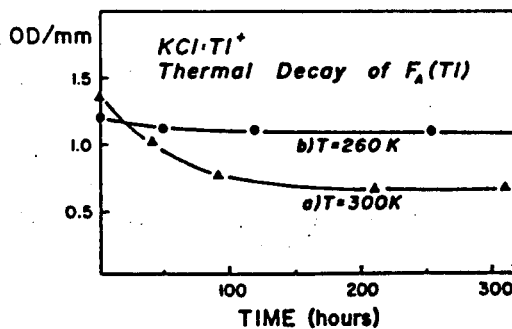


Fig. 3. Absorption of $F_A(Tl)$ centers in KCl as function of storage time at room temperature (a) and in a refrigerator at 260 K (b).

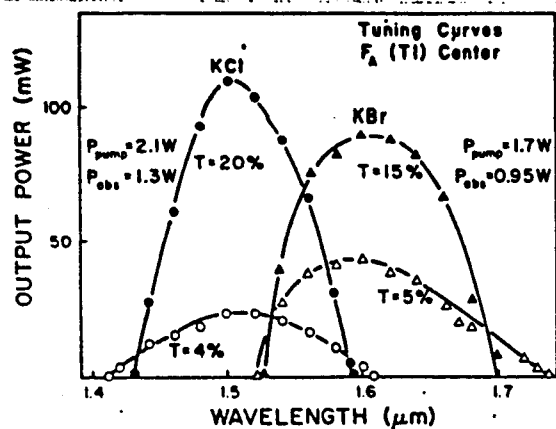


Fig. 4. Tuning curves of KCl and KBr $F_A(Tl)$ -center lasers.

K copper gold finger. Crystal and folding mirrors are placed within an evacuated cavity space having two Brewster oriented CaF_2 windows as exit ports. The tuning element – a Brewster cut sapphire prism – and the end mirrors are placed outside the vacuum to provide easy access.

The possibility to prepare crystals with $F_A(Tl)$ centers ready for laser operation and to store them at RT was only discovered later in this work. Therefore, the actual laser crystals were still prepared with the process used for F_2^+ center production [4]. Crystal slabs of $2 \times 5 \times 8 \text{ mm}^3$ size were cleaved, polished, wrapped in aluminum foil and exposed to a 1.8 MeV, $1.7 \mu\text{A}/\text{cm}^2$ e^- -beam on both sides at temperatures below -50°C . After coloration, the crystals were stored in liquid nitrogen until needed. Prior to use the crystals were briefly repolished, mounted into the resonator cavity, cooled to -40°C and exposed, through a cavity window, to unfiltered light from a small tungsten lamp in order to enhance the $F_A(Tl)$ center concentration via aggregation. After approximately 10 minutes exposure time the crystals were cooled to 77 K operating temperature. In their final stage the crystals absorbed roughly 60% of the pump laser power in the case of KCl and 50% in the case of KBr. In both crystals broadly tunable cw laser operation with excellent optical stability has been obtained.

Tuning curves for both lasers and a typical output versus input power dependence, shown as an example for the KBr laser, are given in figs. 4 and 5. The KCl laser was tunable from 1.41 to 1.61 μm with 24 mW in the peak around 1.5 μm using an output coupler

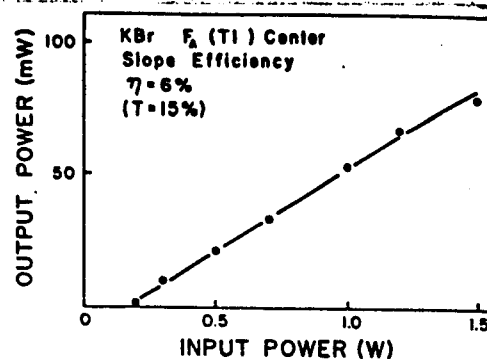


Fig. 5. Input-output power dependence for the KBr $F_A(Tl)$ -center laser.

with 4% transmission. Increase of the transmission to 20% leads to a slight decrease of the tuning range and an increase in peak power to 113 mW. The KBr laser was tunable from 1.522 to 1.738 μm and yielded 44 mW in the peak around 1.6 μm using a 5% output coupler. Change to a 15% output coupler increased the peak output power to 90 mW. For both crystals output power was optimum when the electric field vector of the pump beam was parallel to the plane of incidence and thus lying in a $\langle 100 \rangle$ plane of the crystal.

Output powers were found to increase linearly with increasing pump powers up to a level of 1.8 W of the latter – resulting in a slope efficiency of 6% for the KBr laser and a slightly higher one for the KCl laser. Increase of the pump power to the highest available level (4W) does not lead to further increase or change in cw output power, an effect which we attribute to a heating of the crystal to temperatures above 77 K and a corresponding trade-off between decrease in quantum efficiency and increase in pump power. This limits the useful average pump power to 2 W for the crystal clamping design employed in our resonator. It is expected, however, that harder pumping and a linear increase in output power is possible using an improved thermal contact between crystal slab and cold finger. A further scaling of output power with increasing input power was indeed observed using a light chopper in front of the color center laser which reduced the average pump power to 50%. Thus, at 4 W peak pump power it was possible to extract color center laser "pulses" with exactly double the peak output power compared to 2 W pump power.

It should be pointed out that both $F_A(Tl)$ lasers show a significant stability of the output even under extended operation periods and high pump power levels: no decay in output power was observed when the laser was operated for a test period of one day under four watt pump power excitation, in distinct contrast to the behavior of F_2^+ center systems. In summary, this new class of color center systems supplies for the first time materials for tunable lasers in the 1–2 μm range, which provide excellent optical stability, simplicity of laser operation (no need for auxiliary light irradiation) and long term storage capability at RT of fully prepared laser crystals. At the present time laser experiments are under way to extend the total tuning range of these lasers using $F_A(Tl)$ centers in RbI and similar centers in In^+ - and Ga^+ -doped alkali halides, for which in the latter cases emission bands in the 0.8 to 1.4 μm range have already been identified.

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Added Note:

After completion of this manuscript, a paper has appeared (E. Goovaerts et al., Phys. Rev. B24 (1981) 29) which reports ESR measurements on two thallium defects of $\langle 100 \rangle$ symmetry in x-irradiated $KCl:Tl^+$. One of these defects is interpreted to consist of a Tl^0

atom and an attached anion vacancy, with the unpaired Tl^0 electron being partly delocalised in F center orbitals of the anion vacancy. This is very likely the same type of defect complex we are treating in this work. Experiments to verify the interrelation between the infrared properties of our $F_A(Tl)$ defect and the ESR properties of the $\langle 100 \rangle Tl^0$ defect are under way.

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