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Optical properties of the oxygen-perturbed F_2^+ colour centres in six different alkali halides

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Abstract. We studied the formation and optical properties of $(F_2^+)_H$ centres in six different crystals doped with oxygen: NaCl, KCl, KBr, RbCl, RbBr and KI. The results are entirely new in the case of KI and mostly original for RbCl and RbBr. The absorption and emission bands are compared with those of pure F_2^+ centres in similar host lattices. In order to obtain an interpretation of the relationship between the wavelengths of the low-energy transitions $1s\sigma_g \leftrightarrow 2p\pi_u$ and the nature of the host crystal, we applied a semi-empirical model based on the analogy of F_2^+ -like centres to molecular hydrogen ions immersed in a dielectric medium. This model, with the influence of both lattice parameter and dielectric constant, explains nicely the experimental results, including those for KI, which are inadequately described in the framework of the simpler Mollwo-Ivey law.

1. Introduction

A few years ago, a new kind of F_2^+ -like colour centre, active for laser emission, was obtained with oxygen impurities, first in NaCl crystals doped with OH^- (Pinto *et al* 1986) or O_2^{2-} (Wandt *et al* 1987) and then in O_2^- -doped KCl and KBr (Wandt *et al* 1987). These laser-active media are interesting in comparison with other colour centres such as F_2^+ or $(F_2^+)_A$ centres (stability under high optical pump power, formation by additive colouration, and possibility of obtaining high concentrations) or with other solid state laser media (higher stimulated emission cross section and emission band width; they are particularly interesting when they are used as a tunable single-mode source, or for femtosecond experiments). Laser-active materials which emit between 1.4 and 2 μm are especially valuable for studies of transmission in silica fibres (domain around 1.5 μm) or spectroscopic measurements of gain cross section in crystals doped with rare-earth ions or transition-metal ions. The optical properties of the $F_2^+-O_2^{2-}$ centres in NaCl:OH⁻ or NaCl:O₂²⁻ are outstanding in the ease of pumping (optical excitation by YAG:Nd³⁺ at 1.064 μm), the high value of slope efficiency (purely radiative de-excitation even at room temperature), and the broad band width (laser emission tunable from 1.4 to 1.8 μm).

The usual model for interpreting the microscopic structure of the oxygen-perturbed F_2^+ centre consists of an F_2^+ centre (two adjacent halogen vacancies trapping a single electron) stabilized by an O_2^{2-} impurity. This centre is called $(F_2^+)_H$ by analogy with the F_H centre, meaning that the impurity is substituted for a halogen

ion. Recently, Sennaroglu and Pollock (1991) successfully computed the transition energies of the $(F_2^+)_{\text{H}}$ centre in NaCl:OH^- by the addition of observed energies of the F_2^+ centre in pure NaCl and of corrections, calculated by first-order perturbation, starting from the wavefunctions of the H_2^+ molecular ion. Similar calculations were performed by our group (Doualan *et al* 1992) to extend the model of Sennaroglu and Pollock to $(F_2^+)_{\text{H}}$ centres in other alkali halides and/or with other dopants.

The aim of the present paper is to describe (sections 2 and 3) our experimental investigations on F_2^+ -like centres in new materials such as potassium iodide (KI:O_2^-), or rubidium halides (RbCl:O_2^- and RbBr:O_2^-) †. Moreover, to simplify research about the new active $(F_2^+)_{\text{H}}$ centres—and in particular to predict the wavelengths of optical transitions in absorption (availability of pump laser) and in emission (quest for laser emission wavelengths for specific applications) without the need to know transitions of pure F_2^+ centres in the same matrix (as in the calculations of Sennaroglu and Pollock (1991) or Doualan *et al* (1992)), we developed a very simple empirical law, based on the analogy of F_2^+ centres to the H_2^+ molecular ion. This relation gives results in good agreement with the observed low-energy transitions of $(F_2^+)_{\text{H}}$ centres in oxygen-doped crystals, as shown in section 4.

2. Experimental procedures for $F_2^+:\text{O}_2^-$ centre formation

The crystals used in these experiments were grown in our laboratory by a pulling method—Kyropoulos or Czochralski—from a platinum crucible. We used a pure argon atmosphere for NaCl:OH^- crystals, and a mixture of argon and oxygen (5–10%) for other crystals doped with the superoxide (KO_2). The presence of a partial pressure of oxygen was required to counterbalance the decomposition of superoxide when the temperature increases to the melting point of the alkali halides (600–900 °C):



With NaCl:OH^- crystals, it was possible to measure the final concentration of OH^- impurities after growth by pH titration or by UV absorption (Klein *et al* 1968). Appropriate amounts of OH^- of the order of 5×10^{-4} mol were added to the initial melt in order to achieve, in the crystal, OH^- concentrations in the range $5\text{--}10 \times 10^{-5}$ mol (corresponding to a segregation coefficient between 10 and 20%). The UV absorption measurements have the advantage over pH titration that they are non-destructive.

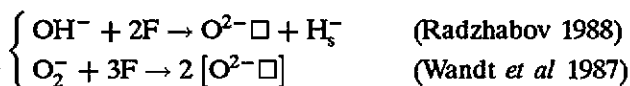
With other crystals (KCl , KBr , RbCl , RbBr and KI) we used potassium superoxide as the impurity. Because of the difficulty in detecting by traditional chemical analysis small amounts of oxygen, we could not estimate the final concentration, but appropriate amounts of KO_2 were around 5×10^{-4} mol in the initial melt to obtain optimized formation of $(F_2^+)_{\text{H}}$ centres. It could be interesting to use thermogravimetric analysis to estimate the final concentration of O_2^- finally incorporated into the crystal host.

For spectroscopic studies, crystals were cleaved with $\{100\}$ -oriented faces and typical dimensions 3 mm \times 10 mm \times 10 mm. Samples were additively coloured in alkali

† Gellermann (1989) has performed some unpublished experimental work on $(F_2^+)_{\text{H}}$ centres in RbCl:O_2^- and RbBr:O_2^- .

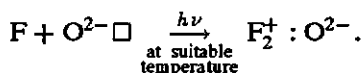
metal vapour at a temperature 50–100°C below the melting point of the material, using a heat-pipe apparatus similar to that described by Mollenauer (1978). The nature of the alkali vapour has no influence on the subsequent formation of colour centres (only halogen ions migrate significantly inside the crystal; alkali ions from the vapour stay on the surface of the sample). Thus we have used sodium vapour for NaCl colouration, and potassium vapour for KCl, KBr, RbCl, RbBr and KI. This choice permitted us to adapt the evolution of saturated vapour pressure versus temperature to the pressure and temperature of colouration (in fact, the temperature of halogen migration in the crystal). It is particularly important to use low pressures ($P < 100$ Torr) to reduce the formation of colloidal aggregates in the crystal. The conditions of colouration are reported in table 1.

During additive colouration, two distinct effects occur. On the one hand, there is the formation of simple F centres or colloids (aggregates of F centres). Before use, the crystals were annealed and quickly quenched on a copper plate in order to convert colloids into isolated F centres. On the other hand, the molecular ions (OH^- or O_2^- depending on the nature of dopant) are converted into $\text{O}^{2-}\square$ by reaction with the F centres (mobile at the temperature of colouration):



(H_s^- represents a hydrogen negative ion in a substitutional position).

Then, an exposure to 'F-band' light at a suitable temperature (see table 1) for a few minutes produces photoionization of F centres, migration of halogen vacancies through the crystal and, by combination with $\text{O}^{2-}\square$ centres and capture of a free electron, formation of the $\text{F}_2^+:\text{O}^{2-}$ aggregate:



We also used UV band light (from a high-pressure Hg lamp) to obtain $\text{F}_2^+:\text{O}^{2-}$ in NaCl or in KI. The $\text{F}_2^+:\text{O}^{2-}$ centre production by UV irradiation could be attributed to slow motion in the crystal of $\text{O}^{2-}\square$ by successive reorientations or to ionization of F centres by transition of the electron into the conduction band.

We can distinguish two different ranges of photoaggregation temperature depending on the crystal (in fact, the temperature of photoaggregation is directly connected to the temperature of the vacancy motion and therefore to the nature of the crystal). NaCl has been converted at room temperature, even though other materials have been transformed at lower temperatures between -30°C (KCl) and -5°C (KI) (see table 1).

In the optical absorption spectra (figure 1 for NaCl, KCl and KBr; figure 2 for RbCl, RbBr and KI), we observe the UV absorption bands characteristic of $\text{O}^{2-}\square$, the visible bands characteristic of intrinsic defects (F, F_2 , etc) and a weak absorption band in the infrared region attributed to $\text{F}_2^+:\text{O}^{2-}$ centres.

3. Optical properties of the $(\text{F}_2^+)_\text{H}$ centres

After photoaggregation (called step (a) below), the low-energy transition of $\text{F}_2^+:\text{O}^{2-}$ centres consists of a weak broad absorption band in the near-infrared region, weakly

Table 1. Crystal growth, colouration and photoaggregation conditions used for the $(F_2^+)_H$ centre formation.

Crystal	Crystal growth conditions			Additive colouration conditions			Photoaggregation conditions		
	Impurity	Quantity added to the melt (mol.ppm)	Melting point ($^{\circ}C$)	Temperature ($^{\circ}C$)	Pressure (Torr)	Time (min)	Wavelength of exciting light (nm)	Conversion temperature ($^{\circ}C$)	
NaCl	NaOH	500-1000	801	650-700	40-100	150	Unfiltered Hg lamp	20	
KCl	KO ₂	500	776	650	30-40	120	546	-30	
KBr	KO ₂	500	730	550-600	20-30	30	546, 647	-10	
RbCl	KO ₂	500	715	500	20-30	30	546	-20	
RbBr	KO ₂	500	687	450	30	30	546	-20	
KI	KO ₂	500	686	500	20-30	30	UV Hg lamp	-5	

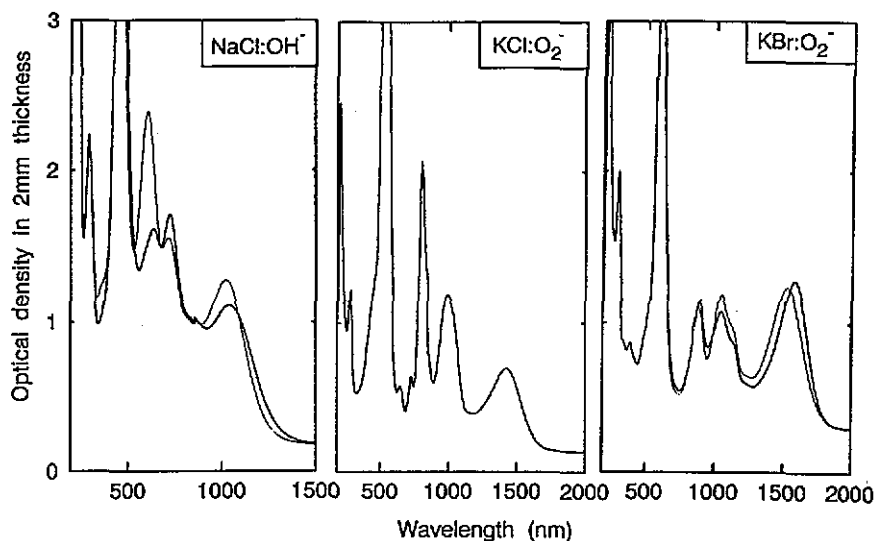


Figure 1. Absorption spectra of NaCl:OH^- , KCl:O_2^- and KBr:O_2^- after photoaggregation, step (a) in the text (—), and after further F-band light exposure, step (b) in the text (---).

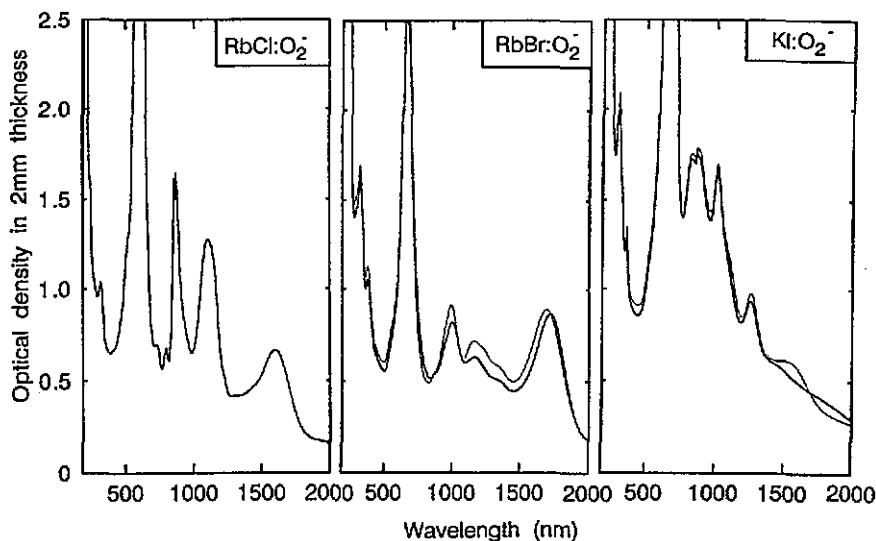


Figure 2. Absorption spectra of RbCl:O_2^- , RbBr:O_2^- and KI:O_2^- after photoaggregation, step (a) in the text (—), and after further F-band light exposure, step (b) in the text (---).

shifted toward long wavelengths with respect to the corresponding absorption band of F_2^+ centres (intrinsic F_2^+ band in the same host crystal).

By a further F-band light exposure at LNT (called step (b) below), this band usually shifts by a few tens of nanometres toward longer wavelengths. The only

exceptions are the $F_2^+O^{2-}$ centres in KCl and RbCl. A similar shift is observed for the low-energy emission band. The transformation (b) was differently interpreted by the Utah (Wandt *et al* 1987) and the Cornell (Georgiou *et al* 1987) groups.

According to the Cornell group, treatment (a) produces pure F_2^+ centres, and treatment (b) ensures the photoaggregation of the F_2^+ with the O^{2-} impurities, forming the final aggregate $F_2^+O^{2-}$. Migration of F_2^+ would arise from step-by-step reorientation during the transition $1s\sigma_g \rightarrow 2p\pi_u$, which corresponds to the 'F band'; such orientation effects are typical of F_2^+ centres (see, for instance, Gellermann (1991)). If we take into account the difference between the transition wavelengths of pure F_2^+ and the species produced after step (a) (table 2), this interpretation seems erroneous.

Table 2. $(F_2^+)_H$ centre low-energy absorption and emission band positions in various alkali-halide crystals (the peaks of the bands were measured at 77 K). The pure F_2^+ centre transition wavelengths are from the work of Gellermann (1991) for NaCl, KCl and RbCl and from the work of Schneider (1981) for KI. The $(F_2^+)_H$ centre transitions have been measured in this work.

Colour centre	Peak of band (nm) for the following crystal hosts					
	NaCl	KCl	KBr	RbCl	RbBr	KI
F_2^+ centre						
$1s\sigma_g \rightarrow 2p\sigma_u$	1020	1380	1470			1610
$2p\sigma_u \rightarrow 1s\sigma_g$	1480	1680	1800			2150
$(F_2^+)_H$ centre, after step (a)						
$1s\sigma_g \rightarrow 2p\sigma_u$	1050	1445	1530	1615	1700	1580
$2p\sigma_u \rightarrow 1s\sigma_g$	1495	1775	1980	1950	2050	2040
$(F_2^+)_H$ centre, after step (b)						
$1s\sigma_g \rightarrow 2p\sigma_u$	1085	—	1580	1615	1725	≈ 1700
$2p\sigma_u \rightarrow 1s\sigma_g$	1580	—	2000	1950	2080	2400

According to Wandt *et al* (1987), the aggregate $F_2^+O^{2-}$ is obtained during step (a), and further exposure permits reorientation of the $F_2^+O^{2-}$ block into the most stable configuration called $(F_2^+)_H$. This interpretation has the advantage of explaining the difference between the peak positions observed for F_2^+ centres and those for centres produced after step (a). On the other hand, we have observed a slow decomposition, probably according to the reaction $(F_2^+)_H \rightarrow F_2^+ + O^{2-}$ when we stored NaCl: O^{2-} for days at room temperature in the dark. After this decomposition, the transformation (b) described above was found to be impossible, which confirms that the species obtained after photoaggregation (a) is a block, constituted by the F_2^+ centre and O^{2-} impurity in relatively close neighbouring positions. Variety $F_2^+O^{2-}$ (a) does not seem to be associated with a specific microscopic structure (configuration 1, 2, 3 or 4 of figure 3) but rather with a mixing of these configurations, while $(F_2^+)_H$ (b) could be attributed to configuration 1 (the oxygen ion and the two halogen vacancies forming an equilateral triangle in the {111} plane). This hypothesis arises from the strong trapping efficiency of doubly negatively charged oxygen impurities for the positive halogen divacancies. Configuration 1 is the closest-packed $F_2^+O^{2-}$ aggregate, in which the influence of O^{2-} impurities (electric field and ion size) can most strongly

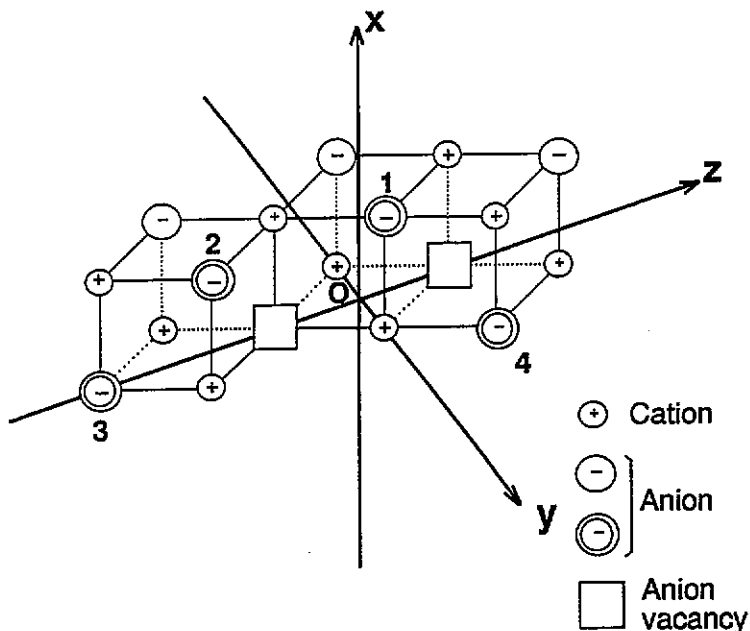


Figure 3. Four different possible configurations of the $(F_2^+)_H$ centre according to Wandt *et al* (1987).

perturb electronic wavefunctions of the F_2^+ defect and explain the large shift observed between pure F_2^+ centres and $(F_2^+)_H$ centres after step (b).

From this point of view, the behaviours of both exceptions (KCl and RbCl) are interesting and have to be discussed separately. In $KCl:O_2^-$, the $(F_2^+)_H$ centres are in their stable configuration already after step (a) (as described by Wandt *et al* (1987)). A further F-band light exposure at low temperatures produces a shift towards short wavelengths for absorption and emission transitions. The band peak positions after step (b) correspond to the $1s\sigma_g \leftrightarrow 2p_u$ transitions of pure F_2^+ centres. This $(F_2^+)_H \rightarrow F_2^+$ conversion is more efficiently performed by using short-wavelength exposure (436 nm) rather than F-band light (about 530 nm). We did not find any explanation for this behaviour in KCl, especially if we assume that the effect of O^{2-} ion impurities is limited to Coulomb field perturbation and lattice deformations due to difference in ionic sizes (both effects would be quite similar in KCl and other alkali halides). In $RbCl:O_2^-$, we observe that, as in $KCl:O_2^-$, the $(F_2^+)_H$ centres are already in their stable configuration after step (a), but a new F-band light exposure at LNT does not produce any variation in the absorption or emission bands. Contrary to the case of $KCl:O_2^-$, $(F_2^+)_H$ centres in $RbCl:O_2^-$ are stable under F-band light exposure at low temperatures.

In order to complement information about $(F_2^+)_H$ centres, we have measured their emission spectra in RbCl, RbBr and KI. Excitation was performed either with a colour-centre laser (CCL) (using $F_A(Tl)$ centres in $KCl:Tl^+$ or $(F_2^+)_H$ centres in $NaCl:OH^-$) or with a filtered quartz tungsten-halogen lamp (interference filters at 1.5 or 1.7 μm). The emission spectra were recorded with a Jobin-Yvon HRS2

monochromator and an InSb detector cooled at LNT.

The absorption and emission bands of $(F_2^+)_H$ low-energy transitions in these three new host crystals are shown in figure 4; the absorption and emission bands are represented by a full curve after step (a), and a broken curve after step (b). Absorption bands have been obtained from the absorption spectra in figure 2, by subtraction of a background (fitted by a second-order polynomial). We have not shown the $(F_2^+)_H$ (b) absorption band in $KI:O_2^-$ because it was too poorly resolved in our spectra. In order to obtain the peak wavelength position of this absorption band, we recorded the excitation spectrum, using a CCL ($(F_2^+)_H$ centres in $NaCl:OH^-$; tunable between 1.45 and 1.75 μm) but, even with this method, the resolution of the excitation spectrum was very poor, similar to the absorption spectrum. Finally, we took the middle of the estimated absorption band, fitted by the polynomial method discussed above, such as the peak wavelength position of $(F_2^+)_H$ (b) in $KI:O_2^-$. The background was fitted by a second-order polynomial. This polynomial was calculated by taking into account absorption at 1300 and 2400 nm.

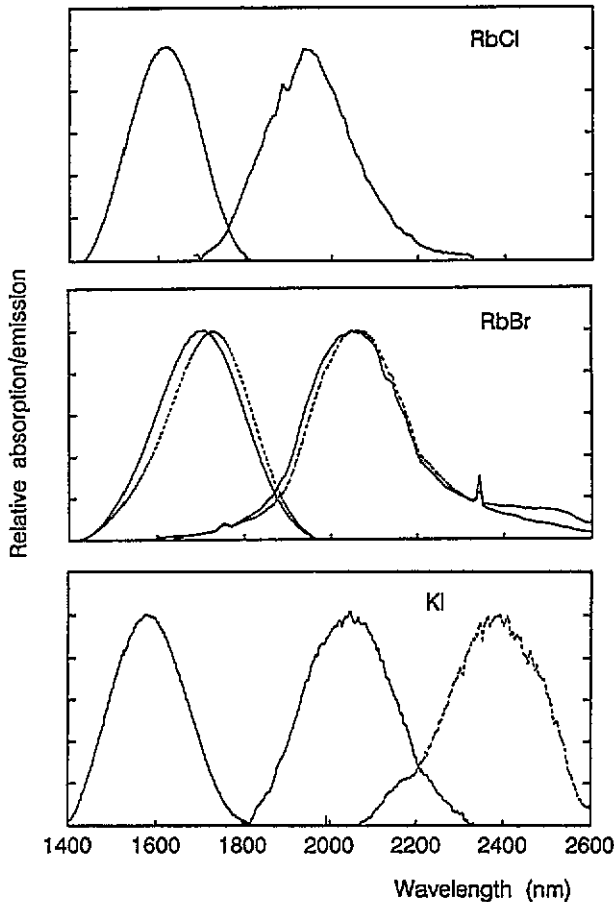


Figure 4. Absorption and emission bands of low-energy transitions of $(F_2^+)_H$ centres in $RbCl:O_2^-$, $RbBr:O_{21}^-$ and $KI:O_2^-$: —, after step (a); - - -, after step (b).

Even if the shift of the absorption band in $KI:O_2^-$ was not measured with good precision, the nature of the centres observed in this material, assumed to be $(F_2^+)_H$ centres, was clearly confirmed by the evolution of the emission band when the sample was exposed to further F-band light at low temperatures; we observed a shift of the emission band from 2040 to 2400 nm which is typical of the $(F_2^+)_H$ centres (step (b)).

4. Semi-empirical model based on the analogy of F_2^+ -like centres to H_2^+ molecular ions

We do not use a theoretical model which permits us to predict reliably peak wavelength positions of the $(F_2^+)_H$ centre absorption or emission bands. Only the disturbing effects of O^{2-} impurities on the F_2^+ species have been estimated by perturbative calculations (Sennaroglu and Pollock 1991, Doualan *et al* 1992). To anticipate experimental results and, consequently, to permit direct identification of absorption bands measured after photoaggregation and reorientation (step (b)) in new host crystals, we have first tried to apply a Mollwo-Ivey relation to $(F_2^+)_H$ centres; similar relations have given results in good agreement with experimental data for simple centres such as F in absorption (Fowler 1968), F_2^+ (Aegerter and Lüty 1971) or even $F_A(Tl)$ (Gellermann 1991) for which the importance of the thallium perturbation could dissuade us from using this kind of model.

From the Mollwo-Ivey relation, optical transitions are assumed to depend only on the lattice constant of the crystal host matrix by

$$\lambda_i = Ad^x$$

where λ_i is the wavelength transition, d is the lattice constant (anion-cation distance in a face-centred cubic lattice), and A and x are empirical parameters which depend on the type of centres and the optical transition under study. On a doubly logarithmic plot (figure 5), we show the absorption and emission wavelengths of the $(F_2^+)_H$ -centre low-energy transitions versus lattice constant; they follow a Mollwo-Ivey relation quite well with $x = 2.34$ for absorption and $x = 1.38$ for emission. However, this law seems inadequate for the transitions of the $(F_2^+)_H$ centre in $KI:O_2^-$.

In order to improve this first approach, we apply a model based on the analogy of the F_2^+ centre to a H_2^+ molecular ion immersed in a dielectric medium. In this model, a pure F_2^+ centre is described by the wavefunction of a hydrogen molecular ion with proton distance R :

$$R = r_{ab}/\epsilon_\infty$$

where r_{ab} is the distance between two neighbouring anion vacancies and ϵ_∞ is the high-frequency relative dielectric constant of the alkali halide. The eigenenergies $E_i(r_{ab}, \epsilon_\infty)$ of the F_2^+ centre are deduced from those of the H_2^+ ion by

$$E_i(r_{ab}, \epsilon_\infty) = (1/\epsilon_\infty^2) E_i'(R)$$

where $E_i'(R)$ are the eigenenergies of the H_2^+ ion, calculated for a proton distance R . Usually (Aegerter and Lüty 1971, Mollenauer 1979), slight adjustments of R and ϵ_∞ are made in order to fit calculated results to experimental data. Unfortunately,

these corrections differ from crystal to crystal and therefore they cannot be taken into account in our present model.

For the group of alkali halides in which we have created $(F_2^+)_{\text{H}}$ centres, R varies only from 1.70 Å (NaCl) to 2.13 Å (RbCl). In the calculated energy scheme of H_2^+ molecule levels as a function of the distance R (figure 11 of the paper by Aegerter and Lüty (1971)), the difference between the energies of the ground state ($1s\sigma_g$) and the first excited level ($2p\sigma_u$) varies nearly linearly with R (for R between 1.7 and 2.13 Å), so that

$$\Delta E(R) = E_{2p\sigma_u}(R) - E_{1s\sigma_g}(R) \simeq aR + b.$$

If we transpose this result to the difference between the energies of the two lowest-energy levels of an F_2^+ centre, we obtain

$$\begin{aligned} \Delta E(r_{\text{ab}}, \epsilon_{\infty}) &= E_{2p\sigma_u}(r_{\text{ab}}, \epsilon_{\infty}) - E_{1s\sigma_g}(r_{\text{ab}}, \epsilon_{\infty}) = (1/\epsilon_{\infty}^2)(ar_{\text{ab}}/\epsilon_{\infty} + b) \\ &= (1/\epsilon_{\infty}^2)(a'd/\epsilon_{\infty} + b) \end{aligned}$$

where d is the anion-cation distance (lattice constant), with $r_{\text{ab}} = \sqrt{2}d$.

Because of the similarity between F_2^+ and $(F_2^+)_{\text{H}}$ centres, we postulate that the wavelength of the $(F_2^+)_{\text{H}}$ absorption and emission bands can be deduced from a similar law:

$$\lambda_t = \epsilon_{\infty}^2 / (\alpha d / \epsilon_{\infty} + \beta)$$

where α and β are two empirical parameters, adjusted from experimental data. We attempted to fit our results for the transition $1s\sigma_g \leftrightarrow 2p\pi_u$ with this model. The best fit thus obtained and the observed absorption and emission band peaks are presented in table 3 and figure 6. Of course, the coefficients α and β (which are assumed to contain relaxation effects on the lattice around the F_2^+ -like centre and perturbative effects of O^{2-} impurities) are different for absorption and emission wavelengths.

Table 3. Comparison of experimental transition wavelengths of $(F_2^+)_{\text{H}}$ centres and those calculated by the semi-empirical model based on the H_2^+ molecular ion. ϵ_{∞} and d are taken from the work of Fowler (1968).

Crystal host	High frequency dielectric constant ϵ_{∞}	Lattice parameter d (Å)	Wavelength of absorption band peak, $1s\sigma_g \rightarrow 2p\sigma_u$		Wavelength of emission band peak, $2p\sigma_u \rightarrow 1s\sigma_g$	
			Experimental	Calculated	Experimental	Calculated
NaCl	2.34	2.82	1085	1101	1580	1628
KCl	2.19	3.147	1445	1417	1775	1793
KBr	2.34	3.298	1580	1532	2000	1985
RbCl	2.19	3.291	1615	1634	1950	1933
RbBr	2.34	3.445	1725	1742	2080	2129
KI	2.62	3.533	~1700	1720	2400	2336

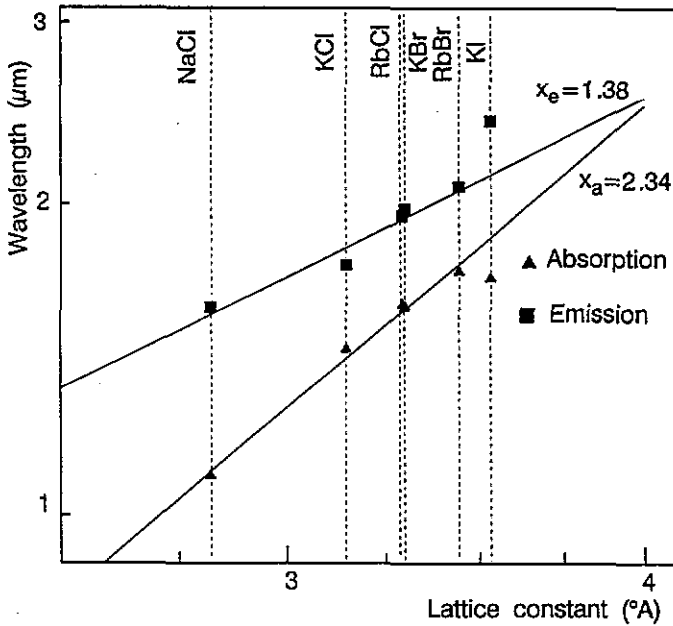


Figure 5. The Mollwo-Ivey law applied to the low-energy transition: $1s\sigma_g \leftrightarrow 2p\sigma_u$ of the $(F_2^+)_H$ centres.

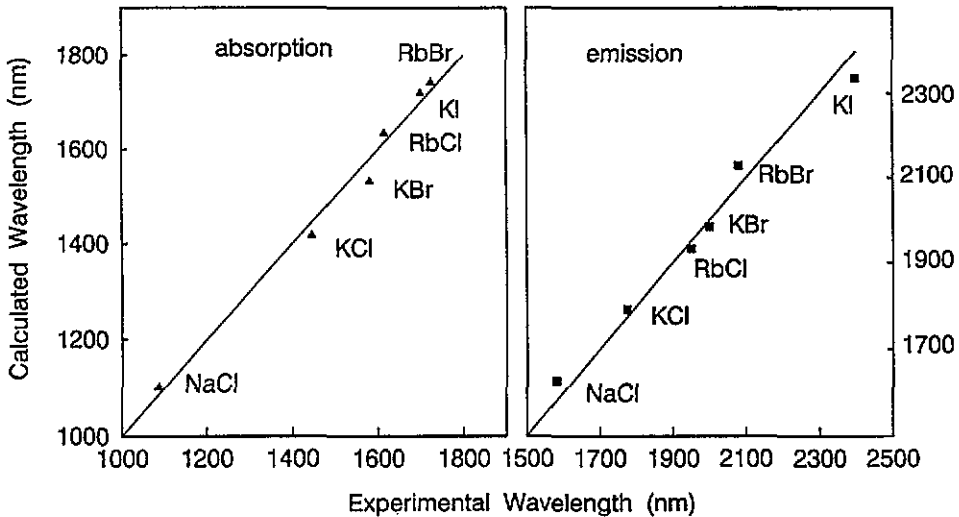


Figure 6. Experimental values for the lowest-energy transitions ($1s\sigma_g \leftrightarrow 2p\sigma_u$) of the $(F_2^+)_H$ centres compared with values predicted by the semi-empirical model based on the analogy with H_2^+ molecular ion.

We obtained $(\alpha_a, \beta_a) = (-6.846 \times 10^{-3}, 1.322 \times 10^{-2})$ for absorption, and $(\alpha_e, \beta_e) = (-2.965 \times 10^{-3}, 6.937 \times 10^{-3})$ for emission (with the wavelength λ in nanometres and the lattice constant d in ångströms). This simple model has the

advantage of explaining the 'anomalous behaviour' observed for $(F_2^+)_{\text{H}}$ centres in $\text{KI}:\text{O}_2^-$ (compare figures 5 and 6) by the high value of the dielectric constant in this material.

We expect a similar behaviour in $\text{NaI}:\text{O}_2^-$ too, but an experimental study of this material failed because we were unable to colour it additively. It will be interesting to study $(F_2^+)_{\text{H}}$ centres in $\text{RbI}:\text{O}_2^-$, in order to confirm the influence of the dielectric constant on wavelength transitions (in our model, the absorption and emission bands of $(F_2^+)_{\text{H}}$ in $\text{RbI}:\text{O}_2^-$ are expected to be at approximately 1900 nm and 2500 nm, respectively).

5. Conclusion

We have obtained $(F_2^+)_{\text{H}}$ centres in three new alkali halides (RbCl , RbBr and KI), extending the emission bands in the infrared region between 2 and 2.5 μm . This work confirms the large extent of the family of crystals in which $(F_2^+)_{\text{H}}$ centres can be created. If laser action can be obtained with the new crystals, the wavelength range of a CCL based on $(F_2^+)_{\text{H}}$ centres will be extended well beyond 2 μm . Similar experiments with other impurities (sulphur, selenium, etc) or combinations of impurities (alkali-oxygen and alkali-sulphur) are at present in progress and will hopefully give better materials for laser action (in terms of stability, emission range, etc).

A semi-empirical model based on the analogy of F_2^+ -like centres to the H_2^+ molecular ion has suggested an empirical law that connects the transition wavelengths of $(F_2^+)_{\text{H}}$ to the dielectric constant and lattice parameter of the host material. The low-energy transitions of $(F_2^+)_{\text{H}}$ centres obtained in six different crystal lattices (NaCl , KCl , KBr and the three 'new' lattices) are in good agreement with this H_2^+ model. Similar laws with modified numerical coefficients will prove to be suitable for other kinds of F_2^+ -like centre.

Acknowledgments

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