Spectroscopic properties of $(F_2^+)_{AH}$ centres in oxygen- and sulphur-doped alkali halides

Spectroscopic properties of $(F_2^+)_{AH}$ centres in oxygen- and sulphur-doped alkali halides

A El Akrmi†, P Ketolainen‡, J L Doualan, E Kawa§, J Margerie§ and B Rocher

Laboratoire de Spectroscopie Atomique, ERS 137 du CNRS, Institut des Sciences de la Matière et du Rayonnement, 6 Boulevard Maréchal Juin, 14050 Caen Cédex, France

Abstract. In search of potential laser-active colour centres, we have created and spectroscopically studied for the first time $(F_2^+)_{AH}$ centres in KCl:Li⁺:O²⁻ and RbCl:Na⁺:O²⁻. We compare them with the 'classical' $(F_2^+)_{AH}$ centres in KCl:Na⁺:O²⁻ and KBr:Na⁺:O²⁻. We describe preparation procedures, and absorption and emission spectra at 100 and 5 K. We study the stability of the centres in the dark at room temperature, an important property for laser applications. Preliminary data concerning $(F_2^+)_{AH}$ centres in KBr:Na⁺:S²⁻ are also reported.

1. Introduction

Recently Wandt and Gellermann (1987) described a new type of laser-active colour centre, namely $(F_2^+)_{AH}$ in KCl:Na⁺:O²⁻ and in KBr:Na⁺:O²⁻. This centre consists of two halogen vacancies in nearest-neighbour positions, decorated with a single electron (this is the F_2^+ centre), with two stabilizing substitutional impurities in the close vicinity: an Na⁺ ion instead of a K⁺ ion (hence the A subscript in the centre's symbol) and divalent oxygen instead of singly charged chlorine or bromine (hence the H subscript). Because of the double pinning of the F_2^+ centre by Na⁺ and by O²⁻, $(F_2^+)_{AH}$ centres were found to be much more stable under IR irradiation at low temperatures than F_2^+ and even $(F_2^+)_H$ are.

In order to obtain $(F_2^+)_{AH}$ centres, one grows a crystal, under partial oxygen pressure, from a KCl (or KBr) melt to which has been added KO₂ and NaCl (or NaBr) impurities (table 1). Then, samples are additively coloured, which produces both F-centres and O²⁻–□ defects. If the concentration of sodium is sufficiently high, these O²⁻–□ defects are associated with a Na impurity (yielding an O²⁻–□–Na⁺ complex). Coloured samples are exposed to 'F light' at a suitable temperature (table 1), in order to induce diffusive motion of the F centres. An $(F_2^+)_{AH}$ centre is formed when a wandering F centre meets an O²⁻–□–Na⁺ complex. This process is called 'photoaggregation'. $(F_2^+)_{AH}$ centres thus obtained are characterized by absorption and emission bands shifted to shorter wavelengths with respect to intrinsic F_2^+ centres in the same host. They are the so-called $(F_2^+)_{AH}$ (a) centres, which turn out to be stable at room temperature, but only metastable at cryogenic

---

† Present address: Département de Physique, Université d'Annaba, BP 12, 23000 Annaba, Algeria.

‡ Permanent address: Physics Department, University of Joensuu, Postal Box 111, SF 80101 Joensuu, Finland.

§ Also at UFR de Sciences, Université de Caen, 14032 Caen Cédex, France.

Table 1. $(F_2^+)_{AH^-}$-centres preparation parameters. In all cases, additive coloration is performed with K vapour and 546 nm light is used for photoaggregation.

	Growth		Coloration			Photoaggregation		100 K (a) → (b) conversion	
	Impurity (mol ppm)	Atmosphere	Temperature (°C)	Pressure (Torr)	Duration (h)	Temperature (°C)	Duration (min)	Wavelength (nm)	Duration (min)
KCl:Na$^+$:O^{2-}	407 KO$_2$ + 991 NaCl	Ar+O$_2$	650	35	2	−10	20	546	10
KCl:Li$^+$:O^{2-}	385 KO$_2$ + 1260 LiCl	Ar+O$_2$	650	35	2	−10^a	20^a	436	20
KBr:Na$^+$:O^{2-}	600 KO$_2$ + 828 NaBr	Ar+O$_2$	600	20–30	1.25	−9	15	546	5
KBr:Na$^+$:S^{2-}	50 Na$_2$S	Ar	600	20–30	2	−6	10	546	10
RbCl:Na$^+$:O^{2-}	850 KO$_2$ + 1380 NaCl	Ar+O$_2$	675	30	2	−13	15	546	20

[a] See section 2 of text.

Table 2. Peak wavelengths of the broad bands $1s\sigma_g \to 2p\sigma_u$ and $2p\sigma_u \to 1s\sigma_g$. LNT is 100 K for this work and 77 K for the data of other workers. For emission bands, we observed no significant shift between LNT and 5 K.

	Peak wavelength (nm)					
	Type (a)			Type (b)		
	Absorption		Emission	Absorption		Emission
	LNT	5 K	LNT	LNT	5 K	LNT
KCl:Na$^+$:O^{2-}	1295[a]	1320[a]	1698[a]	1379[a]	1450[a]	1896[a]
	1290[b]		1660[b]	1390[b]		1860[b]
KCl:Li$^+$:O^{2-}	1330[a]		1703[a]	1430[a]		1878[a]
KBr:Na$^+$:O^{2-}	1379[a]	1390[a]	1882[a]	1585[a]	1622[a]	2040[a]
	1350[c]		1770[c]	1650[c]		2040[c]
KBr:Na$^+$:S^{2-}	~1500[a]			1630[a]		
RbCl:Na$^+$:O^{2-}	1392[a]	1427[a]	1804[a]	1560[a]	1582[a]	2036[a]

[a] This work.
[b] Wandt and Gellerman (1987).
[c] Gellerman (1991).

temperatures. If one irradiates the sample at 77 or 100 K† with a suitable light (table 1), $(F_2^+)_{AH}$ (a) centres are converted into $(F_2^+)_{AH}$ (b), with longer absorption and emission wavelengths (table 2). $(F_2^+)_{AH}$ (b) centres are stable at cryogenic temperatures but unstable at 295 K. Most probably, $(F_2^+)_{AH}$ (a) and $(F_2^+)_{AH}$ (b) correspond to two different ways of accommodating the Na$^+$ and O^{2-} impurities in the vicinity of the F^{2+} centre. Wandt and Gellerman (1987) successfully used $(F_2^+)_{AH}$ (b) centres for CW tunable laser emission at around 1.90 μm and 2.16 μm in KCl and KBr, respectively.

In his review article, Gellermann (1991) suggested that $(F_2^+)_{AH}$ centres should be produced in other crystals and also with other cationic (Li$^+$, K$^+$, etc) and/or anionic (S^{2-}, Se^{2-}, etc) impurities. The purpose of the present paper is to report our work along these lines; we have indeed obtained $(F_2^+)_{AH}$ centres with another cationic impurity (KCl:Li$^+$:O^{2-}), with another anionic impurity (KBr:Na$^+$:S^{2-}) and in another host (RbCl:Na$^+$:O^{2-}). Sections 2, 3 and 4 below will deal with these three new $(F_2^+)_{AH}$ centres, respectively. The experimental apparatus and methods are the same as in our work on the spectroscopic properties of $(F_2^+)_H$ centres (El Akrmi *et al* 1994, section 2). For brevity, throughout the present paper we shall call an $(F_2^+)_H$ centre stabilized by oxygen F$_2^+$:O^{2-}, an $(F_2^+)_{AH}$ centre stabilized both by lithium and oxygen F$_2^+$:Li$^+$:O^{2-}, and similarly for all kinds of $(F_2^+)_H$ and $(F_2^+)_{AH}$ centres.
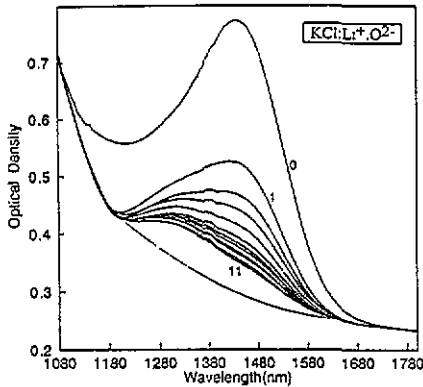
2. $(F_2^+)_{AH}$ centres in KCl:Li$^+$:O^{2-}

A sample of KCl:Li$^+$:O^{2-} after additive coloration and photoaggregation by 546 nm light at $-10\,°C$ is found to behave similarly to KCl:O^{2-} (Wandt *et al* 1987, Lifante *et al* 1990): the same absorption and emission spectra, including the same zero-phonon lines at 5 K,

† Gellermann (1991) briefly mentions that this low-temperature (a) $\to$ (b) conversion of $(F_2^+)_{AH}$ centres in KCl:Na$^+$:O^{2-} has a very low thermal activation energy compared with $(F_2^+)_H$ centres, since it may be performed even at 15 K. We have verified this fact by experiments at liquid-helium temperature: figure 1 shows the modifications of the spectrum by 5 K irradiation with 365 nm light during an increasing amount of time. $(F_2^+)_{AH}$ (a) centres, absorbing at 1320 nm, progressively disappear and are replaced by $(F_2^+)_{AH}$ (b) centres with an absorption band centred at 1450 nm.
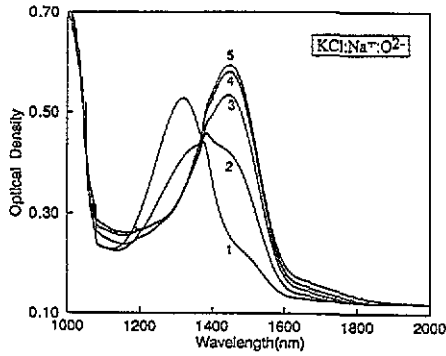
Figure 1. Absorption spectra of $(F_2^+)_{AH}$ centres in KCl:Na$^+$:O^{2-} at 5 K: curve 1, after coloration and photoaggregation at $-10\,^{\circ}$C; curves 2, 3, 4 and 5, after subsequent irradiation at 5 K for 2 min, 5 min, 10 min and 15 min, respectively, with the light of an Osram HBO 100 high-pressure mercury lamp, filtered by a Schott Monochromat 365 and focused by an f/4.5 lens. The sharp irregularity at around 1380 nm is due to absorption by the cryostat windows and should therefore be disregarded.

Figure 2. Absorption spectra of $(F_2^+)_H$ and $(F_2^+)_{AH}$ centres in KCl:Li$^+$:O^{2-} at 100 K: curve 0, just after coloration and photoaggregation at $-10\,^{\circ}$C; curves $1, 2, \ldots, 11$, after subsequent storage in the darkness at room temperature during $1, 2, \ldots, 11$ d. The thin curve is the estimated 'background' (wing of transitions at shorter wavelengths).

and the same conversion into intrinsic F_2^+ centres by F-light irradiation at liquid-nitrogen temperature. Therefore, this sample chiefly contains $(F_2^+)_H$ centres, unperturbed by the lithium doping.

The difference between KCl:Li$^+$:O^{2-} and KCl:O^{2-} appears when one keeps the sample for a sufficiently long time in the darkness at room temperature. Figure 2 shows that the 1450 nm band of F_2^+:O^{2-} does not merely decrease (as would be the case for a KCl:O^{2-} crystal); it also broadens and its centre of gravity shifts towards shorter wavelengths. After 11 d, one clearly sees two components, at around 1350 and 1450 nm respectively. We determined by trial and error two Gaussian profiles α and β, so that suitable linear combinations $a\alpha + b\beta$ of these profiles should allow, within experimental uncertainty, reconstruction of each experimental curve 1–11 of figure 2 (more exactly, reconstruction of the difference between these curves and their common absorption background, represented by a thin curve). As an example, figure 3 shows the observed absorption profile at $t = 1$ d
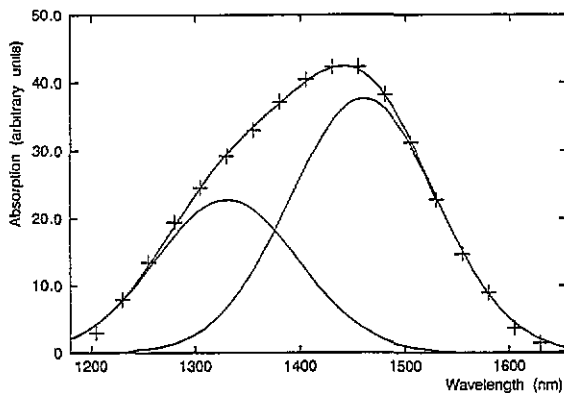
Figure 3. Gaussian components of the absorption spectra in figure 2: +, difference between curve 1 and the background in figure 2; ———, Gaussian components $a\alpha$ (on the left) and $b\beta$ (on the right); ———, reconstructed profile $a\alpha + b\beta$.

(crosses), together with its simulation (bold curve) by the sum of two Gaussian components (thin curves).

This analysis demonstrates the existence of two centres, one of which absorbs at 100 K at 1460 nm (namely the F_2^+:O^{2-} (a) centre, in agreement with the wavelength quoted by Gellermann (1991)) and the other at 1330 nm, which we shall assume to be $(F_2^+)_{AH}$ (a) of KCl:Li$^+$:O^{2-}†. The number densities of these two species, measured in arbitrary units by coefficients a and b of the linear combination, decrease as time elapses. Between 1 and 11 d, this decay can be represented within experimental accuracy by

$$a = 10.0 + 16.5 \exp(-0.277t) \qquad \text{for } (F_2^+)_{AH} \text{ centres} \tag{1}$$

$$b = 6.9 + 41.7 \exp(-0.317t) \qquad \text{for } (F_2^+)_H \text{ centres.} \tag{2}$$

A comparison may be made with the results that we obtained with F_2^+:O^{2-} centres in KCl:O^{2-}. Equation (2) yields a time constant of 3.2 d, to be compared with 2.4 d (table 5 of El Akrmi *et al* (1994)), and a fraction R of centres with an 'infinite' lifetime equal to $6.9/(6.9 + 41.7) = 14\%$, versus 6% observed in KCl:O^{2-}. The agreement is fair, in view of the uncertainties associated with the choice of the absorption background and of the splitting of each curve in figure 2 into two components $a\alpha$ and $b\beta$.

From equations (1) and (2), one can see that in KCl:Li$^+$:O^{2-}, $(F_2^+)_H$ and $(F_2^+)_{AH}$ centres have similar decay constants in the dark at room temperature, but that the proportion R of $(F_2^+)_{AH}$ centres which overlive 'indefinitely' is significantly larger: 38% versus 14%. It is this fact which caused the shape variations of the absorption curves in figure 2, and therefore which allowed detection of the existence of F_2^+:Li$^+$:O^{2-} centres. It should be remarked that, even if they are somewhat more stable than F_2^+:O^{2-} centres in KCl, F_2^+:Li$^+$:O^{2-} centres are noticeable shorter lived than F_2^+:Na$^+$:O^{2-} centres in the same crystal; we observed no decay at all of the latter centres after 35 d at room temperature in the dark.

In the calculations above, we have excluded the starting curve (0 d) in figure 2. It obviously contains, besides components α and β, a supplementary background, arising

---

† 1330 nm is rather close to the central absorption wavelength of $(F_2^+)_A$ centres in KCl:Li$^+$ (1340 nm according to Schneider (1980)). However, the species responsible for the α profile in our experiment is not the $(F_2^+)_A$ centre described by Schneider since it has a quite different emission wavelength (1703 nm versus 2210 nm) and since it shows the customary (a)↔(b) transformation of $(F_2^+)_H$ and $(F_2^+)_{AH}$ centres.

from some centre absorbing at smaller wavelengths and with a short lifetime at room temperature. Moreover, the β component (F_2^+:O^{2-} centres) decreases more rapidly than equation (2) between 0 and 1 d. Such behaviour was also observed for F_2^+:O^{2-} centres in KCl:O^{2-} and KBr:O^{2-}. After photoaggregation, there probably exist some especially unstable F_2^+:O^{2-} centres which disappear in less than 24 h.

When we irradiate by 436 nm light at 100 K a sample of KCl:Li^+:O^{2-} in the state of curve 11 in figure 2, we observe that the $(F_2^+)_{AH}$ band shifts from 1330 to 1430 nm, i.e. from a wavelength shorter than to a wavelength longer than the peak of the intrinsic F_2^+ band (1385 nm in KCl). This is exactly the behaviour of $(F_2^+)_{AH}$ centres in KCl:Na^+:O^{2-} and KBr:Na^+:O^{2-} (Gellerman 1991) and this is one of the chief reasons for ascribing the 1330 nm and 1430 nm bands to types (a) and (b), respectively, of F_2^+:Li^+:O^{2-} centres of KCl.

The fluorescence of these centres is excited at 100 K by a white lamp through suitable interference filters. With the sample in the state of curve 11 in figure 2, one observes at 100 K a fluorescence peak wavelength which depends on the excitation radiation: 1703 nm, 1762 nm or 1798 nm for pumping at 1.3 μm, 1.4 μm or 1.5 μm, respectively. With 1.3 μm, one should excite nearly exclusively $(F_2^+)_{AH}$ (a) centres, with 1.5 μm only $(F_2^+)_H$ (a) centres and with 1.4 μm both these species (see the absorption profiles in figure 3). Therefore, 1703 nm is the approximate emission wavelength of F_2^+:Li^+:O^{2-} (a) centres, while 1798 nm is, within experimental accuracy, the emission wavelength of F_2^+:O^{2-} (a) centres (1778 or 1780 nm according to El Akrmi *et al* (1994) or to Gellerman (1991)). After conversion of the centres by 436 nm light at 100 K, the fluorescence peak is observed at 1878 nm, with both 1.4 and 1.5 μm excitation. 1878 nm is thus most probably the emission peak of F_2^+:Li^+:O^{2-} (b) centres. It is shifted to longer wavelengths with respect to type (a), in agreement with the behaviour of other $(F_2^+)_{AH}$ centres (Gellermann 1991).
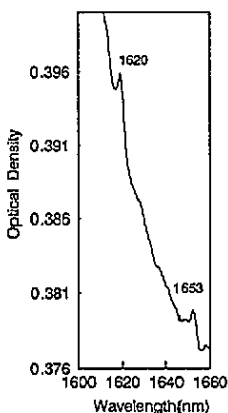

Figure 4. Absorption spectrum at 5 K of KCl:Li^+:O^{2-} in state (b).

At 5 K, with a sample in state (b), we observe two sharp absorption lines at 1620 and 1653 nm (figure 4). The former has already been reported by Wandt *et al* (1987), Lifante *et al* (1990) and El Akrmi *et al* (1994) and it is attributed to F_2^+:O^{2-} centres. It is, however, rather surprising that it should appear in the present spectrum, since F_2^+:O^{2-} centres of KCl are unstable under the 100 K, 436 nm irradiation which was necessary to convert the F_2^+:Li^+:O^{2-} centres from type (a) to type (b). On the other hand, 1653 nm is a new line,

to the best of our knowledge†. In view of its position, just at the long-wavelength foot of the $(F_2^+)_{AH}$ broad absorption band, this 1653 nm line is probably the zero-phonon line of $(F_2^+)_{AH}$ (b) centres in KCl:Li$^+$:O^{2-}.

Let us finally remark that photoaggregation at $-10\,°$C seems to have very different effects in KCl:Na$^+$:O^{2-} and in KCl:Li$^+$:O^{2-}; in the former case, it yields nearly solely F_2^+:Na$^+$:O^{2-} centres, and in the latter, chiefly F_2^+:O^{2-} centres and a comparatively small number density of F_2^+:Li$^+$:O^{2-} centres. This means that, after additive coloration, KCl:Na$^+$:O^{2-} has many of its O^{2-}–□ defects associated with Na$^+$ impurities, whereas KCl:Li$^+$:O^{2-}, after coloration, contains chiefly isolated O^{2-}–□ defects and a small proportion of O^{2-}–□–Li$^+$ complexes. *A priori*, this could arise from a weaker attraction of O^{2-}–□ defects for lithium than for sodium ions. In fact, a chemical analysis of one of our crystals by atomic absorption yielded a molar concentration of lithium of 100 ppm at most, i.e. more than 12 times smaller than the 1260 ppm that we had originally introduced into the melt. It is therefore of interest to investigate how one may grow KCl:Li$^+$:O^{2-} samples with a higher effective concentration of lithium, in order to see whether the photoaggregation process will have comparable effects in KCl:Li$^+$:O^{2-} as in other matrices, and also in the hope of producing F_2^+:Li$^+$:O^{2-} centres more easily, with greater number densities than in the present experiment.

3. $(F_2^+)_{AH}$ centres in KBr:Na$^+$:S^{2-}

After additive coloration and photoaggregation by 546 nm light at $-6\,°$C for 10 min, we observe a broad weak absorption band at around 1500 nm (100 K density, 0.05–0.1 for a sample 2 mm thick). 100 K irradiation by 546 nm light shifts this band to 1630 nm. This is the same behaviour as for the $(F_2^+)_{AH}$ centres described by Wandt and Gellerman (1987). However, since the observed absorption was quite weak, we feared, at first, that sulphur should not have been incorporated into the crystal and that we were observing F_2^+:Na$^+$:O^{2-} centres owing to accidental contamination of the crystal during growth by oxygen from air. This hypothesis was discarded because the position of the absorption band in state (a) is at a wavelength significantly larger than in the case of KBr:Na$^+$:O^{2-} (table 2). Another noticeable difference between F_2^+:Na$^+$:S^{2-} and F_2^+:Na$^+$:O^{2-} centres in KBr is their stability in the dark at room temperature. The latter are found to decay with a time constant of 6.3 d and to be still observable after storage of more than 2 months whereas, for F_2^+:Na$^+$:S^{2-} centres, the decay time constant is only a few hours and the 1500 nm absorption band has completely disappeared after 1.5 d in the dark at room temperature.

Because of this poorer thermal stability, F_2^+:Na$^+$:S^{2-} centres of KBr appear to be a less promising laser material than F_2^+:Na$^+$:O^{2-} in the same crystal. Since the wavelength domains are comparable, we do not think it worthwhile to look for a method to increase the number density of F_2^+:Na$^+$:S^{2-} centres and to carry on their spectroscopic study further (fluorescence, 5 K spectra).

4. $(F_2^+)_{AH}$ centres in RbCl:Na$^+$:O^{2-}

Figure 5 summarizes the three steps required to obtain $(F_2^+)_{AH}$ (b) centres. After additive coloration, annealing and quenching, spectrum 1 shows an UV band at 268 nm, which we

† In particular, the 1653 nm line is not observed if the sample is in state (a).
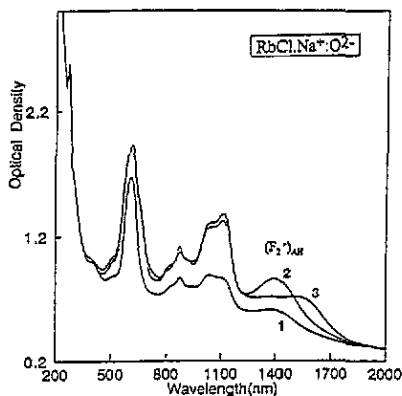
Figure 5. Absorption spectra of colour centres in RbCl:Na$^+$:O^{2-} at 100 K: curve 1, after coloration, annealing and quenching; curve 2, after 15 min, 546 nm irradiation at −13 °C; curve 3, after subsequent 20 min, 546 nm irradiation at 100 K.

tentatively attribute to O^{2-}–□–Na$^+$ complexes, and a weak band at around 1392 nm, which will be revealed as due to (F$_2^+$)$_{AH}$ (a) centres already existing at this step of the process. Irradiation by 546 nm light at −13 °C results in a noticeable increase in the 1392 nm band (curve 2). Finally, 546 nm irradiation of the sample at 100 K results in a large shift of this band towards longer wavelengths. Its maximum is then at 1560 nm; it corresponds to (F$_2^+$)$_{AH}$ (b) centres (curve 3). By letting the sample reach room temperature (and cooling it afterwards to 100 K for the measurement), one obtains the spectrum shown in curve 2 again; (F$_2^+$)$_{AH}$ (b) centres are unstable thermally and convert themselves into (F$_2^+$)$_{AH}$ (a) centres at some temperature between 100 and 295 K. All these properties are exactly similar to those of (F$_2^+$)$_{AH}$ centres in KCl or KBr, as reported by Wandt and Gellerman (1987). Because of this similarity, there is no doubt that the centres that we are studying are indeed (F$_2^+$)$_{AH}$ centres of RbCl.

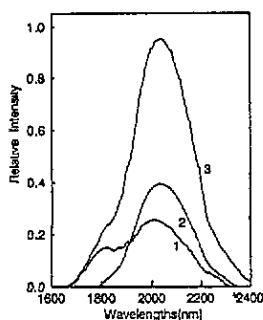**Figure 6.** Emission spectra of (F$_2^+$)$_{AH}$ centres in RbCl:Na$^+$:O^{2-} at 100 K. The sample is in 'state (b)'. The excitation wavelengths are 1.4 μm, 1.5 μm and 1.6 μm for curves 1, 2 and 3, respectively. The vertical scales are not the same for the three curves, because of the different transmissions of the interference filters inserted in the excitation beam.

In either state of the sample, fluorescence spectra at 100 K clearly show two components peaking at 1804 and 2036 nm, respectively; figure 6 shows, for instance, the fluorescence spectra obtained after 100 K photoconversion of centres. Most probably, when the crystal

is in 'state (b)', it contains chiefly $(F_2^+)_{AH}$ (b) centres with emission at 2036 nm, but some centres are still type (a) which emits at 1804 nm. On the other hand, when the crystal is in 'state (a)', it contains chiefly $(F_2^+)_{AH}$ (a) centres, but also a small concentration of $(F_2^+)_{AH}$ (b) centres, already present at this stage†.

Table 3. Mollowo–Ivey law for $(F_2^+)_{AH}$ centres in alkali halides doped with both oxygen and sodium. Experimental data are from table 2 of the present paper for KCl, KBr, RbCl, and from table 3 of El Akrmi *et al* (1994) for the $(F_2^+)_H$ centre of NaCl (considered as a special case of the $F_2^+:Na^+:O^{2-}$ centre).

	A (nm)	x	σ (nm)
(a) Absorption	168.0	1.772	14
(a) Emission	342.2	1.409	41
(b) Absorption	86.7	2.427	20
(b) Emission	239.3	1.799	12

Together with the previously well known cases of KCl and KBr, we now have spectroscopic data for three $(F_2^+)_{AH}$ centres which should be quite comparable with one another since they are all obtained in halides doped with oxygen and with sodium. We can therefore look for an empirical law to account for the position of their absorption and emission bands. From table 2, one can see that, for both type (a) and type (b), peak wavelengths are nearly the same in KBr:Na$^+$:O^{2-} and in RbCl:Na$^+$:O^{2-}. On the other hand, KBr and RbCl have nearly the same cation–anion distance d (3.298 Å and 3.291 Å according to Fowler (1968)). This suggests that currently known spectroscopic data for $(F_2^+)_{AH}$ centres in crystals doped simultaneously with O^{2-} and Na$^+$ should obey a simple Mollwo–Ivey law:

$$\lambda = Ad^x \tag{3}$$

where A and x are constants. Indeed, one obtains a very nice fit of all experimental data to equation (3) (of course, with different sets (A, x) of adjustable constants for type (a) or (b) and for absorption or emission). However, since each fit rests on three measured points only for two adjustable parameters, this agreement may seem of little significance. Therefore, we increased the number of data by considering that $F_2^+:O^{2-}$ centres in NaCl are a special case of $F_2^+:Na^+:O^{2-}$ centres (with a Na$^+$ 'impurity' substituted for a 'regular' Na$^+$ ion). This idea works quite well, as shown in table 3 which lists the best values of A and x for $(F_2^+)_{AH}$ (a) and $(F_2^+)_{AH}$ (b) centres, in absorption and emission, together with the standard deviation σ defined by

$$\sigma = \left(\sum_{i=1}^{n} \frac{(\lambda_{calc} - \lambda_{exp})^2}{n - p} \right)^{1/2} \tag{4}$$

where $n = 4$ is the number of crystals investigated and $p = 2$, the number of adjustable parameters. The agreement is satisfactory, except for the emission of type (a) centres. In this particular case, results can be improved by using the semi-empirical approach of Girard and Doualan (1993), in which the wavelengths of spectral transitions depend both on the lattice parameter and on the high-frequency dielectric constant of the host. With this model,

† This mixture of centres is observed with 'fresh' samples, just after photoaggregation. Type (b) completely disappears from a sample which has been kept in the dark for a few days at room temperature.

the standard deviation for the emission of type (a) is decreased to 29 nm, but then, for the emission of type (b) and for both absorptions, σ is noticeably increased with respect to the Mollwo–Ivey calculation. Therefore, with the small amount of data at present available, it is wiser to hold to the simpler Mollwo–Ivey formula for all four cases. Of course, it seems highly desirable to obtain spectroscopic data for $(F_2^+)_{AH}$ centres in alkali halides with lattice constants very different from those of NaCl, KCl, KBr and RbCl, for instance in RbBr or in KI. This would allow us to decide whether the Mollwo–Ivey formula is really sufficient to describe the positions of absorption and emission peaks of $(F_2^+)_{AH}$ centres or if some refinement is necessary.

By cooling the RbCl:Na$^+$:O^{2-} sample to liquid-helium temperature, absorption bands of both type (a) and type (b) are observed to narrow and to shift towards longer wavelengths (table 2), while fluorescence bands only narrow, with no significant displacements of their maxima. We looked for sharp lines in the 5 K absorption and emission spectra, but we observed none in the wavelength domain where zero-phonon transitions of $(F_2^+)_{AH}$ centres (either (a) or (b)) are expected.

$(F_2^+)_{AH}$ centres in RbCl:Na$^+$:O^{2-} are rather stable in the dark at room temperature: after 47 d, the optical density of their absorption band decreased by 32% only. We verified that the remaining centres have the same optical properties as those of a fresh sample: photoconversion of (a) into (b) by 100 K, 546 nm irradiation, and spectral positions of the emission bands. Therefore, $(F_2^+)_{AH}$ centres in RbCl appear as a promising new material for IR tunable lasers. Their emission domain will be nearly the same as that of $(F_2^+)_{AH}$ centres in KBr, but they will allow easier storage of the samples, because of better stability. (We observed $(F_2^+)_{AH}$ centres of KBr to decay exponentially in the dark at 295 K with a time constant of approximately 6 d.)

It also seems of interest for colour centre lasers to obtain $(F_2^+)_{AH}$ centres in materials such as RbBr:Na$^+$:O^{2-} or KI:Na$^+$:O^{2-} with interionic distances ($d = 3.445$ Å or 3.544 Å) significantly larger than KBr and RbCl. If $(F_2^+)_{AH}$ centres of RbBr and KI are stable enough and if they yield laser action with a good quantum efficiency, they should allow tunable emission in interesting spectral domains; using the Mollwo–Ivey formula, we calculate for the $(F_2^+)_{AH}$ (b) centres of KI:Na$^+$:O^{2-} an emission band centred at 2316 nm. However, a problem will be to find a suitable pump laser.

Acknowledgment

References

El Akrmi A, Ketolainen P, Doualan J L, Kawa E, Margerie J and Rocher B 1994 *J. Phys.: Condens. Matter* **6** 4843

Fowler W B 1968 *Physics of Color Centres* (New York: Academic)

Gellermann W 1991 *J. Phys. Chem. Solids* **52** 249

Girard S and Doualan J L 1993 *J. Phys.: Condens. Matter* **5** 1811

Lifante G, Cussó F, Jaque F and Henderson B 1990 *J. Phys.: Condens. Matter* **2** 8691

Schneider I 1980 *Solid State Commun.* **34** 865

Wandt D and Gellerman W 1987 *Opt. Commun.* **61** 405

Wandt D, Gellerman W, Lüty F and Welling H 1987 *J. Appl. Phys.* **61** 864