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$(F_2^+)_{\text{H}}$ and $(F_2^+)_{\text{AH}}$ centres in KCl and KBr doped with either carbonates or sulphates

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Abstract. In the present paper, it is shown experimentally: (i) that laser-active $(F_2^+)_{\text{H}}$ and $(F_2^+)_{\text{AH}}$ centres may be produced with significant concentrations in CO_3^{2-} -doped KBr (as was already known for CO_3^{2-} -doped KCl); and (ii) that, in contradistinction to the results reported previously, large optical densities of $(F_2^+)_{\text{H}}$ and $(F_2^+)_{\text{AH}}$ centres can be obtained in sulphate-doped alkali halides (KCl or KBr).

1. Introduction

Laser emission of NaCl:OH^- crystals has initiated a new class of laser-active colour centres, called $(F_2^+)_{\text{H}}$ (Pinto *et al* 1986, Wandt *et al* 1987). They are formed of an F_2^+ centre (two neighbouring anion vacancies decorated by a single electron) in the vicinity of a divalent anionic impurity, generally an O^{2-} ion.

Recently, much research has been carried out with the aim of producing this type of centre and of increasing their stability under the intense pump beam of a laser, by substituting another chalcogenic impurity (S^{2-} , Se^{2-} instead of O^{2-}) or by the further insertion of an alkaline substitutional impurity (generally Na^+). One thus obtains $(F_2^+)_{\text{H}}$ and $(F_2^+)_{\text{AH}}$ centres respectively. $(F_2^+)_{\text{H}}$ centres have been widely studied both in NaCl:OH^- and in NaCl:O^{2-} . But Wandt *et al* (1987) have reported that dissociation of OH^- in KCl and KBr matrices is very weak, which prevents formation of significant concentrations of $(F_2^+)_{\text{H}}$ centres in KCl:OH^- and KBr:OH^- . On the other hand, doping of these matrices (along with NaCl and KI) with alkali superoxides, sulphides or selenides such as Na_2O_2 , KO_2 , Na_2S , K_2S and Na_2Se allows formation of various $(F_2^+)_{\text{H}}$ centres (Wandt *et al* 1987, El Akrmî *et al* 1994a). Thermal stability is much higher in NaCl:OH^- , NaCl:S^{2-} , and NaCl:Se^{2-} than in all other crystals (El Akrmî *et al* 1994a).

However, these dopants, especially alkali superoxides, have some drawbacks as regards sample growth: they are strongly hygroscopic and rapidly converted into hydroxides in the presence of moisture. Moreover, doping with alkali superoxides must be performed under a partial pressure of oxygen in order to prevent their thermal decomposition.

More recently, $(F_2^+)_{\text{H}}$ and $(F_2^+)_{\text{AH}}$ centres have been obtained in KCl with easy-to-handle dopants, such as K_2CO_3 , KNO_3 or NaNO_3 . Lifante *et al* (1991) obtain significant concentrations of $(F_2^+)_{\text{H}}$ centres in KCl doped with either K_2CO_3 or KNO_3 and $(F_2^+)_{\text{AH}}$ centres in KCl:NaNO_3 . On the other hand, they fail to obtain such modified F_2^+ centres in KCl doped with K_2SO_4 . The results of Raerinne and Ketolainen (1993) are somewhat different since, for some unknown reason, they obtain $(F_2^+)_{\text{H}}$ centres in KCl:NO_3^- only, and

Table 1. Crystal growth and coloration conditions: crystal growth in open atmosphere (O.A.) or in argon-controlled atmosphere (Ar); additive coloration performed with K vapour.

Sample	Growth		Coloration		
	Impurity (mol. ppm)	Atmosphere	<i>T</i> (°C)	<i>P</i> (mbar)	Duration (h)
KCl:SO ₄ ²⁻	K ₂ SO ₄ (500)	O.A.	650	45	2.5–3
KCl:Na ⁺ :SO ₄ ²⁻	Na ₂ SO ₄ (600)	O.A.	650	45	2.5–3
KCl:Na ⁺ :SO ₄ ²⁻	Na ₂ SO ₄ (600)	Ar	650	45	2.5–3
KCl:Na ⁺ :CO ₃ ²⁻	Na ₂ CO ₃ (700)	O.A.	650	45	2.5–3
KBr:CO ₃ ²⁻	K ₂ CO ₃ (900)	O.A.	600	30	2
KBr:SO ₄ ²⁻	K ₂ SO ₄ (700)	O.A.	600	30	2
KBr:Na ⁺ :CO ₃ ²⁻	K ₂ CO ₃ (800) +NaBr (1200)	O.A.	600	30	2
KBr:Na ⁺ :SO ₄ ²⁻	Na ₂ SO ₄ (800)	O.A.	600	30	2

not in KCl:CO₃²⁻. In a very recent paper (Diaf *et al* 1996), we confirm the results of Lifante *et al* (1991), as opposed to those of Raerinne and Ketolainen (1993): in KCl doped with either K₂CO₃ or (K₂CO₃ + NaCl), it is indeed possible to obtain (F₂⁺)_H or (F₂⁺)_{AH} centres† with the same optical properties as in crystals obtained with the usual dopants, such as KO₂ or Na₂O₂.

In the present paper, we extend this study from the KCl to the KBr matrix and we show, moreover, that one may obtain (F₂⁺)_H and (F₂⁺)_{AH} centres by doping KCl and KBr crystals with sulphate ions, instead of carbonate ones, in disagreement with the results of Lifante *et al* (1991). We describe in section 2 the sample preparation procedure: crystal growth, coloration and optical treatments. Section 3 deals with the optical absorption and emission spectra of the centres obtained as well as with their thermal stabilities. In section 4, we discuss our experimental results and compare them with those already available in the literature.

2. The sample preparation procedure

Most of the crystals were grown in the Annaba laboratory by the Czochralski technique in open air. The starting alkali halide powders (NaCl, NaBr, KCl, KBr) were pure grade

† We recently verified that (F₂⁺)_{AH} centres can also be obtained from KCl doped with CO₃Na₂. This possibility has been included in tables 1 and 2.

Table 2. Absorption and emission band maxima at LNT for $(F_2^+)_H$ and $(F_2^+)_{AH}$ centres in KCl and KBr: (*) $(F_2^+)_H$ centres converted into F_2^+ by 'F-light' irradiation at LNT; and (!) although no sodium was intentionally introduced into the initial powder, we observed $(F_2^+)_{AH}$ centres and not $(F_2^+)_H$ ones (see section 3.1.2).

Crystal	Centre	Dope	Variety (a)		Variety (b)		Reference
			Absorption (nm)	Emission (nm)	Absorption (nm)	Emission (nm)	
KCl	$(F_2^+)_H$	KO ₂	1460	1770	(*)		El Akrmi <i>et al</i> (1994a)
		KO ₂	1450	1780	(*)		Wandt <i>et al</i> (1987)
		K ₂ CO ₃	1454	1780	(*)		Diaf <i>et al</i> (1996)
		K ₂ CO ₃	1450	1780	(*)		Lifante <i>et al</i> (1991)
		KNO ₃	1450		(*)		Raerinne and Ketolainen (1993)
		K ₂ SO ₄	1440		(*)		This work
KBr	$(F_2^+)_H$	KO ₂	1540	1916	1580	1980	El Akrmi <i>et al</i> (1994a)
		KO ₂	1530	1890	1580	1980	Wandt <i>et al</i> (1987)
		K ₂ CO ₃	1510	1956	1578	1987	This work
KCl	$(F_2^+)_{AH}$	KO ₂ + NaCl	1295	1698	1379	1896	El Akrmi <i>et al</i> (1994b)
		KO ₂ + NaCl	1290	1660	1390	1860	Wandt and Gellermann (1987)
		K ₂ CO ₃ + NaCl	1298	1698	1378	1896	Diaf <i>et al</i> (1996)
		Na ₂ CO ₃	1300		1370		This work
		Na ₂ SO ₄	1300		1374		This work
		KBr	$(F_2^+)_{AH}$	KO ₂ + NaBr	1379	1882	1585
		KO ₂ + NaBr	1350	1770	1650	2040	Gellermann (1991)
		K ₂ CO ₃ + NaBr	1390		1578		This work
		Na ₂ SO ₄	1370		1574		This work
		K ₂ SO ₄ (!)	1360		1572		This work

from Réachim, while the dopants (K₂CO₃, Na₂CO₃, K₂SO₄, Na₂SO₄) were provided by Prolabo. One Na₂SO₄-doped KCl crystal was produced, for comparison purposes, in the Caen laboratory by the Czochralski technique, under a controlled argon atmosphere, from Merck Suprapur-grade KCl powder and Prolabo ultrapure-grade Na₂SO₄ dopants. All of the parameters related to the sample preparation are gathered together in table 1.

Parallelepipedic samples, approximately 10 × 10 × 3 mm³, were cleaved from the crystals, coarsely polished and additively coloured (Mollenauer 1978) under conditions summarized in table 1. During the return to room temperature after coloration, aggregates and colloids develop in the sample. Therefore, in order to eliminate them, we performed several two- or three-minute annealings at a temperature 100 °C below the melting point, followed by rapid quenches on a copper plate or into a liquid nitrogen bath. Then we proceeded to the final polishing of the samples, under dim red light in order to prevent photoionization, on a silk cloth stretched over a stainless-steel cylinder. On the surface of the cloth, we placed alumina powder of grain size 1 to 0.3 μm, lubricated by a mixture of ethanol and water initially, and by anhydrous acetone.

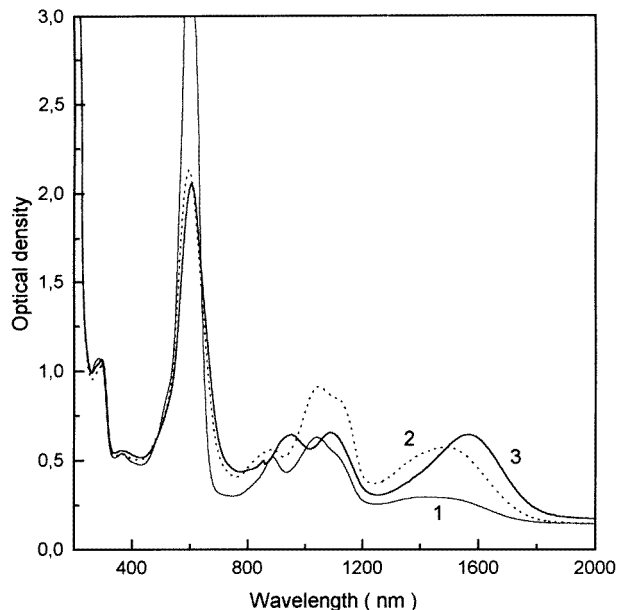


Figure 1. Absorption spectra of KBr:CO_3^{2-} at LNT: (1) after annealing; (2) after photoaggregation with 546 nm light at -10°C for 15 minutes; and (3) after subsequent LNT irradiation with 436 or 365 nm light for 10 minutes.

The sample was then placed into a small nitrogen cryostat, the cold finger of which has a temperature adjustable between 100 and 290 K. Light irradiations were performed at -10°C and at 100 K (LNT) using a high-pressure mercury lamp, Osram HBO 100, and a Schott 546, 436 or 365 nm Monochromat filter. LNT absorption spectra were obtained with a Perkin-Elmer Lambda 9 spectrophotometer which can operate in the 185–3200 nm spectral range. For emission measurements, we use a mechanical chopper, a Jobin-Yvon HRS2 monochromator, a PbS detector and a Stanford Research System SR 510 lock-in amplifier.

3. Experimental results

3.1. Absorption and emission of $(F_2^+)_H$ centres

3.1.1. $(F_2^+)_H$ in KBr:CO_3^{2-} . The LNT absorption spectrum of CO_3^{2-} -doped KBr (figure 1) displays around 290 nm an absorption band assigned to $\text{O}^{2-}-\square$ by Wandt *et al* (1987), a fact which suggests that decomposition of CO_3^{2-} ions has occurred during additive coloration, like in the case of KCl:CO_3^{2-} (Diaf *et al* 1996). Moreover, one already observes at this stage a weak broad band at around 1500 nm. Photoaggregation with the 546 nm line of mercury at -10°C leads to a considerable increase of this band which peaks at 1510 nm. In agreement with data obtained with other dopants (Wandt *et al* 1987, El Akrimi *et al* 1994a), we assign this band to the (a) variety of $(F_2^+)_H$ centres. In fact, when one irradiates this same sample with the 436 nm mercury line at 100 K, the peak absorption is shifted to 1578 nm (figure 1, curve 3) corresponding to the (b) variety of the same $(F_2^+)_H$ centres.

Excitation at LNT of the absorption bands of the (a) or (b) species with a 100 W halogen

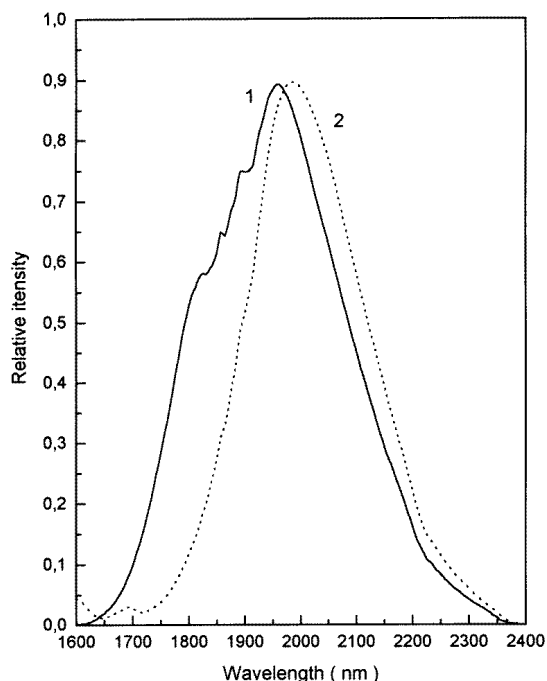


Figure 2. Emission spectra of KBr:CO₃²⁻ at LNT: (1) after photoaggregation with 546 nm light at $-10\text{ }^{\circ}\text{C}$ for 15 minutes (the ‘accidents’ in the 1800–1900 nm range are due to absorption by atmospheric H₂O); and (2) after subsequent LNT irradiation with 436 nm light for 10 minutes.

lamp filtered by a $1.4\text{ }\mu\text{m}$ interference filter leads to an emission band peaking at 1956 nm ((a) variety) or 1987 nm ((b) variety); see figure 2. Table 2 summarizes the positions of (F₂⁺)_H-centre absorption and emission bands in our samples, compared with the values from the literature. The agreement is good. Moreover, a study of the thermal stability of (F₂⁺)_H centres in the dark at room temperature shows the same behaviour as that reported by El Akrimi *et al* (1994a) for the same centres in crystals doped with the superoxide KO₂.

3.1.2. (F₂⁺)_H in KCl:SO₄²⁻ and KBr:SO₄²⁻. Like in the case of KCl:CO₃²⁻ (Diaf *et al* 1996), LNT absorption spectra of coloured KCl:SO₄²⁻ after annealing and quenching show a broad band at 1440 nm, the intensity of which is enhanced by $-10\text{ }^{\circ}\text{C}$ photoaggregation with the 546 nm line. This 1440 nm band is characteristic of (F₂⁺)_H centres. A 436 nm irradiation of this sample at LNT destroys these centres and converts them to intrinsic F₂⁺ centres which absorb at 1378 nm. This behaviour is identical to that observed with superoxide, carbonate or nitrate doping (Wandt *et al* 1987, El Akrimi *et al* 1994a, Lifante *et al* 1991, Raerinne and Ketolainen 1993, Diaf *et al* 1996). However, as pointed out in the introduction, Lifante *et al* were unable to observe (F₂⁺)_H centres in sulphate-doped (or OH⁻-doped) KCl.

In KBr:SO₄²⁻, the spectral position of the absorption bands observed either after $-10\text{ }^{\circ}\text{C}$ photoaggregation or after extra LNT irradiation do not correspond to (F₂⁺)_H, but rather to (F₂⁺)_{AH} centres (see the penultimate line of table 2), as if some contamination with sodium had happened during crystal growth.

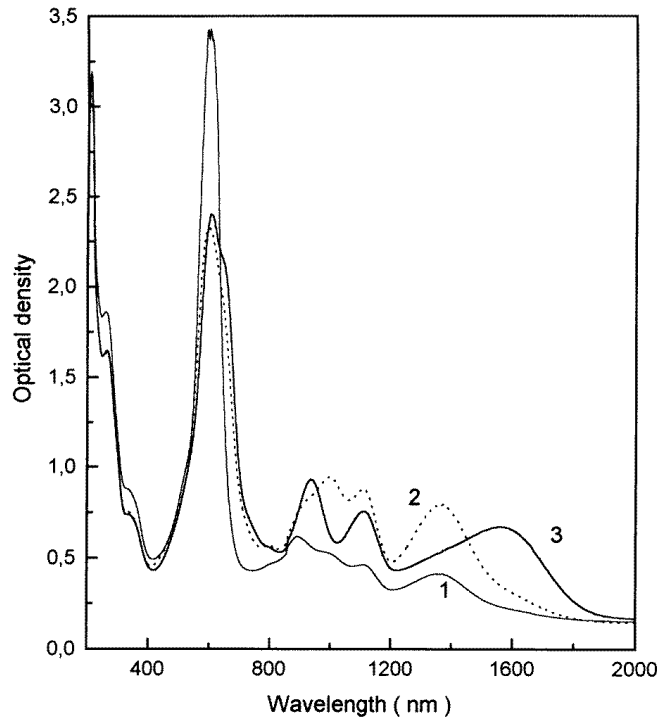


Figure 3. Absorption spectra of $\text{KBr}:\text{SO}_4^{2-}:\text{Na}^+$ at LNT: (1) after annealing; (2) after photoaggregation with 546 nm light at $-10\text{ }^\circ\text{C}$ for 20 minutes; and (3) after subsequent LNT irradiation with 365 nm light for 12 minutes.

3.2. Absorption of $(F_2^+)_{\text{AH}}$ centres

3.2.1. $(F_2^+)_{\text{AH}}$ in $\text{KBr}:\text{CO}_3^{2-}:\text{Na}^+$. Like in the case of $\text{KCl}:\text{CO}_3^{2-}:\text{Na}^+$, the LNT absorption spectrum of $\text{KBr}:\text{CO}_3^{2-}:\text{Na}^+$ after photoaggregation shows a broad infrared band (here located at around 1390 nm), in addition to the 285 nm UV band, which is assigned to $\text{O}^{2-}-\square-\text{Na}^+$ complexes by El Akrimi (1994). In agreement with the results from this reference, LNT irradiation with the 436 nm or even the 365 nm mercury line shifts the infrared band to 1578 nm. According to Wandt and Gellermann (1987), the 1390 nm band is associated with the (a) variety and the 1578 nm band with the (b) variety of $(F_2^+)_{\text{AH}}$ centres. The broad 1390 nm band is asymmetrical and presents a shoulder in the long-wavelength wing; this means that, after photoaggregation, the two species (a) and (b) of $(F_2^+)_{\text{AH}}$ centres coexist. On the other hand, after LNT photoconversion, the band associated with the (b) variety is more symmetrical, which shows that the $(a) \rightarrow (b)$ conversion is practically complete. Table 2 compares the position of (a) and (b) absorption bands with those published in the literature.

3.2.2. $(F_2^+)_{\text{AH}}$ in $\text{KBr}:\text{SO}_4^{2-}:\text{Na}^+$. Figure 3 depicts the optical stages leading to $(F_2^+)_{\text{AH}}$ centres of varieties (a) and (b). Curve 1, for after annealing and quenching, shows a fairly distinct 1370 nm band, in addition to the intense 270 nm one assigned, as above, to

Na⁺-perturbed O²⁻-□ pairs†. After -10 °C photoaggregation with the 546 nm mercury line, the infrared band grows noticeably, reaching an optical density of approximately 0.7 (for a sample of thickness ≈2 mm), which is quite comparable to the value obtained after conventional (KO₂ + NaBr) doping (Möllmann *et al* 1994, El Akrimi 1994). The 1370 nm band is due to the (a) variety of (F₂⁺)_{AH} centres. LNT irradiation of the sample with the mercury 436 or 365 nm line leads to creation of the (b) variety, with an absorption band peaking at 1574 nm. The asymmetry of this band towards short wavelengths shows that the (a) → (b) conversion is incomplete. The observed band positions are in good agreement with the results of El Akrimi *et al* (1994b); see table 2.

3.2.3. (F₂⁺)_{AH} in KCl:SO₄²⁻:Na⁺. Together with the 270 nm band due to O²⁻-□-Na⁺, we observe the presence of the bands assigned to the varieties (a) (after photoaggregation) or (b) (after LNT photoconversion) of (F₂⁺)_{AH} centres in KCl. These bands are at the same location as those observed in KCl:O²⁻:Na⁺ (El Akrimi *et al* 1994b) or in KCl:CO₃²⁻:Na⁺ (Diaf *et al* 1996); see table 2.

4. Discussion

In our previous paper (Diaf *et al* 1996), we confirmed that it is possible to obtain (F₂⁺)_H and (F₂⁺)_{AH} centres in KCl by using carbonate doping, in agreement with the previous results of Lifante *et al* (1991) and at variance with those of Raerinne and Ketolainen (1993). The present work leads chiefly to two further conclusions.

(i) (F₂⁺)_H and (F₂⁺)_{AH} centres may be created, with large densities, in carbonate-doped KBr, exactly like in carbonate-doped KCl. This result may have interesting practical applications, but it is hardly surprising, since colour centres in KBr and in KCl generally have similar behaviours.

(ii) (F₂⁺)_H and (F₂⁺)_{AH} centres in KCl, and (F₂⁺)_{AH} centres in KBr can be obtained in sulphate-doped crystals too. This was quite unexpected in view of the negative result of Lifante *et al* (1991). We must therefore examine our results critically. From the position of the absorption bands both before and after LNT photoconversion, there is no doubt that the centres that we get are identical with those obtained by the more conventional superoxide doping (see table 2). But, since our crystals are grown in open air, one may fear that the oxygen of the (F₂⁺)_H and (F₂⁺)_{AH} centres may have arisen from atmospheric moisture, not from the sulphate dopants. However, it is well known (Wandt *et al* 1987, Lifante *et al* 1991) that OH⁻ doping does not allow substantial formation of (F₂⁺)_H centres except in NaCl; thus it seems very doubtful that the presence of (F₂⁺)_H and (F₂⁺)_{AH} centres in our KCl and KBr samples should be a result of the growth being in open air. Moreover, a direct argument has been obtained by Czochralski pulling one crystal of KCl:Na₂SO₄ in the Caen laboratory facility, under a controlled argon atmosphere and using Merck Suprapur KCl powder. After additive coloration and -10 °C photoaggregation, this crystal had exactly the same optical properties as the ones obtained by open-air growth at Annaba (peak absorptions at LNT: 1370 and 1574 nm respectively before and after LNT photoconversion, which is characteristic of the (F₂⁺)_{AH} centre in KCl). Therefore, we consider that (F₂⁺)_{AH} centres in KCl are genuinely obtained by a decomposition of SO₄²⁻ during additive coloration, which

† Because of a significant slope of the absorption background which increases toward short wavelengths, it is impossible to measure accurately the spectral position of these O²⁻-□ absorptions. Therefore, one should not consider as significant the differences between the 270 nm observed here, the 285 nm of section 3.2.1 and the 278 nm quoted by El Akrimi (1994).

provides the O^{2-} 'building block' of this centre. By analogy, we think that $(F_2^+)_{\text{H}}$ centres in KCl and $(F_2^+)_{\text{AH}}$ centres in KBr also arise genuinely from the decomposition of the sulphate dopants of our samples.

This conclusion raises the question of the cause of the difference between our positive result and the negative one of Lifante *et al* (1991). We have currently no answer on this point. Let us only remark that the possibility of creating $(F_2^+)_{\text{H}}$ and $(F_2^+)_{\text{AH}}$ centres seems to depend critically on some minute details in the crystal growth procedure; indeed this problem of the sulphate doping is not the only one—there is also the question of the carbonate doping for which Raerinne and Ketolainen (1993), on one hand, and Lifante *et al* (1991) and Diaf *et al* (1996), on the other hand, arrive at opposite conclusions.

From the practical point of view, crystal growth is easier in open air than under a controlled atmosphere. Therefore, the results of the present paper, together with those of Diaf *et al* (1996), may prove valuable for preparing laser-active samples. With our air-grown crystals, we have observed optical spectra and thermal behaviours identical with those of samples produced by the usual technique (superoxide doping and an inert atmosphere). The optical densities of modified F_2^+ centres attained are high, especially in the case of $(F_2^+)_{\text{AH}}$ centres in $\text{KBr}:\text{Na}_2\text{SO}_4$. It would therefore be very interesting to perform the crucial test, i.e. to obtain induced emission from our crystals and to compare their laser performance with that of conventionally prepared samples.

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