Cryst. Res. Technol. **38**, No. 12, 1052 – 1057 (2003) / **DOI** 10.1002/crat.200310135

Preparation of (KBr-KCl)(OH^-):$(F_2^+)_H$ color center laser crystal series and their spectral characteristics

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Received 10 February 2003, revised 16 May, accepted 2 July 2003
Published online 15 November 2003

Key words laser crystal, color center, alkali halides, single crystal growth.
PACS 42.55.Rz

In order to adjust and broaden the absorption spectrum and emission spectrum of the $(F_2^+)_H$ type color center so as to match up to the pumping and to fit in with the demand of application, a (KBr-KCl)(OH^-):$(F_2^+)_H$ color center laser crystal series was prepared by the process of single crystal growth, additive coloration, anneal, and light aggregation at 290 K and 77 K. The spectral characteristics of (KBr-KCl)(OH^-) crystals are investigated. It is found that the absorption and emission band of the $(F_2^+)_H$ color centers in KBr-KCl complex host crystals has a considerable adjustment and extensions compared to the color centers in single KBr or KCl crystal.

1 Introduction

The color center laser has become an active field in the solid state tunable lasers because it has fine comprehensively laser properties compared with other lasers and has good application prospect in high technology field [1,2]. In order to overcome the instability of the pure $(F_2^+)_H$ color center, adjust and broaden the absorption spectrum and emission spectrum of $(F_2^+)_H$ type color center so as to match up to the pumping and to fit in with the demand of application, F. L. Mollenauer et al. [3,4], E. Georgiou et al. [5], F. Luty et al. [6] and W. Gellermann et al. [1] made research on doping anions and cation ions into the crystals. As expected, the perturbation of the doping ion shows a significant effect on the stability of centers, but it shows no encouraging effect on the laser spectrum of $(F_2^+)_H$ type color center.

The authors believe, it is possible to adjust and broaden the spectral region of $(F_2^+)_H$ type color center by choosing a complex host crystal consisting of two or more compounds as a complex unit and preparing the crystal with multi-center co-existent color centers. As an example, a (KBr-KCl)(OH^-):$(F_2^+)_H$ color center crystal series was prepared and the absorption and emission spectra of the crystals were characterized.

2 Experiment and results

2.1 Single crystals growth

The preparation of F_2^+-like color center crystals has to pass through the processes of single crystal growth, additive coloration, annealing and light aggregation. KBr, KCl and KOH with a suitable ratio were evenly mixed at room temperature, the mixture was put into a platinum crucible, then the mixture was overheated at 800 ºC for 24 h. If necessary, the processes of crystallization and melt-out was repeated. (KBr-KCl)(OH^-)

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single crystals were grown by the Czochralski method under the following conditions: start temperature of about 720 ºC, descend temperature rate of 2 ºC/h, seed rotation rate of 360 rph and raise rate of 2 mm/h, Ar atmosphere. After that, transparent (KBr-KCl) (OH^-) single crystals with well cleavage and evenly dispersed dopant ions were obtained.

2.2 Additive coloration

Color centers were incorporated into the crystals by using a rather crude but simple additive coloration technique [7]. Cleaved sections of a crystal approximately 20 mm × 20 mm × 6 mm were placed together with a about 3 g a potassium metal in a bomb consisting of two hollowed-out blank Conflat flanges tightly bolted together with a Cu gasket to form a hermetic seal. The bomb was placed in a 650 ºC oven for 60 min under the pressure of potassium vapor of 8×10^3 Pa, then removed and allowed to cool down to room temperature by freely. After additive coloration, the crystals had a uniform purple-palm color, which was due to the absorption bands from the various types of color centers present as well as from colloids of potassium metal in the crystal.

2.3 Anneal process

In order to eliminate unuseful and colloid color centers and to enhance the concentration of useful color centers in the crystal, the colored crystal was annealed for several minutes at 600 ºC, after which the crystal had an orange-yellow color. The duration of the anneal process depended on the crystal thickness, varying from 3 to 7 minutes for crystals from 2 to 4 mm thick. The absorption spectra of the annealed crystals showed that there are higher concentrations of F and F_2 color centers and that a moderate O^{2-}-F^+ defect remained in the crystal.

2.4 Light aggregation

The annealed piece was irradiated for 5 min by a light source with a wavelength less than 365 nm from a 200 W high pressure mercury lamp filtered through a 10-cm cell filled with a $CuSO_4$ solution at 275 K, the color center thus obtained was designated as $(F_2^+)_{H1}$ color center. As an example, the absorption peak wavelength for the $(F_2^+)_{H1}$ color center in a (20 mol. % KBr - 80 mol. % KCl) complex host crystal is at 1300 nm and the emission peak wavelength is at 1740 nm, respectively. After that, the piece was cooled down to 77 K and irradiated by the same light source for 5 min, the color center thus obtained with an absorption peak wavelength at 1380 nm and a emission peak wavelength at 1820 nm was designated as $(F_2^+)_{H2}$ color center in (20 mol. % KBr - 80 mol. % KCl) complex host crystal. It is noticeable that the $(F_2^+)_{H1}$-type color center is not a laser-active color center, while the $(F_2^+)_{H2}$-type color center is a laser-active color center [1].

2.5 Analysis

The kinds and concentration of color center in crystal was determined from the absorption spectra of the samples measured by using a Shimadzu Model UV-3100 UV-VIS spectrophotometer. The emission spectra of samples were measured using a Nd^{3+}:YAP laser with wavelength at 1340 nm as exciting source. The chemical elements, such as K^+, Br^- and Cl^- ions, in the crystal were determined by inductively coupled plasma atomic emission spectroscopy (Seiko SPS-1200A), after dissolving the crystal samples in distilled water. The concentration of OH^- incorporated in the crystals was determined from Fourier-transform infrared spectroscopy (Nicolet Maga-IR 750 instrument) measurements of the OH^- vibration band at 3654 cm [1,8].

3 Results and discussion

3.1 Single crystal growth

The (KBr-KCl)(OH-) system is chosen as a research object based on the following: (1) (KBr-KCl) is a complex system with complete solubility in liquid and solid state (Fig. 1) [9], which is propitious to grow single crystal in any ratio mix. (2) The recrystallization of complex crystal is unobservable under ordinary conditions and temperature, which proves the stability of the complex crystal. (3) The research on $(F_2^+)_H$ type color center in single KCl or KBr host crystal is ripe, which is useful for comparison and utilization. (4) The optical property of $(F_2^+)_H$ color center is different in KCl(OH^-) and KBr(OH^-), after ultraviolet light irradiation at 77K, the absorption peak of $(F_2^+)_H$ color center in a KCl(OH^-) crystal shows a "blue shift"; and the absorption peak of $(F_2^+)_H$ color center in a KBr(OH^-) crystal shows a "red shift" comparing to the absorption peak of $(F_2^+)_H$ color center before the ultraviolet light irradiation (Figure 2 and Figure 3), which enables spectral adjusting of the complex system. (5) The emission peak wavelength for $(F_2^+)_H$ in KBr(OH^-) crystal is at 1980 nm and the absorption peak wavelength at 1580 nm, which is difficult to match by a pump light source. Now, it is possible to shift the absorption peak wavelength to a suitable position and match the pump light source, which is significant for application.

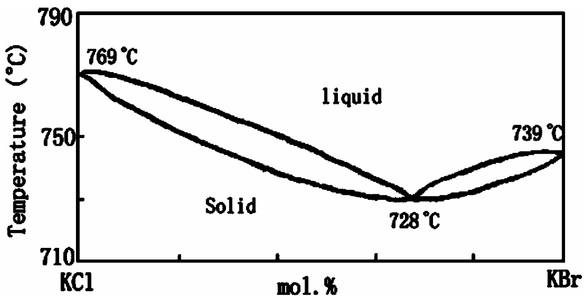

Fig. 1 Phase diagram for KBr-KCl system.

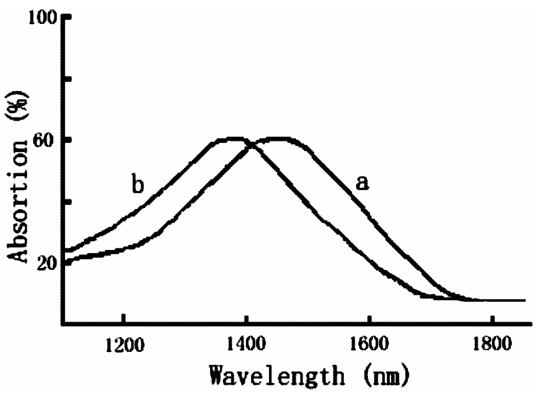

Fig. 2 Absorption spectra of KCl(OH^-) crystal (a) after light aggregation at room temperature; (b) after light aggregation at liquid nitrogen temperature.

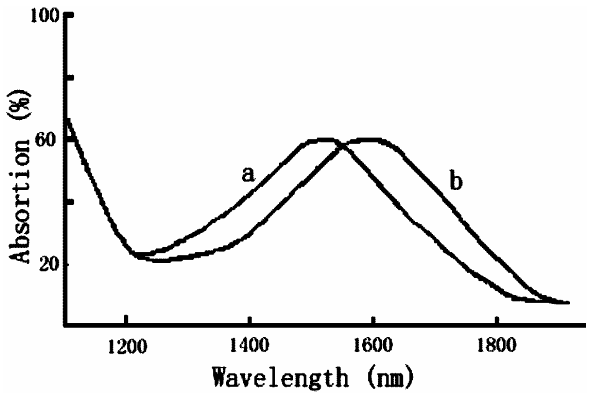

Fig. 3 Absorption spectra of KBr(OH^-) crystal (a) after light aggregation at room temperature; (b) after light aggregation at liquid nitrogen temperature.

The composition and structure of the crystals were characterized with x-ray structural analysis and electron probe microanalysis. It was found that there are serious double crystals, twin crystals, various tresses, uneven OH^- distribution, and also uneven Br^- and Cl^- distribution in (KBr-KCl)(OH^-) complex host crystals grown under routine growth conditions. In order to solve the homogeneity problem for the crystals, the following techniques are employed: evenly mixing the materials based on proportion; overheating the melt at high temperature for a long time; controlling the growth speed, making it two or three times slower than that of a single host single crystal; if necessary, repeating the processes of crystallization and melt-out. Eventually, a homogeneous OH^- doped (KBr-KCl) complex host single crystal was generated.

The OH^- concentration in a complex host crystal is a decisive and hardly controllable factor. A too low OH^- concentration restricts the formation of the $(F_2^+)_H$ color center. A higher OH^- concentration, however, inhibits the formation of the F color center and promotes the conversion of the F color center into F aggregate color centers, consequently, the decrease of the F color center restricts the concentration of the $(F_2^+)_H$ color center as well. By comparing different experiments, an OH^- concentration of 0.15 ~ 0.25 mol % in the melt is proved to be appropriate under the conditions now available.

3.2 The formation of color centers

During additive coloration, both the generation of the F color center in adequate amount and the decomposition of OH^- into F^+-O^{2-}, *i.e.* oxygen vacancy pair, are required. The coloration temperature is different for (KBr-KCl) complex host crystals of different compositions. The coloration temperature *vs.* the composition of the complex host crystal is shown in Table 1.

Table 1 The coloration temperature vs. the composition of complex host crystal.

KCl (melt) (mol. %)	Temperature (ºC)	KCl (melt) (mol. %)	Temperature (ºC)
0	680	45	660
5	680	80	680
10	670	90	690
20	670	100	700

The $(F_2^+)_H$ color center will be produced during the light aggregation process. The temperature for the light aggregation is somewhat lower for a complex host crystal than that for a single host crystal, and the formation mechanism of the $(F_2^+)_H$ color center in the complex host crystal is similar to that in a single host crystal which have been investigated before by us [10]. The light aggregation of color centers reactions (1) and (2) takes place at 275 K and 77 K, respectively.

$$F + O^{2-}\text{-}F^+ \xrightarrow{\text{275K, UVL, 5min}} F_2^+\text{-}O^{2-} = (F_2^+)_{H1} \qquad (1)$$

$$(F_2^+)_{H1} \xrightarrow{\text{77K, UVL, 5min}} (F_2^+)_{H2} \qquad (2)$$

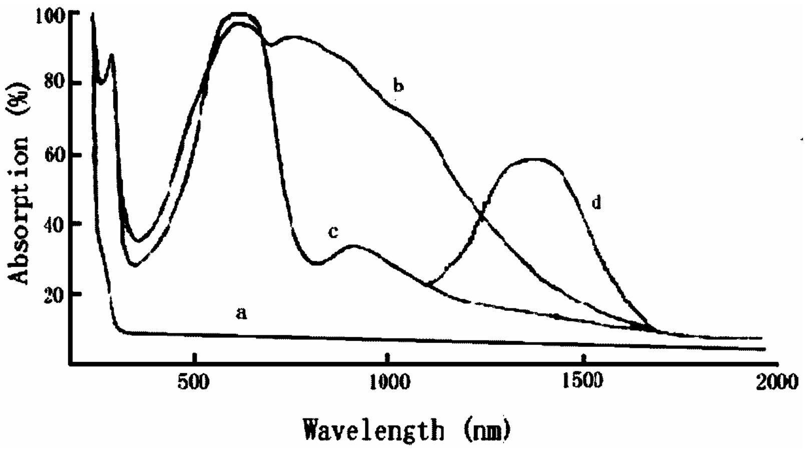

Fig. 4 Absorption spectra of (a) (20 mol. % KCl - 80 mol. % KBr):OH^- monocrystal, (b) additively colored crystal, (c) annealed crystal, (d) light aggregated crystal.

As an example, the absorption spectra for (a) (20 mol. % KCl - 80 mol. % KBr)(OH^-) single crystal, (b) additive colored crystal, (c) annealed crystal, (d) light aggregated crystal are shown in Figure 4. From Figure 4, the absorption band wavelength less than 200 nm in curve (a) presents the OH^- ion effectively doped in the crystal, and the concentration of OH^- is about 50 ppm determined by FTIR analysis. After additive coloration [curve (b)], various color centers are formed, such as the F color center, the F_2 color center, the F_3 color center and the F_4 color center, and so on, which formed an absorption band from 400 nm to 1400 nm. Meanwhile, the OH^- is decomposed into O^{2-}-F^+ and H_i^0 with absorption peak wavelength at 290 nm and 190 nm, respectively. In curve (c), it can be seen that the concentration of F and F_2 color centers is enhanced and the concentration of other F-type aggregated color centers is declined which is the purpose of the anneal process. After light aggregation at 275 K, the $(F_2^+)_{H1}$ color center is formed. Under light irradiating at 77 K, the $(F_2^+)_{H1}$ no laser-active color center changes into the $(F_2^+)_{H2}$ laser-active color center with an absorption wavelength band in the range of 1100 - 1700 nm [curve (d)].

3.3 Spectral characteristics of (KBr-KCl)(OH^-)

The spectrum of the complex host crystal regularly shifts along with the change of complex composition. The relation between the composition of the complex host crystals and the absorption peak wavelength of F color and $(F_2^+)_H$ color centers are shown in Table 2 and Table 3, respectively.

Table 2 The composition of crystal *vs.* the absorption peak wavelength of F color center.

KCl (melt) (mol. %)	Absorption peak wavelength (nm)	KCl (melt) (mol. %)	Absorption peak wavelength (nm)
0	600	45	582
5	590	80	570
10	590	90	570
20	588	100	560

Table 3 The composition of crystal *vs.* the absorption peak wavelength of $(F_2^+)_H$ color center.

KCl (melt) (mol. %)	Peak wavelength of $(F_2^+)_{H(1)}$ (nm)	Peak wavelength of $(F_2^+)_{H(2)}$ (nm)	Shifting value (nm)
0	1530	1580	50
5	1420	1480	60
10	1340	1410	70
20	1300	1380	80
45	1280	1280	0
80	1390	1370	–20
90	1420	1380	–40
100	1450	1380	–70

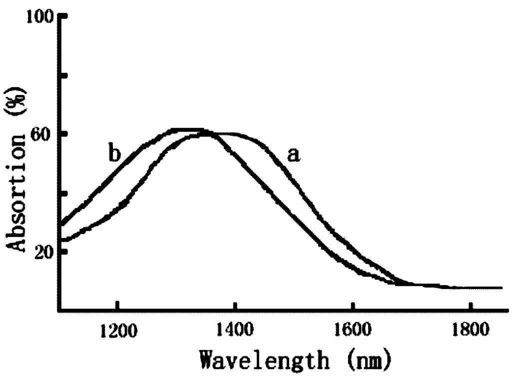

Fig. 5 Absorption spectra of (20 mol. %KCl-80 mol.%KBr):OH^- crystal (a) after light aggregation at room temperature; (b) after light aggregation at liquid nitrogen temperature.

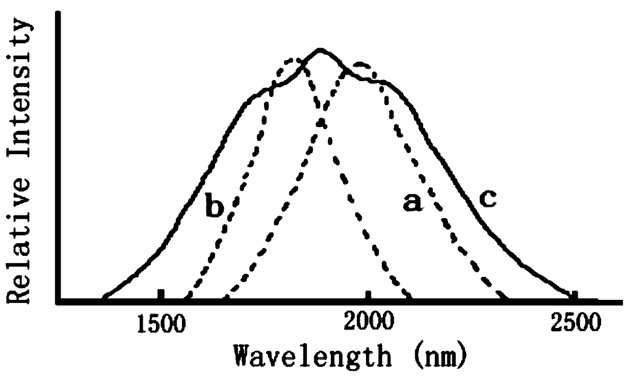

Fig. 6 Emission spectra of (a) KBr:OH^-; (b) KCl:OH^-; (c) (20 mol. % KCl - 80 mol. % KBr):OH^-.

As well known, the spectrum of a KBr(OH^-):$(F_2^+)_H$ color center laser has a tunable range between 1700 ~ 2100 nm and a power peak wavelength at 1900 nm, which is a very applicable laser spectral band. However, it is very deficient to an appropriate pumping source for its absorption peak wavelength at 1900 nm. From Table 3, it can be seen that the wavelength of the absorption peak has been shifted to 1380 nm, that is: (20 mol. % KBr - 80 mol. % KCl), (10 mol. % KBr - 90 mol. % KCl), and (80 mol. % KBr - 20 mol. % KCl), with the absorption peak wavelength at 1370 nm, 1380 nm and 1380 nm, respectively, so that a Nd^{3+}:YAP laser can be effectively adopted as pumping source.

The absorption spectra for KBr(OH^-):$(F_2^+)_H$, KCl(OH^-):$(F_2^+)_H$ and (80 mol. % KBr - 20 mol. % KCl)(OH^-):$(F_2^+)_H$ crystals are shown in Figure3, 2 and 5, respectively. The emission spectrum for KBr(OH^-):$(F_2^+)_H$, KCl(OH^-):$(F_2^+)_H$ and (80 mol. % KBr - 20 mol. % KCl)(OH^-):$(F_2^+)_H$ crystals are shown in Figure 6.

The results in Figure 6 further reveal the excellent laser spectral characteristics of the complex host crystal, namely, its emission spectrum completely covers and exceeds the summation of the emission spectra of single KBr or KCl host crystals. It has a tunable range of 1500 ~ 2300 nm, with a plateformlike peak part of 400 nm (the part of highest emissive power), unlike the narrow peak (100 nm) for single KBr or KCl host crystal.

From the absorption and emission spectra for (80 mol. % KBr - 20 mol. % KCl)(OH^-):$(F_2^+)_H$ complex host crystals, it is found the wider absorption and emission range for (KBr-KCl) complex host crystal than that of KBr or KCl single crystal. It is suspected that (KBr-KCl):$(F_2^+)_H$ color center, (KBr):$(F_2^+)_H$ color center and (KCl):$(F_2^+)_H$ color center co-exist in (KBr-KCl) complex host crystal.

4 Conclusions

The above experiment results confirm the authors' expectation that $(F_2^+)_H$ color center can be obtained from a complex host crystal. The absorption and emission wavelength range of color center in (KBr-KCl) complex host crystal has a considerable adjustment and extensions compared with that in single KBr or KCl host crystal. As an example, the tunable wavelength range up to 800 nm and peak wavelength range of 400 nm for (80 mol. % KBr - 20 mol. % KCl)(OH^-):$(F_2^+)_H$ complex host crystal, manifold exceeding that in single KBr or KCl host crystal. The considerable shift of absorption wavelength peak is convenient for matching with effective pumping source.

From the analysis of the spectral characteristics of (KBr-KCl)(OH^-):$(F_2^+)_H$ color center laser series and the trend of their evolution, the authors have an initial impression as following: $(F_2^+)_H$ color center in the complex host crystal possesses the property of recombination. It is recombined in a certain form from KBr(OH^-):$(F_2^+)_H$, KCl(OH^-):$(F_2^+)_H$ and (KBr-KCl)(OH^-):$(F_2^+)_H$, the form and extent of its recombination depend upon the proportion of KBr and KCl as well as the control of the conditions affecting the whole processes form crystal growth to the formation of color center.

The results reported here belong obviously to the exploration in a new field. A lot of theoretical and technological problems pertaining to the crystal growth, color center formation and spectral characteristics remain to be further studied. However, it will surely be a valuable new field of color center laser studies.

Acknowledgements The authors thank for the jointly supporting by Natural Science Foundation of China (No. 50082003 and No.69178025)

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