Photothermal Conversion of F-centres in Additively Coloured Potassium Chloride Crystals with Cationic and Anionic Impurities

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Abstract

The compensating influence of cationic (Ca^{++} ions) and anionic (OH^{-} ions) impurities doped into additively coloured potassium chloride crystal on the process of photothermal conversion of F-centres is detected. “Brightening” in the absorption band of the F-centres is revealed that achieves 90%. It is not accompanied by the appearance of centres absorbing in the visible range. Double vacancies and the complexes $Ca^{++}(OH^{-})_2$-cationic vacancy are shown to be responsible for this phenomenon. Basing on those results, a new system for holographic recording is suggested that uses the compensating effect of cationic and anionic impurities .

Key words: volume holograms, KCl crystals, cationic impurities, anionic impurities

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1. Formulation of problem

Photothermal conversion of F-centres in additively coloured potassium chloride crystals is now widely used for different scientific and engineering purposes. The colour centres are nano-sized objects, which seem to be interesting in what concerns both the fundamental and applied fields, e.g. in studying the properties of nano-objects and improving technologies for their control. In particular, these processes have been used for recording “thick” three-dimensional transmission holograms [1] and creating high-precision optoelectronic measuring systems of different types [2]. The processes of photothermal conversion of the F-centres characterize the properties of crystals and depend essentially upon the available impurities [3]. Therefore, targeted doping of these crystals with impurities may enable one to control the considered processes and optimise them for solving each specific task.

As it is known [4], irradiation of pure KCl crystals, containing only F-centres, with a “homogeneous” light from the spectral region of 450-650 nm at temperatures higher than 200ºC results in the appearance of X-band in the absorption spectrum of crystal, which is stipulated by quasi-colloid particles of potassium (or X-centres) formed due to coagulation of the F-centres under the action of both light and temperature. Doping of KCl crystal with the anionic impurities, e.g., OH, CO_3 and SO_4 [5-10], facilitates considerably the colloid formation process. The colloids of metallic potassium of rather large sizes would be generated in these crystals, which can be observed with the help of optical microscopy [8,9]. The divalent cationic impurities Ca, Ba and Sr impose a complex influence, depending on the concentration of impurities entered into KCl crystal. So, their small amounts accelerate forming the potassium colloids [11], though the latter are not generated in crystal if the impurity concentration is large enough [12,13], and the impurity colloids become segregated [14].

Starting from these results, there appears a natural problem: which properties will have the process of conversion of F-centres in KCl crystals that contain both cationic and anionic impurities? Besides of a case of homogeneous light fields, the features of these processes peculiar for stationary spatially periodic light fields (SSPLF) with high enough spatial frequency, which is characteristic for recording of holograms, are also of especial interest. That is why, the purpose of the present work is to analyse a common influence of cationic and anionic impurities on the process of photothermal conversion of the F-centres in additively coloured KCl crystals and check a possibility for using this process in three-dimensional holographic recording. We have selected Ca as a cationic impurity and OH as anionic one.

2. Experimental Results

KCl crystals grown from especially pure raw materials with the aid of Czochralski technique in the open atmosphere were utilized for the experiments. The impurities were introduced into crystals while adding the appropriate compounds to the raw material during the crystal growth. The grown crystals were split into separate plates with the typical sizes of $1\times1\times0.1$ cm^3 and additionally coloured through locating them together with the metallic potassium, annealing within one hour at the temperature ~600ºC and then cooling the samples rapidly down to the room temperature. The concentration of the F-centres was calculated as being equal to 10^{16}-10^{17} cм$^{-3}$, using the *Smakula* formula based on the absorption spectrum characteristics and ignoring the impurity sort (see Fig. 1, curve 1).

In case of KCl:OH crystals, which contain no Ca impurity and are irradiated with He-Ne laser (the wavelength λ=632.8 nm) at the temperatures higher than 160°C, formation of the potassium colloidal colour nano-centres is observed, with the absorption band maximum located at ~720 nm (see Fig. 1, curve 4). In KCl:Ca crystals without a specially inserted OH impurity and at the temperatures higher than 160°C, the thermooptical F-centre conversion caused by He-Ne laser irradiation is accompanied with formation of small colloids of calcium (the relevant sizes being ~15 nm). Then the absorption maximum is centred at λ=540 nm (Fig. 1, curve 2) and the crystal acquires a characteristic brown-red colouring [14,15].

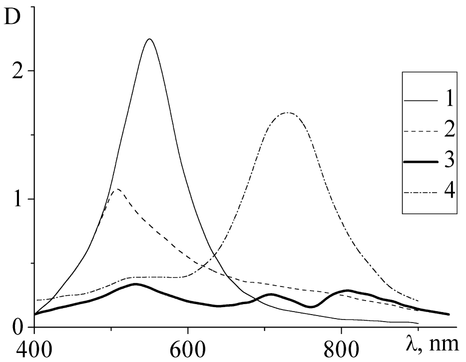

Fig. 1. Absorption spectra detected for the cases of (1) highly pure KCl with specially entered impurities, irrespective of their kind, after quenching from 640°C down to the room temperature in darkness; (2) KCl+0.2 mol.% $CaCl_2$ without specially entered OH impurity after irradiating with He-Ne laser light (λ=632.8 nm) at 200°C; (3) KCl+0.2 mol.% $CaCl_2$+0.2 mol.% KOH after irradiating with He-Ne laser at 200°C; and (4) KCl+0.2 mol.% KOH after irradiating with He-Ne laser at 200°C.

Simultaneous availability of OH and Ca impurities with the concentration ratio 1:1 (or 2:1) has the following result. The thermooptical F-centre conversion owing to the radiation of He-Ne laser at the temperatures higher than 160°C is not accompanied with the appearance of any pronounced absorption bands in the visible and IR spectral regions under test (see Fig. 1, curve 3). Moreover, a “brightening” in the F-absorption band during the irradiation achieves 90%.

Thus, the data obtained above certify undoubtedly that there exists a compensating effect of cationic and anionic impurities on the photothermal conversion of F-centres in additively coloured KCl crystals. It is imposed by the fact that the colloids of neither potassium nor calcium are formed in such the crystals. Therefore, the phenomenon of compensation influence of the cationic and anionic impurities in KCl crystals would be accompanied with the absence of notable absorption in all the visible and near-IR spectral ranges during the process of photothermal F-centre conversion.

Having established this compensation effect caused by simultaneous introduction of Ca and OH impurities, we have further studied the photothermal F-centre conversion in the above crystals under the SSPLF effect.

The spatially periodic light field was shaped, using two He-Ne laser beams inclined at the angle of 40°. The spatial frequency of this interferential SSPLF was about 1000 lines/mm. The SSPLF stabilization and control of the relative diffraction efficiency η ($\eta=I_d/(I_d+I_t)\times100\%$, where I_d and I_t are the intensities of diffracted and reference beams, respectively) were performed with the technique described in brief in [16]. The sample was prepared after annealing at 200°C during 20 minutes. The system was reversible, i.e. the previous record might be completely erased with the aid of annealing.

The kinetics of the lattice formation is shown in Fig. 2 (curve 1). After reaching the maximum diffraction efficiency in ~30 s, the crystal was taken out of furnace and so cooled almost instantly. Then we measured its absorption spectrum (see Fig. 3, curve 2).

It follows from Fig. 3 that the concentration of F-centres decreases by ~40 % after the record and the “colloidal” absorption bands are not produced. Probably, a residual absorption in the F-absorption band is caused by the F-centres that have remained in the nodes of the diffraction lattice.

In order to verify this conjecture, the crystal was placed back into furnace and annealed at the temperature 200°C for 20 minutes. Then the diffraction lattice was repeatedly formed during ~30 seconds. After that recording the SSPLF was displaced along the crystal by the half-period with respect to the lattice formed earlier and the hologram was therefore erased. Fig. 2 (curve 2) illustrates the kinetics of this process, whereas the absorption spectrum of the crystal detected after such the procedure is shown in Fig. 3 (curve 1).

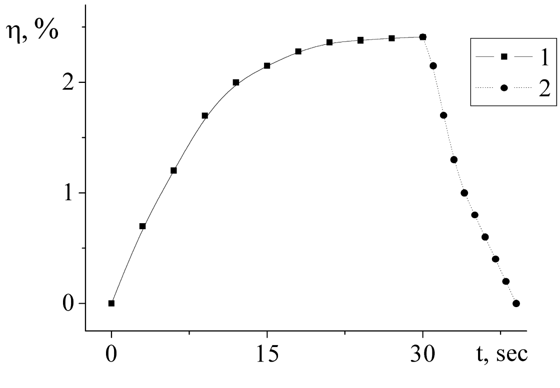

Fig. 2. Kinetics of relative changes in the diffraction efficiency η detected at recording (1) and erasing (2) the holograms (the “half-period” migration time for the interference pattern is equal to 30 s). The record is done with KCl+0.2 mol.% $CaCl_2$+0.2 mol.% KOH at 180°C. The spatial frequency of the interference pattern is 1000 lines/mm and the recording wavelength 632.8 nm.

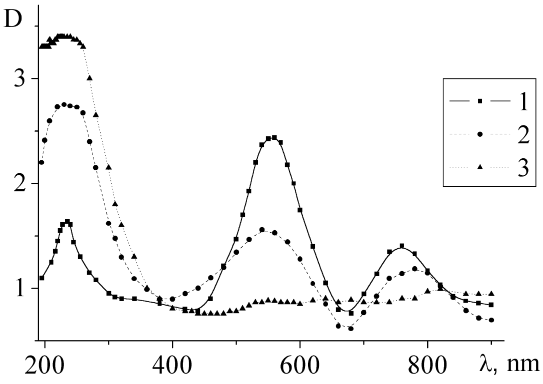

Fig. 3. Absorption spectra of KCl+0.2 mol.% $CaCl_2$+0.2 mol.% KOH crystals detected after annealing (1), 30-second irradiation with spatially periodic light field (2) and 30-second irradiation with the SSPLF shifted by the half-period (3).

As seen from Fig. 3 (curve 3), the F-centres practically disappear. Therefore, after the first record, the remained F-centres are indeed concentrated in the nodes of the registered diffraction grating. All these results testify that the photothermal conversion of the F-centres under consideration is modulated by the interference pattern and may be utilized for a three-dimensional holographic recording. A more detailed analysis of characteristics of such the holographic record requires a separate study.

3. Discussion

The spectral studies of KCl crystals containing Ca and OH impurities in the ratios 1:1 and 1:2 have revealed a presence of absorption maxima in the IR range near 2.8 μm. They originate from the complexes "Ca^{++}-OH^{-}-cationic vacancy" and "Ca^{++}-OH^{-}-OH^{-}-cationic vacancy" [15]. The ions of the impurity Ca^{++} in those complexes are allocated at the cationic nodes of the lattice, while the ions OH^{-} at the anionic ones.

Let us consider in a more detail the photochemical processes occurring in the given system, which produce such the complexes. If MX crystal contains the cationic impurity Ca^{++}, the hydroxyl ions OH^{-} and the vacancies $\boxed{}$ (let the notation $\boxed{-}$ mean the cationic and $\boxed{+}$ the anionic one), the reactions of formation of the complexes referred above may be presented using the following equations:

$$\mathrm{Ca}^{+}_{\mathrm{M}} + \boxed{-} + (\mathrm{OH})^{-}_{\mathrm{X}} \rightarrow [\,\mathrm{Ca}^{+}_{\mathrm{M}}(\mathrm{OH})^{0}_{\mathrm{X}}\boxed{-}\,]^{0} \qquad (1)$$

$$\mathrm{Ca}^{+}_{\mathrm{M}} + \boxed{-} + 2\,(\mathrm{OH})^{-}_{\mathrm{X}} \rightarrow [\,\mathrm{Ca}^{+}_{\mathrm{M}}(\mathrm{OH})^{0}_{\mathrm{X}}(\mathrm{OH})^{0}_{\mathrm{X}}\boxed{-}\,]^{0} \qquad (2)$$

Here the subscripts denote the places in the regular nodes of M (metal) or X (halogen) lattices and the superscripts define the signs of the ionic charges with respect to the neutral MX lattice. It is known [17] that the mentioned complexes are thermally unstable and their destruction under the effect of temperature is accompanied with splitting the bonds in the hydroxyl ions. To our opinion, this can be represented with the following reactions:

$$[\mathrm{Ca}^{+}_{\mathrm{M}}(\mathrm{OH})^{0}_{\mathrm{X}}\boxed{-}\,]^{0} \leftrightarrow [\mathrm{Ca}^{+}_{\mathrm{M}}\mathrm{O}^{-}_{\mathrm{X}}\,]^{0} + \mathrm{H}^{0}_{\mathrm{M}} \qquad (3)$$

$$[\mathrm{Ca}^{+}_{\mathrm{M}}(\mathrm{OH})^{0}_{\mathrm{X}}(\mathrm{OH})^{0}_{\mathrm{X}}\boxed{-}\,]^{0} \leftrightarrow \leftrightarrow [\mathrm{Ca}^{+}_{\mathrm{M}}\mathrm{O}^{-}_{\mathrm{X}}\,]^{0} + \mathrm{H}^{0}_{\mathrm{M}} + \mathrm{OH}^{0}_{\mathrm{X}} \qquad (4)$$

$$\boxed{-} + [\mathrm{Ca}^{+}_{\mathrm{M}}(\mathrm{OH})^{0}_{\mathrm{X}}(\mathrm{OH})^{0}_{\mathrm{X}}\boxed{-}\,]^{0} \leftrightarrow \leftrightarrow [\mathrm{Ca}^{+}_{\mathrm{M}}\mathrm{O}^{-}_{\mathrm{X}}]^{0} + 2\mathrm{H}^{0}_{\mathrm{M}} + \mathrm{O}^{-}_{\mathrm{X}} \qquad (5)$$

$$[\mathrm{Ca}^{+}_{\mathrm{M}}(\mathrm{OH})^{0}_{\mathrm{X}}(\mathrm{OH})^{0}_{\mathrm{X}}\boxed{-}\,]^{0} + \boxed{-\ +} \leftrightarrow \leftrightarrow [\mathrm{Ca}^{+}_{\mathrm{M}}\mathrm{O}^{-}_{\mathrm{X}}]^{0} + 2\mathrm{H}^{0}_{\mathrm{M}} + \mathrm{O}^{-}_{\mathrm{X}} + \boxed{+} \qquad (6)$$

The binary reactions (5) and (6) describe a destruction process, which is stimulated by interaction of the complex derived via the reaction (2) with the cationic vacancy (see Eq. (5)) and the double vacancy $\boxed{-\ +}$ (see Eq. (6)). According to our reckoning, the probability of reaction (6) is higher than that of (5), since the double vacancies in KCl crystals have much higher mobility, when compare to the cationic vacancies [18].

In case of KCl containing the F-centres, the presence of the complexes CaOH and $\mathrm{Ca(OH)_2}$, whose stability depends on the content of double vacancies in the crystal, results in thermal decay of F-centres, acquiring some features associated with a generation of double vacancies and mobile electrons e^{-} [19]. These processes may be described by the following reactions:

$$\mathrm{F} + h\nu + kT + \boxed{-} \rightarrow \boxed{-} + \boxed{+} + e^{-} \rightarrow \boxed{-\ +} + e^{-} \quad (7)$$

$$\mathrm{H}^{0}_{\mathrm{M}} + \mathrm{F} + h\nu + kT \rightarrow \rightarrow \mathrm{H}^{0}_{\mathrm{M}} + kT + \boxed{+} + e^{-} \rightarrow \boxed{-} + \mathrm{H}^{+}_{\mathrm{X}} \qquad (8)$$

$$\mathrm{H}^{+}_{\mathrm{X}} + e^{-} \rightarrow \mathrm{H}^{0}_{\mathrm{X}} \qquad (8^{*})$$

Double vacancies promoting destruction of the complexes $\mathrm{Ca(OH)_2}$ according to Eqs. (6) and (8), give rise to formation of the effective traps $\mathrm{H}^{+}_{\mathrm{X}}$ for electrons. This is because a "defect" $\mathrm{H}^{0}_{\mathrm{X}}$, having locked electron released after ionisation of the F-centre, passes from the cationic lattice node to the anionic one. Then, locking one more electron, according to Eq. (8*), will turn $\mathrm{H}^{0}_{\mathrm{X}}$-centre into what is usually named as a U-centre [5].

In view of this, the process of photothermal conversion of the F-centres observed in KCl crystal, containing both the cationic and anionic impurities, can proceed following the schemes

$$[\mathrm{Ca}_\mathrm{M}^{+}(\mathrm{OH})_\mathrm{X}^{0}\ \boxed{-}\ ]^{0}+\boxed{-\ \ +}\leftrightarrow$$
$$\leftrightarrow[\mathrm{Ca}_\mathrm{M}^{+}\mathrm{O}_\mathrm{X}^{-}]^{0}+2\mathrm{H}_\mathrm{X}^{0}+2\ \boxed{-} \qquad (9)$$

$$[\mathrm{Ca}_\mathrm{M}^{+}(\mathrm{OH})_\mathrm{X}^{0}(\mathrm{OH})_\mathrm{X}^{0}\ \boxed{-}\ ]^{0}+3\ \boxed{-\ \ +}+4e^{-}\leftrightarrow$$
$$\leftrightarrow[\mathrm{Ca}_\mathrm{M}^{+}\mathrm{O}_\mathrm{X}^{-}]^{0}+2\mathrm{H}_\mathrm{X}^{0}+\mathrm{O}_\mathrm{X}^{-}+3\ \boxed{-} \qquad (10)$$

Again, here the charges are indicated with respect to the neutral lattice. As follows from these reactions, the process of photothermal conversion of the F-centres is accompanied with formation of $\mathrm{H}_\mathrm{X}^{0}$ (or U) centres, as well as O^{-}-centres. Their absorption should fall in the short-wavelength UV region (200-240 nm) [5]. The latter fact is confirmed by the spectral data of Fig. 3.

4. Conclusion

Thus, we have shown in the present work that the thermal conversion of F-centres in additively coloured KCl crystals with cationic and anionic impurities reaches 90% at the temperatures higher than 160°C. The process is followed by formation of photolysis products, which do not absorb light in the visible and short-range IR ranges, as it takes place in the pure KCl or the crystals containing Ca or OH impurities. The conversion of F-centres in such the crystals lies in follows. The electrons and double vacancies generated as a result of conversion of thermal F-centres interact with $\mathrm{Ca(OH)_2}$ complexes. These processes activate creation of U- and O^{-}-centres that absorb in the UV spectral range.

Besides, we have revealed that the photothermal conversion of F-centres under study may be used for registration of three-dimensional transmission holograms.

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