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Optical spectroscopy and thermoluminescence of electrolytically colored KCl:Tl$^+$ crystals

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The paper presents the spectroscopic properties of electrolytic colored KCl:Tl and KCl:Tl+Ca crystals and the assignments of the new defects which are formed during electron injection process. The new formed defects Tl^o and Tl^o+Ca^{2+} with the metal in the anionic sites, presents very high photoluminescence properties in the near infrared region. Together with those centers, the F-centers, their aggregates and the holes centers are formed during electrolytic coloring process. Their properties were studied by optical absorption (OA), photoluminescence (PL) and thermoluminescence (TL) measurements and compared with those obtained by ionizing irradiation in uncolored KCl:Tl crystals. The results suggest a more efficient Tl$^+$→Tl^o process in the case of Ca^{2+} codoped samples due to the prolonged time of electrons injection, low temperature and high electric field.

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1. Introduction

The light emission observed in alkali halide (AH) crystals doped with heavy metals positive ions subjected to the electrolytic coloring or X-ray irradiation, represents a promising approach for near infrared media lasers [1-8].

In AH single crystals doped with Tl$^+$ ions (KCl:Tl$^+$, NaI:Tl$^+$, KBr:Tl$^+$) new defects that contains Tl ions in different electron configurations are created in a controlled manner by the electrolytic coloring process. These new defects present very intense near infrared emissive properties and they have been proposed to be used as new active media for lasers with crystalline-solid active medium [2].

Similar behaviors are observed in the case of the Ag$^-$, Tl^o, Ga^o and In^o in AH crystals, but this time, they are obtained by X-ray irradiation at low temperatures, up to 80 K [9-13]. The A$^+$ monovalent ions are situated in the cationic position of the crystals and, after X-ray irradiation, can trap electrons as well as holes to form A^o and A^{++} centers which gives characteristic absorption and emission bands, together with those of F and F-aggregates centers. Their photoluminescence and their thermoluminescence are connected with $\{A^o+V_k\}$ pairs.

The electrolytic coloring process consists in the injection of electrons at high temperature (500° C) and low electric field [1, 2] into doped AH crystals, the heavy metal ions of dopant acting like an electron trap and less as a hole trap like in the X-ray irradiated samples, because the present method is in the excess of electrons. When bivalent ions, optically inactive, like in the case of Ca^{2+} ions were added during crystal growth process, the thermal and electric conductivity of the Tl$^+$-doped crystal is increased and the conditions of electrolytic coloration are changed. The electric field must be increased around one order of magnitude and the temperature of coloration is reduced down to 200° C. The injection process time is increased from tens of seconds to 15-20 minutes, allowing a more efficient process of electron capture, and also an increasing of A^o centers concentration.

The new defects show a very high time stability of the absorption and emission properties which is explained by the changing of the heavy metal dopant valence during electrolytic coloring due to the electronic trapping (i.e. electron excess) [2]. The heavy metal dopant valence (Tl) is changing successively from the cationic state with the charge +1 (Tl$^+$) to an intermediary atom state (Tl^0) and finally to (Tl^o +F centers) aggregates.

The aim of this paper is to present the optical spectroscopic properties of electrolytic colored KCl:Tl and KCl:Tl+Ca for a better understanding of the new formed defects, especially in the case of Ca^{2+} ions codoped samples, because the OA and PL measurements are combined with the TL method.

2. Experimental procedure

KCl;Tl$^+$ and KCl:Tl$^+$+Ca^{2+} crystals were grown by the Czochralski method using a standard heating furnace and platinum crucible under nitrogen atmosphere. The raw material consists of a mixture of KCl, TlCl and CaCl$_2$ salts with ratio of 60 g/0.5 g/1 g in the highly doped and codoped crystals or only 60 g/0.5 g in the simple doped samples.

The concentration of Tl$^+$ ions was kept in the range of $5*10^{16}$-10^{17} ions/cm^3 to avoid formation of metallic colloids of thallium during the electrolytic coloring process. The concentration of Ca $^{2+}$ ions is higher compared with Tl$^+$ ions (about four Ca^{2+} to one Tl$^+$)

because the segregation coefficient is almost 1 in KCl crystals. The grown crystal with a size of 50 mm length and 15 mm diameter was cut to in platelets of 10x5x1 mm for the spectroscopic measurements. Details about the electrolytic coloring techniques can be found in [2].

Absorption and photoluminescence spectra in the uv-vis region were measured with standard commercial spectrophotometers. For infrared photoluminescence measurement, a photodiode with sensitivity at 800-2500 nm has been used. Absorption and photoluminescence spectra were investigated at various temperatures between 10 and 300 K in the spectral region 200-2500 nm. An Ar^+ ionized laser was used for determining the dependence of the photoluminescence in the infrared region which was measured using an optical analyzer between 800-1750 nm.

Thermoluminescence (TL) measurements were carried out with a home-made setup at the heating rate of b = 5°C/sec using a photomultiplier as light detector. A filter was installed in front of the photomultiplier in order to eliminate the thermal radiation of the heater.

3. Results and discussions

The absorption spectrum of KCl:Tl shows the main characteristics of ns^2 ions in AH crystals [5] with the A-band at 5.01 eV as a spin-orbit allowed transition, the vibronic B-band at 5.96 eV which is temperature dependent and the spin allowed C-band at 6.2 eV, similar with those described by Jabobs in [14]. When Ca^{2+} ions are added, a small band at 4.1 eV appears as a result of Tl^+ ions perturbation figure 1. The photoluminescence of KCl:Tl+Ca crystals shows both transitions A_T at 4.13 eV from a tetragonal symmetry of Tl^+ ions and also another transition at 3.5-3.6 eV probably from a trigonal symmetry which results from the perturbations due to the Ca^{2+} ions.

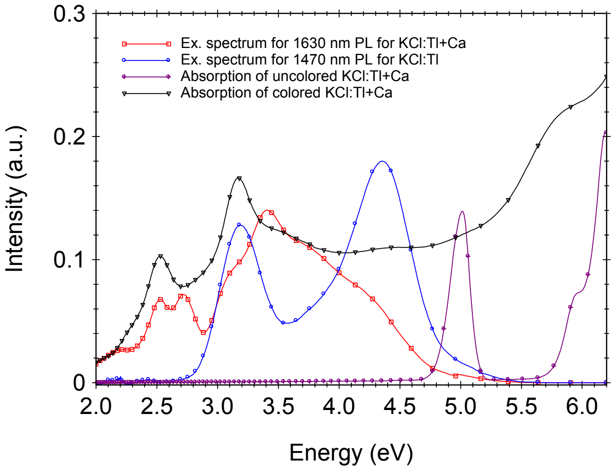

Fig. 1 Absorption and excitation spectra of uncolored and electrolytic colored KCl:Tl, KCl:Tl+Ca crystals

Electrolytic coloring process change the spectroscopic behaviors of the KCl:Tl and KCl:Tl+Ca samples. If the coloration process is long enough time to produce an injection of electrons in the whole sample, the spectral characteristics of Tl^+ ions disappear and new OA and PL bands appear both in the visible and near infrared regions. The process of electron injection strongly depend by the conductivity of the samples, because the Ca^{2+} co-doped samples allow a deep penetration of the electrons, together with formation of hole centers like V_k type. The absorption bands are stronger in the co-doped crystals than in the KCl:Tl^+ samples [15], which means that the concentration of the new defects is higher in those samples. At least two main absorption bands appear at 2.5 eV and 3.2 eV more intense in the case of electrolytic colored KCl:Tl+Ca samples.

The PL excited on those bands exhibits a large photoluminescence in the near infrared region, especially between 1.2 eV to 0.5 eV (figure 2). The photoluminescence bands from 1.02 eV and 1.14 eV (the PL of M-centers [16]) are connected with the formation of F-center aggregates, which gives also very weak absorption bands in the visible range between 2.3 eV for F centers and 1.5 eV for M centers (figure 2). The other peaks at the 0.985 eV, 0.94 eV to 0.56 eV are due to the new formed defects during electrolytic coloring process. At least two peaks appear at 0.84 eV (1470 nm) and 0.56 eV in KCl: Tl samples and another two peaks at 0.76 eV (1630 nm) and 0.63 eV for KCl:Tl+Ca samples. The excitation spectra give the explanation of the observed peaks from the absorption spectrum. Similar, the absorption spectrum in the near infrared region measured by Delbeque is shown [19].

The absorption and photoluminescence spectra can be connected with the optical characteristics with the electronic transitions of free Tl atoms. The main transition is $6\ {}^2P_{1/2} \rightarrow 6\ {}^2P_{3/2}$ as intra-center luminescence in the infrared region and $6\ {}^2P_{1/2} \rightarrow 7\ {}^2S_{1/2}$, $6\ {}^2P_{1/2} \rightarrow 7\ {}^2D_{3/2}$, $6\ {}^2P_{1/2} \rightarrow 7\ {}^2S_{1/2}$, have the excited stats in the conduction band of KCl crystal. The first one appears as a result of Jahn-Teller effects and it is forbidden in the free Tl^o but in the crystalline field appears as a double band in the infrared region. Similar very weak bands were obtained in the absorption spectra by Delbeque [19].

The peaks observed in the excitation spectrum for 0.84 eV (1470 nm) gives two bands centered at 3.17 eV (390 nm) and 4.35 eV (287 nm) similar with those from the absorption spectrum (figure 1). The excitation for 0.77 eV (1630 nm) gives another two bands at 2.52 eV (490 nm), probably a double band and 3.17 eV (390 nm) as a shoulder. As we expected in the second excitation spectrum for KCl:Tl+Ca increases the band from 3.4 eV (364 nm) and the 2.3 eV which is due to the F-center absorption appears in the both samples. A broad band peaked at 3.55-3.6 eV can be observed also in the excitation spectrum for the 0.76 eV (1630 nm) photoluminescence in the KCl:Tl+Ca samples.

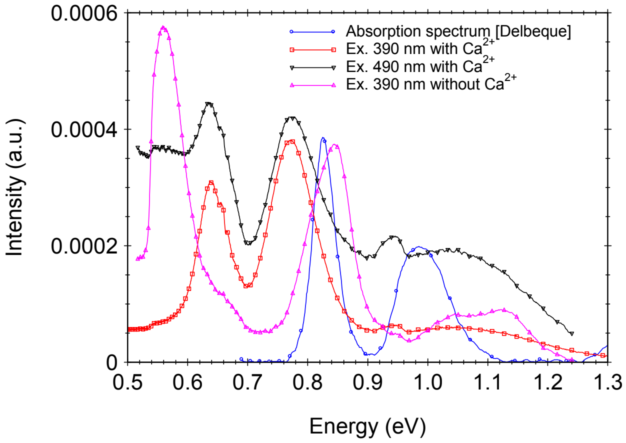

Fig. 2 Photoluminescence spectra of electrolytic colored KCl:Tl, KCl:Tl+Ca crystals at RT.

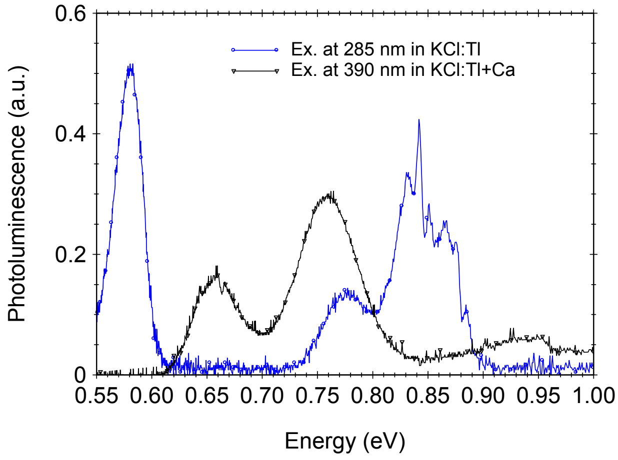

Fig.3 Photoluminescence spectra of electrolytic colored KCl:Tl, KCl:Tl+Ca crystals recorded at low temperature (13K)

A very interesting result is the PL spectra at low temperature (13 K) excited at 4.35 eV (285 nm) and 3.17 eV (390 nm) which shows beside the F-center aggregates bands between 1 eV and 1.2 eV and some vibronic lines at 13 K, the PL bands from 0.84 eV, 0.76 eV and 0.56 eV (figure 3). In fact the first band of the new formed centers is shifted at 0.775 eV in the KCl:Tl sample compared with 0.76 eV in KCl:Tl+Ca at low temperature.

To prove the origin of the photoluminescence from 0.76-0.775 eV, we excited the KCl:Tl and KCl:Tl+Ca with 488-512 nm Ar ionized laser and monitored those two PL bands with an optical analyzer which gives the power of emission versus power of the laser between 800 to 1750 nm. The measurements shows the same dependence for the two emissions from 0.76 eV in KCl:Tl+Ca and 0.775 eV for the KCl:Tl sample (figure 4).

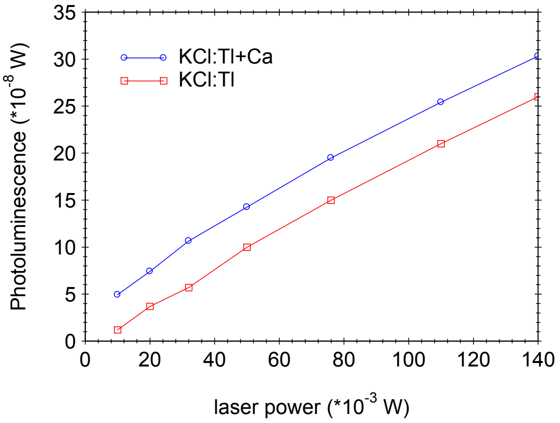

Fig. 4 Intensities of photoluminescence spectra excited with Ar^{+} laser versus excitation power

We excited those PL peaks with an energy between 2.54 eV and 2.42 eV, close to the K-band of F centers situated at 2.55 eV at room temperature (2.71 eV at 90 K, [17]).

The TL curves recorded on both KCl:Tl and KCl:Tl+Ca samples are shown in the figure 5.

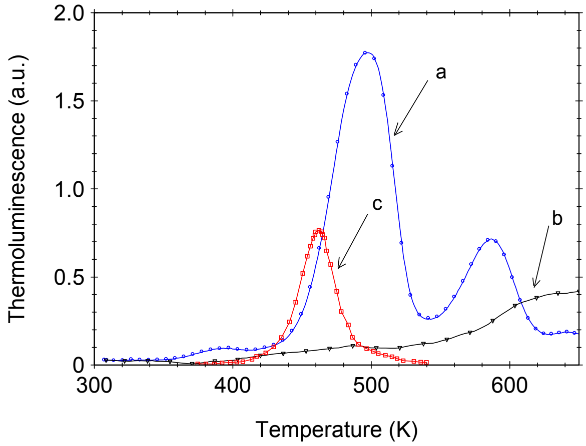

Fig. 5. The spectra of termoluminescence (TL) for KCl:Tl and KCl:Tl+Ca samples: a) KCl:Tl+Ca electrolytic colored (5kV, 250^{o}C); b) KCl:Tl electrolytic colored (500 V, 500^{o}C); c) KCl:F X-ray irradiated.

For comparison, the TL curve recorded on X-ray irradiated KCl with F centers is shown [18]. The sample of KCl:Tl present a very weak TL signal which means a low concentration of $\{A^{o}+V_{k}\}$ pairs. In contrast, the TL signal was very high in the case of KCl:Tl+Ca^{2+} ions. This fact suggests a large concentration of $\{A^{o}+V_{k}\}$ pairs which present different mechanisms of recombination. In the same graph we computed the spectrum obtained by Austin [18], in order to substract the F-center recombination band produced in X-ray irradiated KCl crystals.

The presence of Tl^o-defects produced by ionizing radiation, which have also laser activity, was measured by ESR techniques by Heynderickx et al [20]. On the basis of their production, thermal and optical stability conclude that these centers consists essentially of a Tl^o atoms in the anionic sites, which involves a site switching from the cationic to anionic position when the Tl^+ ions change their valency. Similar properties were determined by Polosan et al [15], measuring the magnetic circular dichroism absorption on the electrolytic colored KCl:Tl and KCl:Tl+Ca crystals.

4. Conclusions

The obtained results allow us to study formation of Tl^o-centers in the KCl:Tl and KCl:Tl+Ca, after electrolytic coloring processes, together with the F-centers and their aggregates. The process of coloration is more efficient in the case of KCl:Tl+Ca samples due to their prolonged injection of electrons, together with some hole centers, probably V_k centers which can efficiently recombine with Tl^o and F centers during the thermal procedure of thermoluminescence.

The photoluminescence of Tl^o more or less perturbed by other defects like Ca^{2+} ions or vacancy centers is very intense in the near infrared region between 1.2 to 0.5 eV. These PL spectra may be also excited in the F-band from the high excited levels K, L_1 and especially L_2 which appears at 4.35 eV (285 nm). This may be connected with the trapping of electron from the conduction band or by means of a tunneling process of Tl^+ centers. The excited (Tl^o*) state of Tl^o centers arises and the transition into the ground state is accompanied by photoemission. This photoemission is similar with that of the direct Tl^o or Tl^o+Ca^{2+} photoluminescence, having the same spectral dependence as the intra-center photoluminescence of Tl^o centers. The phenomenon is analogous with the photoluminescence of F centers which arises under stimulation in the K and L bands.

Acknowledgements

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