

OPTICAL PROPERTIES OF T-CENTERS UNDER GAMMA IRRADIATION

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Electrolytic coloring of KCl:Pb crystals, leads to formation of negative metal ions with an intense emission in infrared region. These new color centers were named T centers, most probably configuration could be Pb_2^{2-} , due to the lack of EPR or DCM signals. In order to destroy these structures, the crystals were irradiated with γ -rays at high doses. The results were the detachment of electrons from T centers and appearing of Pb^{2+} -ions. It cannot be excluded the possibility of existence of Pb^+ and Pb^0 centers in the samples, because these centers do not exhibit any optical properties on this spectral region.

Key words: Electrolytic coloring, color centers, γ -irradiation.

Introduction

Alkali halide crystals containing impurity ions with the s^2 ground state electronic configuration (e.g. Ga^+ , Tl^+ , In^+ , Pb^{2+} , Sn^{2+}) exhibit four absorption bands due to the s^2 ions which are called A, B, C and D in order of increasing energy [1-8]. Excitation (especially in A band) give rise to two emission bands by the excitation in the A band, which are named A_X and A_T emission bands for the low and high energy bands, respectively. The A_X and A_T emission bands are caused by the electronic transition from the Jahn-Teller minima with trigonal and tetragonal symmetries on the adiabatic potential energy surface (APES) of the 3P_1 excited state of the s^2 ions, respectively [1,2,4,5].

In the case of Pb^{2+} centre, only the A_T emission band has been observed (see e.g. [3]). Studies of emission spectra of KCl:Pb crystals, co-doped with a small quantity of Li^+ ions lead to another emission band which has been believed to be attributable to A_X emission band, besides the A_T emission band [9-12]. The reason why the A_X emission does not appear in Pb^{2+} centre has not been clarified. To understand the reason, it is suggested that the study of the Pb^{2+} centre perturbed by a nearby impurity is helpful.

Electrolytic coloring of KCl crystals doped with Pb^{2+} -ions (about 10^{17} ions/cm³), produce so called T_a centers in samples grown by high purity raw salt [13]. Optical properties of these centers depend upon the co-doping with alkali (Na^+ , Li^+ , Rb^+ - so called T_b and T_c centers [14]) and Ca^{2+} ions (in the case of so called T_d and T_x centers) [15]. The most probably model of these T-centers is a Pb_2^{2-} molecule situated in two adjacent negative vacancies, more or less perturbed. The reason of adding small quantities of bivalent ions was to reduce the temperatures used during electrolytic process and to decrease the number of injected electrons into the samples.

When the quantity of Ca^{2+} -ions added into the crucible during growing of the crystals, extend by two times the quantity of lead ions, present special features on the optical properties of the negative ions, obtained during the electrolytic process.

Considering the analogy between Ag^- ions obtained by electrolytic coloring in KCl crystals, the case of so-called T centers would be Pb^- ions with outer electron configuration $6p^3$, isoelectronic with Bi^0 atoms which have the fundamental state $^4\text{S}_{3/2}$. Due to this fact, the crystals containing T centers would be present DCM or EPR signals. Obviously, considering overlapping of the wave functions, there would be explain the lack of EPR signal, but in the case with T_a , T_b and T_c centers, the DCM signal are missing even at 1.4 K. Following the above considerations, the T-centers obtained at high temperature and low electric field, would be probably Pb_2^{2-} which explain the lack of DCM and EPR signals.

The aim of this paper is attempting to destroy these centers by gamma irradiation and to obtain isolated Pb^- centers.

Experimental procedures and results

Some Pb^{2+} and co-doped of KCl crystals with Ca^{2+} were grown by Kyropoulos method in nitrogen atmosphere, from dry Merk p.a. salts. The impurity was enclosed as CaCl_2 p.a. grade salt. All samples used in this work were thermally treated at 600°C for 30 min. in order to reduce formation of clusters from the growing process.

Electrolytic colouring where performed in air into a set-up device describe in [13] by two methods:

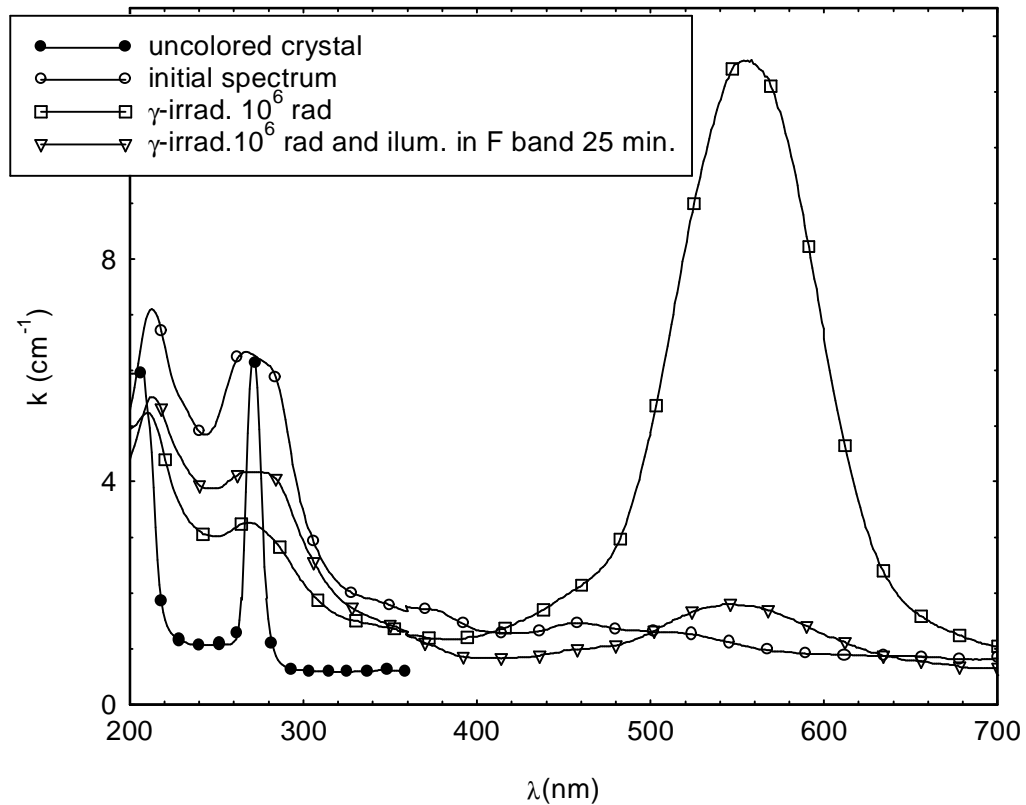
- for the samples containing Ca^{2+} ions, the process was made in high electric field (around 5 kV/cm) and low temperature (between 180 to 300°C).
- for the samples without Ca^{2+} ions, the process was made in low electric field (500V/cm) and high temperature (around 500°C).

Coloured crystals where irradiated with γ -rays form a ^{60}Co source at a dose about 10^6 rad.

Optical measurements were performed into Carry 17 D spectrophotometer for the absorption spectra and Perkin-Elmer spectrofluorimeter for emission spectra.

The absorption and emission spectra were recorded in four steps: before electrolytic colouring, after electrolytic colouring and removing the F centres by changing the polarity of electric field during electron injection, after γ -rays irradiation and after illumination in F band in order to remove the F-centres form the samples. It is well known that a large among of F-centres is formed during γ irradiation, even in pure alkali halide crystals.

Optical absorption of so-called T_a centres is shown in the figure 1.

KCl:Pb, electrolytic coloured and γ -irradiatedFig.1 - Absorption spectra of T_a centres in KCl crystals

From the figure 1 is observed the disappeared of the A band characteristic for Pb^{2+} , after electrolytic colouring and subsequence appearing a new bands in visible and u.v range spectrum. After γ irradiation is observed a diminishing of intensities of the absorption bands and a very intense F-band appear. Removing the F-centres by illumination into F-band, lead to a small increasing of T_a absorption bands.

Emission spectra of T_a centres reveal disappearing of the bands characteristics for Pb^{2+} , after electrolytic colouring process (figure 2). After γ irradiation and illumination in F-band, it is observed re-appearing of the emission bands of Pb^{2+} and the excitation spectra show the A-band of ns^2 ions. A small influence of some impurities, like Li^+ or Na^+ , presented in the KCl salt, produce the second emission band of Pb^{2+} , so-called A_X -band at 345 nm and a split of A-band at 286 nm, revealed in the excitation spectrum.

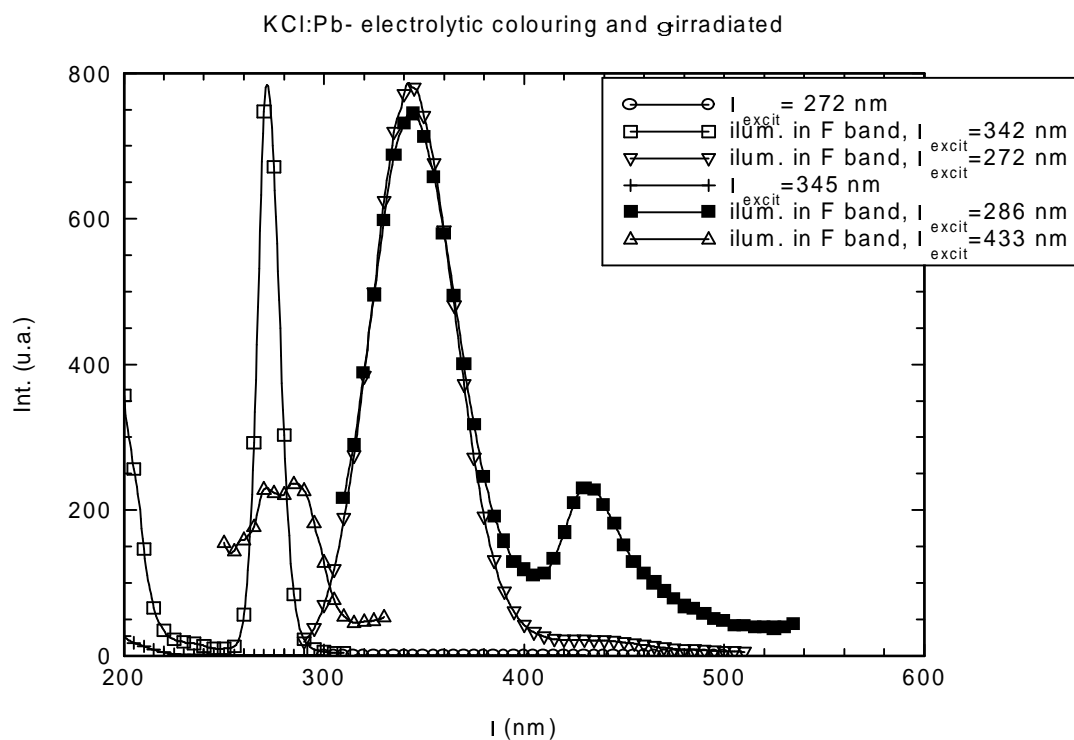


Fig. 2 - Excitation and emission spectra of T_a centres.

The same features were obtained in the case of T_d samples. The absorption spectra mark a decreasing of the absorption bands, characteristics for T_d centres (figure 3).

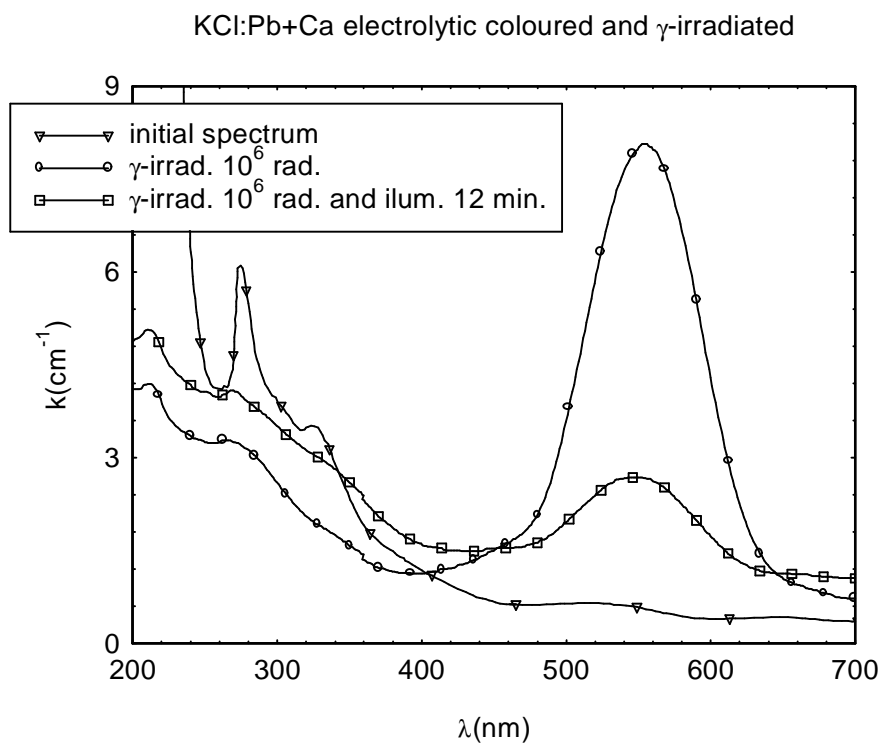


Fig. 3 - Absorption spectra of T_d centres.

Concerning the emission spectra, the presence of a large quantity of Ca^{2+} -ions as a co-doped impurity, lead to an increasing of the intensities of the emission bands which are analogue with those obtained in the crystals co-doped with Li^+ ions []. Both A_2 -band (which are specific for ns^2 ions with a weak coupling with crystal field) and the A_X -band obtained as a result of dynamic Jahn-Teller effect, increase with the concentration of Ca^{2+} -ions (figure 4).

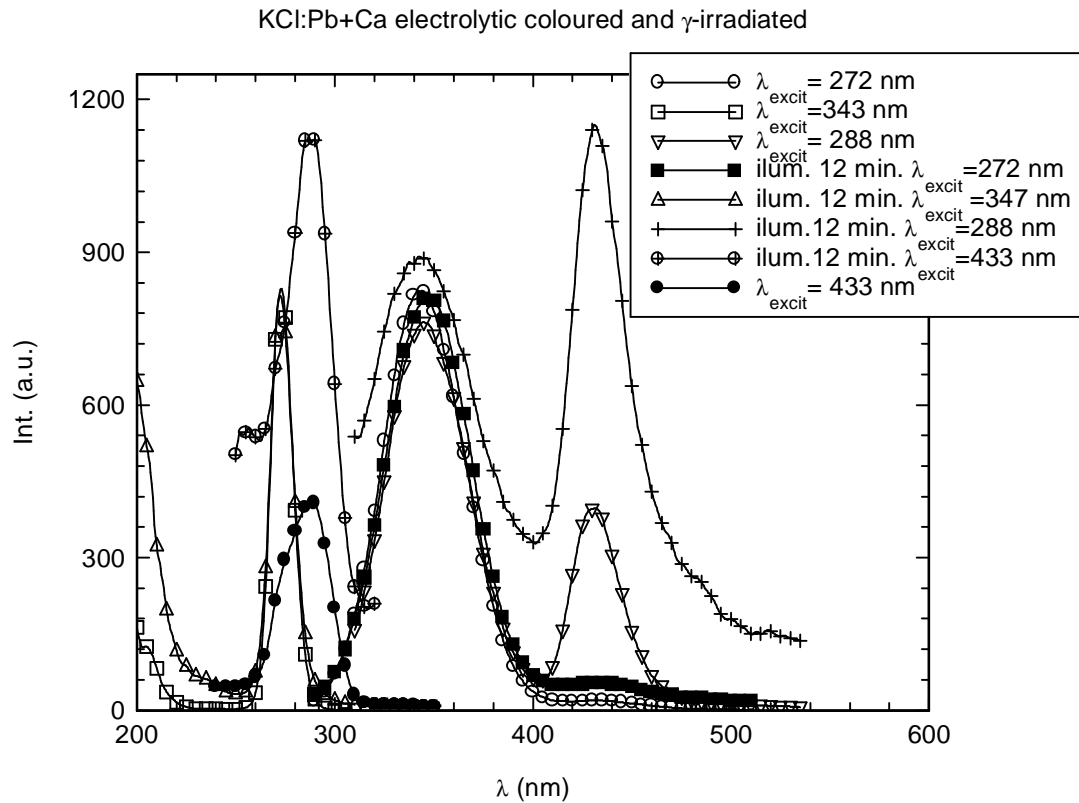


Fig. 4 - Excitation and emission spectra of T_d centres.

Conclusions

At room temperature, the irradiation process of crystal samples containing T_a , T_b , T_c , T_d and T_x centers, change the optical properties of them, as follow:

- the intensities of absorption bands in the u.v. range of T_a , T_b , T_c , T_d centers are diminished by gamma irradiation
- the emission spectra of T_b , T_c , T_d and T_x exhibit clearly bands similar with A_T and A_X emissions of Pb^{2+} -ions. The intensity of so called A_X -band, in the case of T_d centers, is higher than in other cases due to the concentration of Ca^{2+} -ions which extend by two orders of magnitude the number of Pb^{2+} -ions.
- the illumination process are made in order to remove the F-centers, which appear with very high intensity after gamma irradiation, leads of increasing of Pb^{2+} -ions emission.

The explanations of these features are made based on the fact that the production of Pb^{2+} -ions by more easily detachment of electrons from Pb^- and Pb^0 centers comparing with Cl^- ions. It cannot be excluded the possibility of existence of Pb^+ and Pb^0 centers in the samples, because these centers do not exhibit any optical properties on this spectral region.

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