

## NEAR – INFRARED EMISSION SPECTRA OF NEGATIVE METAL IONS AGGREGATES

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In this review paper we attempt to summarize the achievements of the near infrared emission studies of negative metal ions ( $\text{Me}^-$ ) obtained by nonstandard electrolytical colouring. We present the emission characteristics of  $\text{Pb}^-$  ions aggregates in KCl crystals at 300 and 4.2 K by excitation in the UV and visible range of different laser lines. These centres perturbed by  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Rb}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  cations,  $\text{Tl}^-$  and  $\text{Tl}^- + \text{Ca}^{2+}$  ions aggregates and the negative aggregates of  $\text{In}^-$  and  $\text{Ga}^-$  in KCl crystals are, also, discussed.

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### 1. Introduction

Topa in 1967 [1] and, independently, Kleeman in 1968 [2] proposed in electrolytically coloured alkali halide crystals (AHCs), the model of the  $\text{Ag}^-$  ion in anionic position. This model was later called the negative metal ion ( $\text{Me}^-$ ). Meantime, the family of these exotic ions has increased, including:  $\text{Cu}^-$  in 1968 [2,3];  $\text{Pb}^-$  in 1969 [4];  $\text{Au}^-$  in 1970 [5];  $\text{Sn}^-$  and  $\text{Ge}^-$  in 1973 [6];  $\text{Tl}^-$  in 1977 [7];  $\text{Tl}^- + \text{Ca}^{2+}$  in 1978 [8];  $\text{Pb}^- + \text{Ca}^{2+}$  in 1992 [9];  $\text{Pb}^- + \text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$  in 1995 [10];  $\text{In}^-$  in 1996 [11] and  $\text{Ga}^-$  in 2001 [12].

Topa in his thesis [1] stated that all cations of chemical elements, which have the electronegativity, in Pauling scale, more than 1.5 can change their valence state to a negative one. Our work, extending over more than 35 years, proved that the most convenient method to convert absolutely all heavy metal cations embedded in AHCs in  $\text{Me}^-$  ions in anionic sites, is electrolytical colouring.

The other two important methods for changing the valence of the heavy metal cations are: i) additive colouring [13], and ii) irradiation with ionizing radiations [14]. The first method is very suitable for the formation of the colour centres in pure AHCs and the second method converts only partially the heavy metal cations in both electronic and hole defects [15].

We used the electrolytical colouring in two versions:

i). standard colouring ( $\sim 500^\circ\text{C}$ , 300-400 V/cm, 3-10 mA and 5 minutes). In this situation besides  $\text{Me}^-$  ions also F-centres ( $10^{18}$  centres/cm<sup>3</sup>) are present which are removed completely from crystals by changing the polarity of the electrodes [4, 16, 17]

ii). nonstandard colouring (250-300 °C,  $\sim 10^4$  V/cm, 0.5-1 mA, 20-30 minutes, always codoping with  $10^{17}$   $\text{Ca}^{2+}$ -ions/cm<sup>3</sup>), where the colouring takes place apparently without F-centres [8, 18, 19]. The Ca atoms having electronegativity 1.0, their cations do not change their valence state during nonstandard colouring [20] but, due to compensation cations vacancies, the colouring temperature is lowered down to 250-300 °C.

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Our team has used successfully these two versions, for all the  $\text{Me}^-$  - ions above mentioned, taking care of appropriate concentrations of heavy metal impurities cations. It is well-known that, if this concentration overpasses a limit (which depends on the impurity nature), the majority of impurity cations are transformed directly in nanoclusters of the metal atoms impurities, ( $\Sigma \text{Me}^0$ ), and only a little amount of  $\text{Me}^-$  - ions are present in the sample [17].

The optical absorption (OA), optical emission (OE), magnetic circular dichroism (MCD), electron paramagnetic resonance (EPR) and the thermal treatment in a flux of  $\text{H}_2$  have been used by us as experimental methods for studying these exotic ions. The last one, very sensible and precise method, improved by our team [21], was used as an indubitable test concerning the existence in electrolytically coloured AHCs, doped with heavy metal cations, of  $\text{Me}^-$  - ions. Unfortunately, the method cannot give any indication about the structural model of these new species.

In this review paper we attempt to summarize the investigations by NIR emission of  $\text{Me}^-$  - ions, because NIR emission spectra provide more information about the structures of these metal negative species than the optical absorption spectra.

We analyzed and discussd the emission characteristics of the following groups of  $\text{Me}^-$  - ions, or  $\text{Me}^-$  - ions aggregates by excitation in the UV and visible range with different laser radiations:

a) The  $\text{Pb}^-$  ions aggregates ( $T_a$  - centres) obtained by standard colouring of K-halides crystals doped only with  $\text{Pb}^{2+}$ [19, 22], and  $\text{Pb}^-$  - ions aggregates perturbed by  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{Rb}^+$  - ions ( $T_b$ , and  $T_c$  - centres).

b) The  $\text{Pb}^-$  - ions and  $\text{Pb}^-$  - ions aggregates in  $\text{KCl:Pb}^{2+}$  crystals, codoped with  $\sim 10^{17}$   $\text{Ca}^{2+}$  ions/ $\text{cm}^3$  ( $T_d$  and  $T_e$  centres) [22, 23].

c) The  $\text{Pb}^-$  - ions aggregates in  $\text{KCl:Pb}^{2+}$  co-doped with  $10^{18}$  ( $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  -  $\text{Ba}^{2+}$  )-ions/ $\text{cm}^3$  ( $T_x$  - centres)[24].

d) The  $\text{Tl}^-$  and  $\text{Tl}^- + \text{Ca}^{2+}$  - ions aggregates in  $\text{KCl}$  crystals [25]

e) The negative aggregates of  $\text{In}^-$  and  $\text{Ga}^-$  in  $\text{KCl}$  crystals [11, 12].

The points b,c,d and e have been approached by the nonstandard colouring method.

## 2. Group of the $\text{Pb}^-$ - ions and $\text{Pb}^-$ - ions aggregates

### 2.1. Standard colouring of AHCs doped with $\text{Pb}^{2+}$ - ions

The AHCs grown by the Kyropoulos or Bridgman method from purified salts and doped with  $\sim 10^{17}$   $\text{Pb}^{2+}$  - ions/ $\text{cm}^3$  can be electrolytically coloured only at temperatures which exceed  $500^\circ\text{C}$  and in this case about  $10^{18}$  F-centres/ $\text{cm}^3$  are, also, present in the samples.

After removing of the F- centres, the coloured  $\text{KCl}$  samples exhibit a beautiful and uniform pink colour only in the part of the sample where the F- centres have been initially present. This experimental fact proves that the conversion of the  $\text{Pb}^{2+}$  - ions takes place only with the participation of F-centres (anion vacancy which captures one electron) and not by the electrical current which passes across the sample. The absorption spectrum of this sample consists of several well-resolved bands – called T-bands which belong to the  $T_a$  - centres [6]. The 14 T- bands have been found in  $\text{KCl}$  crystals at 4.2 K in the spectral range 200-600 nm. These bands can be divided in two groups: 1) The  $T_1 - T_7$  with low absorption coefficients and 2)  $T_8 - T_{14}$  about sevenfold more intense than the first group. Fig. 1 (curve 1) shows the absorption spectrum of the first group at 20 K [26]. We have not found traces of  $\text{Pb}^{2+}$  - ions in the coloured sample even by excitation spectra. This proves that all the  $\text{Pb}^{2+}$  - ions are converted into new trapping electron species, due to the method of colouring. It is demonstrated in [6] that, in the process of colouring the  $\text{Pb}^{2+}$  - ions are transformed in  $\text{Pb}^-$  ions because three F-centres are needed for this conversion. We also proved that the  $\text{Pb}^-$  - ion is in an anionic site and not in an interstitial position by two solid state reactions verified by optical absorption in initial and final stages:



where  $Pb^-$  and  $H^-$  are negative ions in anionic sites,  $Pb_i^0$  is lead atom in interstitial position,  $\Sigma Pb^0$  means nanoclusters of lead. The first reaction takes place at 700 °C and the second at 550 °C. Without anionic vacancies and electrons, the above reactions are not possible. These reactions prove, undoubtedly, that only  $Pb^-$  - ions or  $Pb^-$  - ions aggregates can supply for F- centres and  $H^-$  - ions, the electrons and anion vacancies required for their formation.

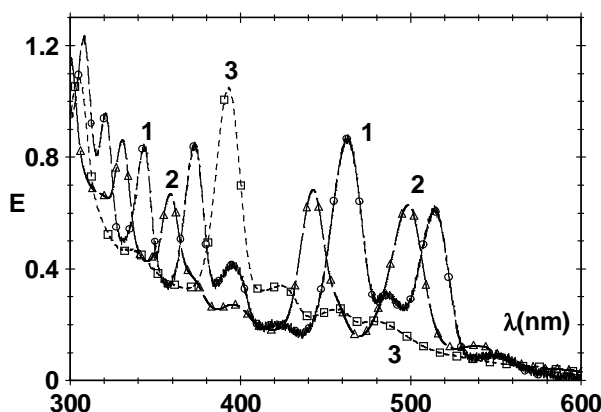


Fig. 1. OA spectra at 20K for: 1) KCl:Pb<sup>2+</sup>; 2) KCl:Pb<sup>2+</sup> + Na<sup>+</sup>, standard coloured 3) KCl:Pb<sup>2+</sup>+Ca<sup>2+</sup> nonstandard coloured.

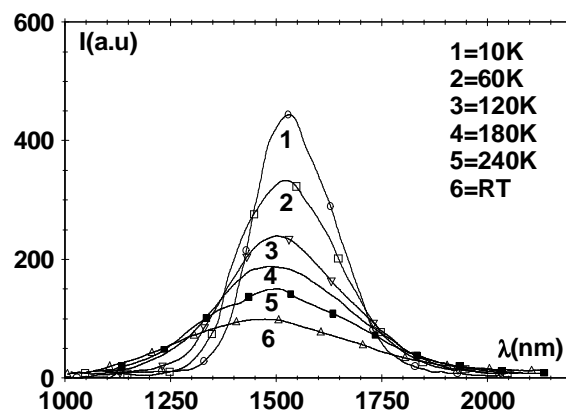


Fig. 2. Emission spectra of Ta - centres in KCl:Pb<sup>2+</sup> standard coloured.

Surprisingly, no emission in the 250-1000 nm spectral region by excitation in the part of the UV and visible T-bands is found. As reported for the first time in [27] the excitation in the T<sub>1</sub>, T<sub>2</sub>, and T<sub>3</sub> bands of the T<sub>a</sub>-centres gives rise for the KCl, KBr, and KI crystals to one simple broad emission band peaking at 1500, 1550 and 1590 nm, respectively. After 22 years, the emission studies of the T<sub>a</sub> - centres in KCl have been continued especially concerning the temperature dependence of the 1500 nm emission band and the following results have been got:

By decreasing temperature, the 1500 nm emission band presents the modifications to be seen in Fig. 2, namely: 1) augmentation of the intensity; 2) diminution of the half width, 3) shifting of the maximum towards shorter energies (unusual behaviour for which we have not yet an explanation). As concerns the decay time, we established that: 4) the decay time (150 μs at 10 K and 200 μs at 300 K) observed at λ = 150 nm is a singular one and strictly exponential as a function of time proving, that no energy transfer occurs. 5) at 300 K the decay times for 1200 nm and 1700 nm are the same as for 1500 nm. This is another argument that this emission band is a singular one. These features belong to a simple Pb<sup>-</sup> centre or to a negative aggregate species of Pb<sup>-</sup> - ions.

Very important is to stress that as recent measurements show [26] the same emission band at 1500 nm is obtained by excitation with 266, 364, 450, 512 and 633 nm laser lines. Because the temperature dependence for all 14- absorption T- bands is quite the same, it was concluded [6] that these bands originate from the same fundamental level. From the dependence as function of temperature of the emission spectra, the same conclusion results as for the absorption spectra.

The above two experimental facts permit to construct a diagram of energy levels for the T<sub>a</sub> - centre in KCl samples (Fig. 4). The black arrows show the energy transition of used laser lines [26].

These results prove the presence in the samples with T<sub>a</sub> -centres of one relatively simple absorbing and luminescent centre. The simplest model can be Pb<sup>-</sup> -ion in anionic site, but the lack of any EPR signal and the fact that MCD measurements certify the presence in T<sub>a</sub>- samples only of diamagnetic centres (see Fig. 3), suggest to speculate about two adjacent Pb<sup>-</sup> - ions in anionic sites. T<sub>c</sub> - centre is probably a T<sub>a</sub> - centre in a perturbing environment.

It is important to mention that T<sub>a</sub>- centres emission in KBr:Pb<sup>2+</sup> grown by the Bridgman method, standard electrolytically coloured and excited with λ = 514 nm, exhibit NIR emission band with the intensity fiftyfold as in the KCl:T<sub>a</sub> - centres, emission made in the same experimental conditions. The later emission was obtained from the crystal grown by the Kyropoulos method.

In the  $\text{KCl}:\text{Sn}^{2+}$  crystals grown by Bridgman method after standard electrolytical colouring we found the same spectral features in optical absorption as for  $\text{KCl}:\text{Pb}^{2+}$ . The emission band in NIR region in the same colouring conditions as for  $T_a$ -centres in  $\text{KCl}:\text{Pb}^{2+}$  are also the same only with an emission peak shifted towards higher energies (see Fig. 5) [28].

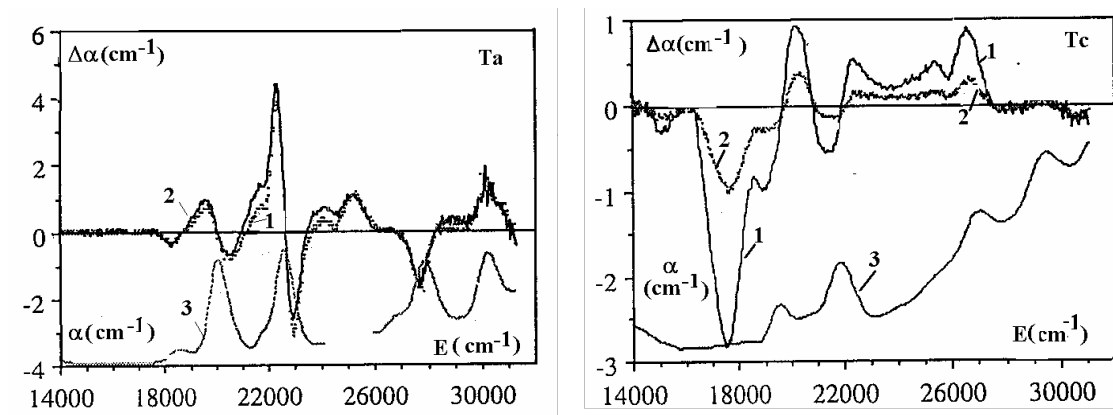


Fig. 3.  $T_a$  and  $T_c$  - centres in KCl crystals; MCD at 4.2 K (curves 1) and 1.3 K (curves 2); OA, (curve 3, at 4.2 K).

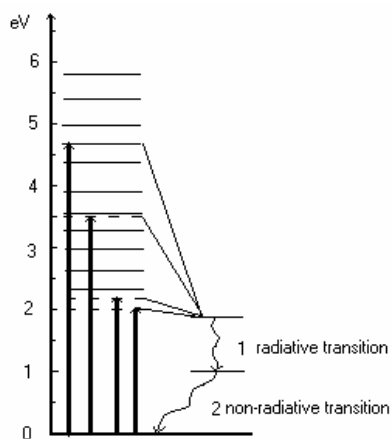


Fig. 4. The diagram of the energy levels for  $T_1 - T_{10}$  -bands of KCl  $T_a$ -centres.

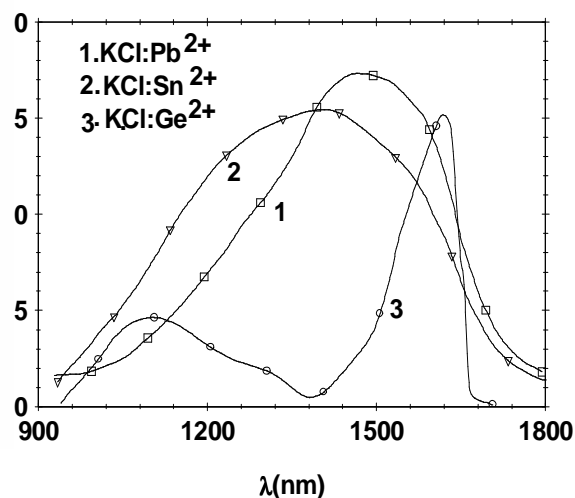


Fig. 5. Emission of  $T_a$ -centres for three  $ns^2$ -ions.

The  $T_a$ -centres emission of the coloured  $\text{KCl}:\text{Ge}^{2+}$  also grown by the Bridgman method is less similar than for the  $T_a$  - emission in  $\text{KCl}:\text{Pb}^{2+}$  and  $\text{KCl}:\text{Sn}^{2+}$  coloured crystals (see Fig. 5, curve 3) The emission band at 1600 nm has a narrower half-width and a second emission band appears at 1100 nm (may be because the sample contains also  $10^{18}\text{F}$ -centres/ $\text{cm}^3$ ). The final conclusion about  $T_a$ -centres in K-halide crystals is that all divalent isoelectronic  $ns^2$  ions ( $\text{Pb}^{2+}$ ,  $\text{Sn}^{2+}$  and  $\text{Ge}^{2+}$ ) standard coloured have the same spectral behaviour [28]. These centres probably are  $\text{Pb}^-$ , or  $\text{Pb}_2^{2-}$  -ions in anionic positions and the crystals with these exotic ions are new and optically very stable materials, with intense NIR emission at room temperature.

## 2.2. Standard colouring of $\text{KCl}:\text{Pb}^{2+}$ crystals co-doped with $\text{Na}^+$ , $\text{Li}^+$ and $\text{Rb}^+$ - ions

In the first experiments concerning the  $T_a$  - centres in KCl samples it was reported that few crystals standard coloured, doped with  $\text{Pb}^{2+}$ - ions, show the T-bands with maxima shifted in both directions from the wavelength of  $T_a$  - centres. These bands have been called  $T_b$  and  $T_c$  - centres [19].

Very interesting was that these centres exhibit the same emission band at  $\lambda = 1500$  nm and  $T_b$ -centres as MCD measurements prove, are total diamagnetic, while the  $T_c$  – centres contain at least one paramagnetic defect (Fig. 3 curve 1,  $T_c$ ). In [29] it was proved that  $T_b$  – centres belong to the  $T_a$  – centres perturbed by the presence of an alkali impurity ion (Li – ion, Fig. 1 curve 2). The emission bands for these codoped KCl:Pb with alkali ions are less spectacular as the optical absorption bands. At room temperature only the coloured samples of KCl:Pb<sup>2+</sup> + Li<sup>+</sup> show a shift of the maximum band at 1500 nm toward longer wavelengths, shift which is more accentuated at 4.2 K. The emission of coloured KCl:Pb<sup>2+</sup> + Na<sup>+</sup> and KCl:Pb<sup>2+</sup> + Rb<sup>+</sup> displays an emission band quite similar to the  $T_a$  – center [26].

### 2.3. Nonstandard colouring

#### 2.3.1. Nonstandard colouring of KCl:Pb<sup>2+</sup> + Ca<sup>2+</sup> ( $c_{Ca^{2+}} \sim 10^{17} Ca^{2+}$ - ions/cm<sup>3</sup>)

In [19,22] we have reported the formation of new T- centres by performing the electrolytical colouring in the nonstandard variant for decreasing the colouring temperature and to preserve the defects which at the 550 °C (the standard colouring temperature) are destroyed. As optical absorption of samples coloured at 250 °C shows (see Fig. 6) the  $T_a$ - absorption band do not exist any longer in the sample and different optical absorption bands appear by the disappearance of initial Pb<sup>2+</sup>- ions. We called the new produced centres  $T_d$  and  $T_e$  - centres because as a function of the colouring condition and the purity of salts used to grow in crystals one or another centre appears but both belong to new paramagnetic centres (see Fig. 6).

The OA spectra of  $T_d$  and  $T_e$  – centres are different from those of  $T_a$  - centres and obviously the colour of the samples with these centres are also different from the colour of  $T_a$ - centres. These OA spectra of  $T_d$  and  $T_e$  exhibit less resolved bands and are extended down at least to 1000 nm in the NIR (compare Fig. 3 and 6).

Additionally the MCD spectra are also quite different from those of  $T_a$  or  $T_b$  – centres and prove the presence of at least two paramagnetic centres in every sample. Fig. 6 displays the OA and MCD spectra at 4.2 K and 1.3 K and it is obviously from it that for  $T_d$  and  $T_e$  – centres the wavelengths at which appear the MCD bands for paramagnetic centres are different.

The emission of  $T_e$  – centres is very complex (see Fig. 7) [22].

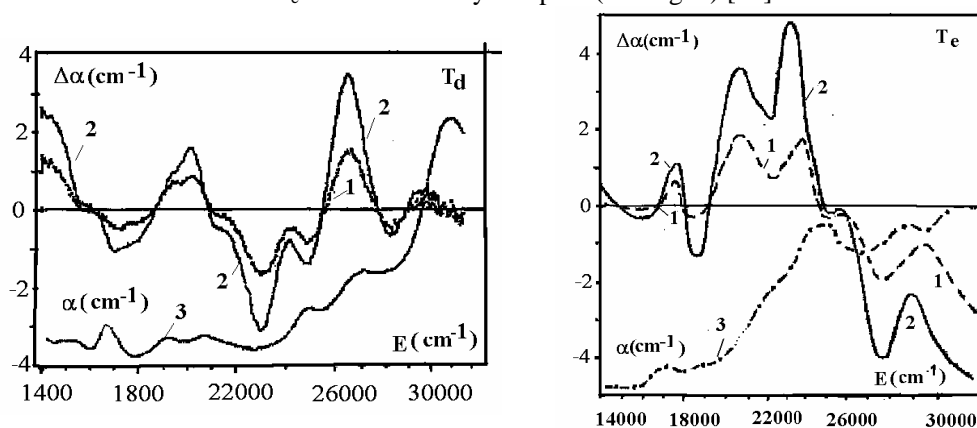


Fig. 6. MCD (curves 1 at 4.2 K and curves 2 at 1.3 K) and OA (curves 3 at 4.2 K) spectra for  $T_d$  and  $T_e$  – centres, obtained by a nonstandard colouring method in KCl:Pb<sup>2+</sup> + Ca<sup>2+</sup> ( $c_{Ca^{2+}} \sim 10^{17}$  ion/cm<sup>3</sup>).

The temperature dependence for the emission spectra of  $T_e$  – centres is quite different from the same dependence of  $T_a$  –centres (see Fig. 2). Two main groups of bands are observed: one below 1.600 nm and the other above this wavelength. Around 1400 nm a vibronic structure with three sharp lines is clearly visible at the lowest temperatures. In the high wavelength region one observes two broad features around 2.060 and 1.960 nm. The latter band occurs only as a weak shoulder at 10 K

and it grows gradually during heating until it dominates the spectrum above 180 K. From the emission spectrum of  $T_e$  – centres as a function of temperature it is obvious that an energy transfer occurs between at least two different centres.

The paramagnetic centres detected in samples with  $T_d$  and  $T_e$  – centres by MCD have been proved by the EPR method [23]. For the first time it was directly demonstrated that in the  $KCl: Pb^{2+} + Ca^{2+}$  samples nonstandard coloured, exist several negatively charged lead centres [19, 22]. By EPR spectra a new type of monomer  $Pb^-$  - centre ( $6p^3$ ) has been observed at  $T \leq 35$  K. The EPR spectra are characterized by single, strongly anisotropic line, flanked at both sides by weaker doublets. The ratio of the integrated intensities of singlet to doublet lines is always roughly 3.5:1. It means that the EPR spectra originate from the centre involving a single Pb nucleus. The angular variation of the EPR line positions shows that the centre called  $Pb^-(Rh)$  possesses orthorhombic symmetry with a set of axes  $x, y, z$ , being  $[110]$ ,  $[001]$  and  $[1\bar{1}0]$ , respectively. The  $g$  – and the values of  $hf$  –principal tensor proved that the  $Pb^-(Rh)$  centre is a negatively charged  $Pb(6s^3)$  ion in an orthorhombic crystal field. It has been found that the  $Pb^-(Rh)$  centres exhibit specific properties under illumination with visible light. All samples containing such centres show a decrease down to half in the concentration in the  $Pb^-(Rh)$  centres after being kept in dark at RT for about 20 hours, and decay completely after about 1 week of such a treatment. However, their initial concentration is restored by keeping the sample at RT, under ambient light for about 15 minutes. These experimental facts prove that  $Pb^-(Rh)$  – centres are unstable at RT, being continuously formed from an EPR silent precursor under illumination with visible light. The growing of the  $Pb^-(Rh)$  – centre from its precursor is not a simple electron (hole) process but also involves ion (vacancy) movement. Indeed, as shown by in situ optical formation experiments, under illumination at various temperatures, the  $Pb^-(Rh)$ centres are formed only at  $T \geq 225$  K (i.e. temperatures where the vacancies of the KCl lattice are mobile). Additional experiments have shown that the  $Pb^-(Rh)$  – centres are formed in a broad spectral range extending at least from 14000 to 26000  $cm^{-1}$ .

Two other EPR spectra, consisting of a stronger central singlet line flanked on both sides by weaker doublets, have also been observed at  $T \leq 35$  K. The spectra attributed to paramagnetic species called  $Tr_1$  and  $Tr_2$  exhibit axial symmetry. The symmetry axis being along one of the trigonal  $\langle 111 \rangle$  axes. The ratio of integrated intensities of the singlet to doublet lines is roughly 1.8:1 for both centres suggesting in each case a dimer structure involving two lead ions/atom probable  $Pb_2^-$  - molecular ion. The results of EPR studies show that the  $T_d$  and  $T_e$  – centres are a new type paramagnetic negative charged lead centres quite different from the  $T_a$  – centres. These results demonstrated that the electrolytical colouring at low temperature also produces lead negative aggregate centres (at least  $Pb_2^-$  - centres) quite similar to the  $Ag^-$  - aggregates obtained in the same colouring condition [30].

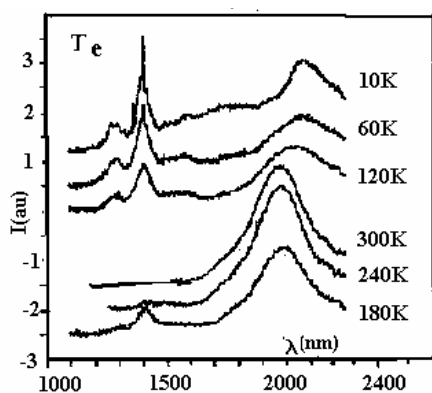


Fig. 7. Emission spectra of  $T_e$  - centres as a function of the temperature  
 $\lambda_{exc} = 514$  nm.

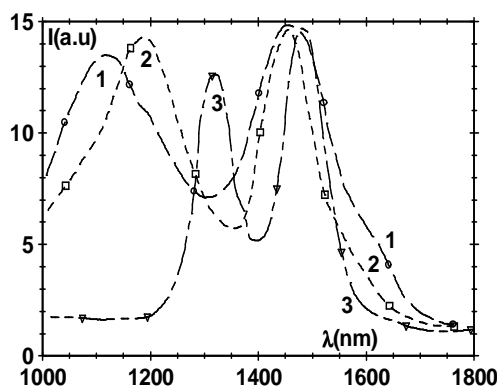


Fig. 8. Emission spectra:  
1.  $KCl: Pb^{2+} + Ca^{2+}$ ; 2.  $KCl: Pb^{2+} + Sr^{2+}$   
3.  $KCl: Pb^{2+} + Ba^{2+}$   $\lambda_{exc} = 514$  nm.

### 2.3.2. Nonstandard colouring of $\text{KCl:Pb}^{2+} + (\text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+})$ crystals ( $c_{\text{Ca}^{2+}} \sim 10^{18}$ ions/cm<sup>3</sup>)

As we have demonstrated in [10], by the increasing of the  $\text{Ca}^{2+}$ - ions concentration in  $\text{KCl:Pb}^{2+}$  crystals one order of magnitude more than the concentration of  $\text{Pb}^{2+}$  - ions (which usually is about  $10^{17}$   $\text{Pb}^{2+}$ - ions/cm<sup>3</sup>) the nonstandard colouring produces, new defects with optical absorption spectra quite different from spectra of  $T_a$ ,  $T_d$  or  $T_e^-$ -centres. This absorption spectra recorded at low temperature consist in two stronger well-resolved (in range of 3100-4140 nm) and at least four weaker bands situated between 6200-4200 nm. The dependence of this optical absorption spectrum on recording temperature (300-20 K) exhibits all characteristic behaviours of absorption spectra arising from electronic transition between two levels: 1<sup>0</sup>, increasing of the intensity of absorption bands; 2<sup>0</sup>, decreasing of half width; 3<sup>0</sup>, shift of max  $\lambda$  with decreasing of temperature. Surprisingly, the shift of the maxima of the bands is in opposite direction as usually, as curve 3 Fig. 1 proves. For the sake of clarity we called the new defects  $T_x$  – centres.

In [10] we have also reported that by changing the divalent  $\text{Ca}^{2+}$  - ions with  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  - ions, the maxima of absorption due to the  $T_x$  – type centres shift to decreasing energy in comparison with absorption maxima of the  $\text{KCl:Pb}^{2+} + \text{Ca}^{2+} T_x$  - centres. This experimental fact demonstrates that the defects responsible for those spectra must contain in their structural model at least one of divalent co-doping ion because the position of the absorption maxima observed depend on the nature of co-doping cations. An important argument in the favour of this assignments is that the emission spectra (see Fig. 8) of nonstandard coloured samples of  $\text{KCl:Pb}^{2+}$  codoped with  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$ - ions depend also on the co-doping cation. As the Fig. 8 shows, the emission ( $\lambda_{\text{exc}} = 514$  nm) of  $T_x$  – centres consist of at least two bands well resolved which are quite different from the emission spectra of  $T_a$ ,  $T_d$ , and  $T_e^-$  – centres.

It is important to mention that, also in nonstandard coloured  $\text{KBr:Pb}^{2+} + \text{Ca}^{2+}$  and  $\text{KBr:Pb}^{2+} + \text{Ba}^{2+}$ , we obtained the same two emission bands in the 1200-1600 nm range as for  $T_x$  – centres in  $\text{KCl}$  samples (Fig. 9). But in  $\text{KBr:Pb}^{2+} + \text{Ba}^{2+}$  nonstandard coloured samples under excitation with He-Ne laser 5 mW,  $\lambda_{\text{exc}} = 633$  nm, beside the two emission bands mentioned above other two emission bands appear in the 750-1150 nm spectral range [31].

By changing the position of the exciting spot the intensities of these two bands change also (Fig. 9, curve 1 and 2). This experimental fact proves that in the process of nonstandard colouring the production of these defects is not uniform.

### 2.3.3. Nonstandard colouring of $\text{KCl:Tl}^+ + \text{Ca}^{2+}$ crystals

In order to verify if the monovalent  $ns^2$  ions (namely  $\text{Tl}^+$  - ions) are converted also in  $\text{Me}^-$  - ions by nonstandard colouring, like the divalent  $ns^2$  – ions discussed above, we have used two  $\text{KCl:Tl}^+$  crystals, Bridgman grown, firstly co-doped with  $\sim 10^{17}$   $\text{Ca}^{2+}$  ions/cm<sup>3</sup> and secondly with  $\sim 10^{18}$   $\text{Ca}^{2+}$  ions/cm<sup>3</sup>. The  $\text{Tl}^+$  -ions concentration was about  $\sim 10^{17}$   $\text{Tl}^+$  ions/cm<sup>3</sup>. The concentration of  $\text{Ca}^{2+}$  - ions was chosen appropriate for obtaining  $T_d$  and  $T_x$  – type centres. We found in the two above mentioned crystals, after nonstandard colouring, all characteristic properties of  $\text{Me}^-$  - ions. On the expense of all  $\text{Tl}^+$  - ions new defects are formed and detected by new absorption and emission spectra. Thermal treatment in air of coloured samples produces F – centres and in flux of  $\text{H}_2$ , the  $\text{H}^-$  - centres and nanoclusters of  $\text{Tl}$  atoms [17].

The experimental results really prove that during electrolytical colouring all  $\text{Tl}^+$  -ions are converted to  $\text{Tl}^-$  - species perturbed by the presence of the  $\text{Ca}^{2+}$  - ion and probably also by a cation vacancy (existent in the sample for charge compensation) like  $T_d$  and  $T_x$  – centers in  $\text{KCl:Pb}^{2+} + \text{Ca}^{2+}$  samples coloured in the same experimental conditions. Surprisingly, the absorption spectrum in coloured samples of  $\text{KCl:Tl}^+ + \text{Ca}^{2+}$  with low concentration of  $\text{Ca}^{2+}$  - ions is different from that given by  $T_d$  – centres in nonstandard coloured  $\text{KCl:Pb}^{2+} + \text{Ca}^{2+}$ . This spectrum exhibits three well resolved absorption bands in the 250-400 nm spectral range [8]. The absorption spectrum for the sample with a high  $\text{Ca}^{2+}$  - ions concentration is very similar to the spectrum represented in Fig. 1 curve 3 for  $T_x$  – centres in  $\text{KCl:Pb}^{2+} + \text{Ca}^{2+}$ . The emission spectra [25] displayed in Fig. 9, curves 3 and 4 exhibit two bands well-resolved for the low  $\text{Ca}^{2+}$  concentration and less – resolved for high  $\text{Ca}^{2+}$  - ions concentration. Unexpectedly, the wavelength for these two bands are situated around the same values

as for  $\text{KCl:Pb}^{2+} + \text{Ca}^{2+}$ , coloured samples (compare the curves 3 and 4 Fig. 9 with curve 1, Fig. 8). The intensity of emission band of the sample with low concentration of  $\text{Ca}^{2+}$  is comparable with the intensity of Ta emission spectra. Unfortunately, the emission spectra of both samples were recorded only at room temperature.

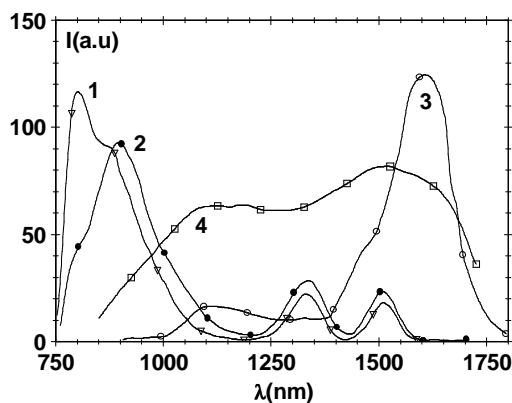


Fig. 9. Emission spectra (RT), 1.  $\text{KBr:Pb}^{2+} + \text{Ba}^{2+}$ ; 2.  $\text{KBr:Pb}^{2+} + \text{Ba}^{2+}$ , (different positions of exciting spot) 3.  $\text{KCl:Tl}^+$  4.  $\text{KCl:Tl}^+ + \text{Ca}^{2+}$  nonstandard coloured samples 1,2  $\lambda_{\text{exc}} = 633 \text{ nm}$ ; 3,4  $\lambda_{\text{exc}} = 514 \text{ nm}$ .

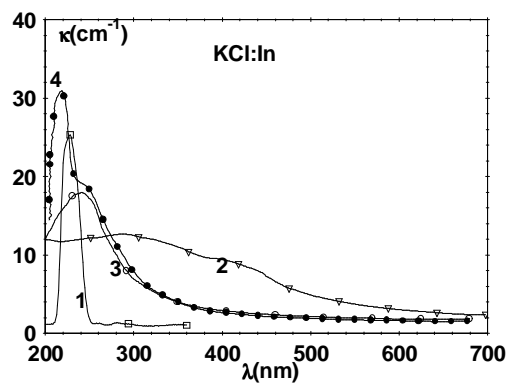


Fig. 10. Absorption spectra of  $\text{KCl:In}^+$  1. uncoloured; 2. nonstandard coloured 2. nonstandard coloured sample 3. After  $\text{N}_2$  treatment 4. After  $\text{H}_2$  treatment.

### 2.3.4. Nonstandard colouring of $\text{KCl:In}^+$ and $\text{KCl:Ga}^+$ codoped with $\sim 10^{17} \text{ Ca}^{2+}$ - ions/ $\text{cm}^3$

As expected, in both  $\text{KCl:In}^+$  and  $\text{KCl:Ga}^+$  codoped the  $\text{Ca}^{2+}$  - ions with the concentration above mentioned, in the electrolytical colouring processes occurs the same changing as for  $\text{Pb}^{2+}$  and  $\text{Tl}^+$  - ions embedded in a KCl crystal. Fig. 10 shows a typical absorption spectrum for a noncoloured  $\text{KCl:In}^+$  sample (curve 1 in which one can see the most intense characteristic absorption band of  $\text{In}^+$  - ions, peaking at 227 nm)[32]. After colouring,  $\text{In}^+$  - ions do not exist any longer in the sample and the new less intense absorption spectrum appears (curve 2). The thermal treatment in  $\text{N}_2$  and  $\text{H}_2$  flux produces a nanocluster band at 240 nm for the  $\text{N}_2$  flux and a  $\text{H}^-$  - ions band (214 nm, well known U-band) and the same nanocluster band at 240 nm. These results prove that the reaction in solid state (2), takes place also in coloured  $\text{KCl:In}^+$  crystals and the existence of  $\text{In}^-$  - ions in anionic positions is demonstrated. Fig. 11 shows that by exciting the  $\text{KCl:In}^+$  coloured sample with 514 nm laser line two well-resolved emission bands appear at 1080 and 1600 nm. Surprisingly, apparently they are the same as, for  $\text{KCl:Pb}^{2+} + \text{Ca}^{2+}$  with high concentration of  $\text{Ca}^{2+}$  - ions. It is obvious, from the emission spectra of Fig. 11, curves 1 and 2, that in the coloured samples there exists at least two luminescent centres because the two bands appear either together (curve 3) or separately (curve 1 or 2). The emission spectrum of a coloured  $\text{KCl:In}^+$  crystal with only 1060 nm emission band at RT, as in Fig. 12, exhibits at 4.2 K an energy transfer which occurs between at least two different centres. Also similar to the case of the emission spectrum at 10 K for Te - centres, several vibronic narrow bands do appear, for  $\text{KCl:In}^+$  coloured sample [11]. This experimental fact demonstrates that the centres present in this sample are aggregate of  $\text{In}^-$  - ions. We suggested in [33] that most probably these aggregates are composed of two adjacent  $\text{In}^-$  - ions ( $\text{In}_2^-$ ) because an EPR signal is not found at 20 K, but more diamagnetic complex defects, with more  $\text{In}^-$  - ions, are not excluded.

By the nonstandard colouring in the  $\text{KCl:Ga}^+$  crystals we have found the same absorption and emission bands, as for the coloured  $\text{KCl:In}^+$  crystals. In Fig. 11 (curve 4) the emission of  $\text{KCl:Ga}^+$  coloured sample is depicted. This spectrum is practically the same as the emission spectrum of the  $\text{KCl:In}^+$ . Also at 4.2 K an energy transfer process occurs and the vibronic lines are present. The similarity with the case of  $\text{KCl:In}^+$  coloured crystals is obvious.



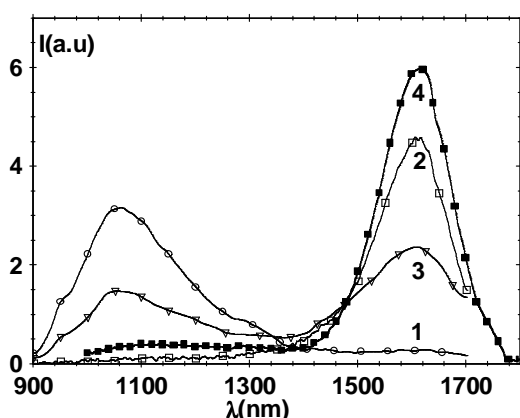


Fig. 11. Emission spectra at RT for;  
KCl:In<sup>+</sup> (curves 1,2,3)  
KCl:Ga<sup>+</sup> (curve 4)  
 $\lambda_{exc} = 514 \text{ nm}$   
nonstandard coloured samples.

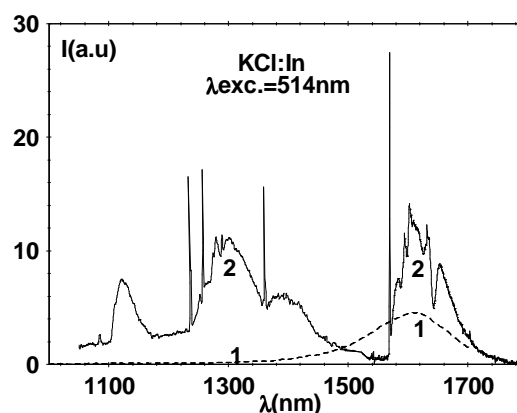


Fig. 12. Emission spectra for KCl:In  
at RT (curve 1) and at 4.2 K (curve 2)  
nonstandard coloured samples.

### 3. Discussion

The above experimental results prove that the nonstandard electrolytical colouring changes the valence state of all heavy metal ions with  $ns^2$ -electronic configuration until negative one, both for the monovalent Ga<sup>+</sup>, In<sup>+</sup> and Tl<sup>+</sup> - ions and for the divalent Pb<sup>2+</sup>, Sn<sup>2+</sup> and Ge<sup>2+</sup> - ions. Because the electronegativity, in Pauling scale, for these ions ranges from 1.6 for Ga to 1.8 for Tl, Pb, Sn, and Ge atoms, the ability to capture two or three electrons supplied by F<sup>-</sup> centres is sufficiently high that even in the situation when the number of the F<sup>-</sup> centres in the nonstandard electrolytical colouring is less than twofold (for monovalent  $ns^2$  - anions) or threefold (for divalent  $ns^2$ - ions) the number of  $ns^2$  impurity ions, the process of electron capture takes place and apparently the colouring is produced without F<sup>-</sup> centers. In the process of colouring the detachment of the electron from Me<sup>-</sup> ions is unavoidably involved and we stress in [33] that the electrons after detachment are captured directly by ions or atoms of impurity and do not pass into the conduction band. A strong argument in the favour of this hypothesis is the experimental fact, that even when the duration of the colouring process is around 30 minutes the nanoclusters are not formed for all  $ns^2$  investigated ions at concentration of impurity ion about  $10^{17}$  ions/cm<sup>3</sup>. By relatively long thermal treatment at temperatures higher than 400 °C for which the electrons detached from Me<sup>-</sup> ions or Me<sup>-</sup> aggregates can leave the crystals, we obtained nanoclusters of doping impurities. This was demonstrated by optical absorption spectra and by transmission electron microscopy techniques [34,35].

The luminescence properties in NIR region are interesting and important taking into account the high intensity of these emission spectra even at room temperature.

### 4. Conclusions

The above results demonstrate that the nonstandard electrolytical colouring is a very useful technique, which if applied to doped AHCs with  $ns^2$  - ions can be used for obtaining new advanced materials with stable and intense emission in the NIR range at room temperature. It is also demonstrated that for all monovalent and divalent  $ns^2$  - ions embedded in KCl crystals are produced the Me<sup>-</sup> ions and Me<sup>-</sup> ions aggregates in anionic positions. For KBr and KI doped with Pb<sup>2+</sup> ions the same results are obtained. In KCl:Pb<sup>2+</sup> crystals codoped with Li<sup>+</sup>, Na<sup>+</sup> and Rb<sup>+</sup>, and coloured, these negative metal species are perturbed by the presence of these alkali ions, in neighbouring position, as in the well known case of F<sub>A</sub> - centres. By codoping of KCl:Pb<sup>2+</sup> and KBr: Pb<sup>2+</sup> with Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>- ions, perturbed defects of Me<sup>-</sup> ions aggregates like F<sub>Z</sub> - centres are obtained after nonstandard

colouring. These perturbed defects have as nearest neighbours the divalent cations and not cation vacancies, as in the case of  $F_z^-$  centres.

If the conversion in several negative species of  $ns^2$  cations, during nonstandard colouring is indubitable proved, the structural atomic models are obtained only for the monomer  $Pb^-$  (Rh) centre and for  $Tr_1$  and  $Tr_2$  centres with  $Pb_2^-$  dimer structure.

Future studies for new negative metal species, will comprise a lot of complex experiments concerning: the improvement of nonstandard colouring technique with the aim to get a uniform distribution of these negative metal species in the bulk of the coloured sample and the attribution of absorption and emission bands to the definite centers.

The striking result concerning the similarity of absorption and emission spectra of the  $T_x$  – centres obtained in  $KCl:Pb^{2+}+Ca^{2+}$  and  $KCl:Tl^++Ca^{2+}$  must be explained. The extension of the study for  $KCl:In^++Ca^{2+}$  and  $KCl:Ga^++Ca^{2+}$  with high concentration of  $Ca^{2+}$ - ions is suggested.

Of great importance is the comparison of the above results with those obtained by the standard colouring method.

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