

Dedicated to Acad. Prof. Dr. Margareta Giurgea with the occasion of her 90-th anniversary

NEW EXOTIC NEGATIVE IONS OF *In* AND *Ga* IN KCl CRYSTALS

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In this paper we present the experimental proofs that in KCl:In⁺ and KCl:Ga⁺ crystals, after non-standard electrolytical colouring, all impurity ions are converted in negative species and occupy anionic positions. The optical absorption and emission, electron paramagnetic resonance, thermal treatment in a flux of N₂ or H₂ and the electrons migration from negative metal species of coloured part to uncoloured part driven by an electric field, have been used as experimental methods for the demonstration of the conversion of In⁺ and Ga⁺-ions in negative exotic ions. The last two methods are very important for proving the existence of negative metal ions in crystals. The first one was improved by our team in [1], and the second one reported here for the first time, was used as an indubitable test for the evidence of *In* and *Ga* negative metal ions in anionic sites, in electrolytical coloured samples.

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1. Introduction

In ionic compounds, especially in alkali halide crystals (AHCs), the impurity cations are embedded in a variety of valence states, as a function of the electronic configuration of each chemical element. It is obvious that different impurities charge states affect, in some cases even drastically, the majority of physical and chemical properties of the crystals in which these have been incorporated. This is the reason why the scientific community considered, long time ago, that studies of the methods of changing the valence state of cations in crystals and also the mechanisms by which the usual valence state of cationic impurity are modified, are of great importance, both for science and practical applications. It is well known that the capacity of valence changing of cations impurities is related very strongly with their electronegativity. Long time ago, Topa stated in [2] that all chemical elements which have the electronegativity more than 1.5 on Pauling scale, are able to change their valence state even to a negative one. Our team demonstrated using the method of electrolytical colouring, that the Ca²⁺, Sr²⁺, Ba²⁺, Eu²⁺ and Sm²⁺ (with electronegativity situated between 0.9 to 1.2) do not change their valence state [3], but Cu⁺, [4], Ag⁺ [5], Au⁺ [6], Ga⁺ [7,8], In⁺ [7,9], Tl⁺ [10], Ge²⁺, Sn²⁺ [11,12] and Pb²⁺ [11,12,13,14,15], could change their valence state until they become negative ions.

The most important properties of the negative metal ions (NMI) are [17]:

a) NMI, appear only in the part of the sample where F-centres are present after electrolytical colouring; (the F-centre is an anion vacancy which captures an electron)

b) NMI can be formed by the migration in electrical field in a sandwich arrangement from a pure crystal which contains a number of F-centres much more than the number of the impurity ions in the doped samples; no correlation between the intensity of the absorption bands of NMI and F-band exists;

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- c) after electrolytic colouring absorption, emission and excitation bands for all doping cations are not present, which it proves that the valence changing was produced;
- d) on the expenses of previous bands of Me^+ or Me^{2+} -ions in coloured samples, new absorption and emission bands appear;
- e) the intensities of these new bands are proportional to Me^+ or Me^{2+} -ions concentrations;
- f) if the concentration of the heavy metal ions surpasses a limit, which depends on the nature of the impurity, electrolytical colouring will produce directly heavy metal nanoclusters and only traces of NMI $-$ ions.

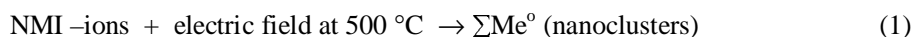
The aim of this paper is to demonstrate that all the In^+ and Ga^+ -ions embedded in KCl crystals by electrolytical colouring, change their valence until a negative one, forming In_a^- , Ga_a^- -ions and their aggregates*. Preliminary results about In^- and Ga^- -ions were reported in [7,8,9].

2. Used methods

2.1 Methods which prove the total conversion of Me^+ -ions in NMI $-$ ions after electrolytical colouring

Obviously, the total disappearance of characteristic absorption and emission bands of heavy metal ions, initially present in KCl samples and the appearance of new absorption, emission and excitation bands prove that all initial impurities present in the studied samples do not exist any more after electrolytical colouring and that new species of defects are formed but nothing is indicated about valence state of these defects. In principle, electrolytical colouring produced only electronic centres by the capture of electrons injected from the pointed cathode in the sample. Using this method, Me^+ -ions can be converted in Me^0 or Me_a^- -ions and their aggregate. To demonstrate that in the process of electrolytical colouring the new produced defects are indeed NMI -ions, a possible method consists in the counting the number of the F-centres which are necessary to convert a heavy metal ion (Me^+ -ion) in a Me_a^- -ion. This is obtained by the migration in an electric field at about 500 °C of a known number of F-centres from a pure KCl crystal in a noncoloured sample doped with Me^+ -ions. The two samples are positioned in a sandwich arrangement. This method can be used only if the number of Me^+ -ions are precisely. This demonstration has been applied for electrolytical coloured KCl:Pb samples [11]. It is not the case for In^+ and Ga^+ -ions because we are not able to determine with precision the number of In^+ and Ga^+ -ions present in our samples. For these impurities we applied the same method of migration in electric field at 500°C for KCl: In^+ and KCl: Ga^+ samples but coloured less than a half.

If the coloured part of samples contains Me_a^- -ions, the electrons of NMI $-$ ions (at 500 °C in a 10^3V/cm electric field) are detached and move to the uncoloured part of the sample and in this way the Me_a^- -ions in the coloured part of sample are converted in In^0 , Ga^0 (which due to the thermal agitation, coagulate in nanoclusters of In and Ga). The electrons lost by the Me_a^- -ions converted the In^+ or Ga^+ -ions in the uncoloured part also into In^0 or Ga^0 , because the number of electrons is not enough for the formation of NMI $-$ ions. If the solid state reaction in the coloured part of the sample is:



and in the initial uncoloured part of the sample is the solid state reaction:



the uncoloured volume of the sample must be equal to the initial coloured volume. In the two parts of the studied crystal there are only nanoclusters, whose absorption spectra have been shown in section 5. Obviously, if the NMI $-$ ions are paramagnetic, the MCD and RES techniques could

* The index "a" means anionic site

demonstrate the existence of these ions, as in the case of T_d -centres in $KCl:Pb^{2+}$ in non-standard coloration [15].

2.2. Methods to obtain NMI- centres

There are three most important ways to produce colour centres in the pure alkali halide single crystals which lead also to the appearance of NMI –ions doped with heavy metal cations crystals.

1. Irradiation with ionizing radiation (which produces NMI-ions only in few cases: Ag, Cu, Pb, Sn).
2. Additive colouring (in general besides NMI-ions, produces also nanoclusters).
3. Electrolysis or electrolytic colouring. This method is in our opinion the best and efficient way to obtain the NMI-ions. We use the method of the electrolytical colouring in two versions:
 - a) The standard method with the parameters: 500 °C, 300-500 V/cm, 3-10 mA and the colouring time - ~ 5 minutes.
 - b) The non-standard method with the parameters: 250-300 °C, 10^3 - 10^4 V/cm, 0.5-1 mA, and the colouring time ~25 minutes.

The second version can be applied only for the sample which contains 10^{17} Ca^{2+} ions/cm³ (which do not change their valence during the colouring, as it was mentioned above). In this case several new negative metal centres which are not destroyed at these relatively low temperatures are present in coloured samples, like the aggregate centres of Ag^- [18], Cu^- [19] or Pb^- -centres (so called T_d -centres) [15].

2.3. Why electrolytical colouring

The electrolytical colouring is the best method because it can produce:

- only electronic centres; visual pursuit of the colouring process (the oven is made of transparent quartz); the interruption of the coloration process at any time (only a part of the sample can be coloured);
- samples only with new centres produced by changing the polarity and moving the F-centers out of the sample;
- large possibilities to change the colouring conditions (temperature, electrical field, time) which allows to obtain different new centres in the same doped crystals;
- colouring seemingly without F-centres (version 2). In this case different new centres are formed if compared to version 1;
- possibility to freeze the situation at the colouring temperature by plunging the coloured sample in CCl_4 or even in liquid nitrogen;
- only few minutes for colouring (very important to avoid the nanoclusters formation).

3. Experimental details

3.1 Crystal growth

The attempts to growing $KCl: In^+$ and $KCl: Ga^+$ by the Kyropoulos method in dry nitrogen flow using a mixture of $InCl_3$ and KCl salts or $GaCl_3$ and KCl salts led to crystals without any trace of In^+ and Ga^+ -ions. KCl single crystals containing In^+ and Ga^+ -ions of concentration $5 \times 10^{15} - 3 \times 10^{17}$ ions/cm³ were grown by the Bridgman method in sealed quartz ampoules in argon and CCl_4 pressure in two steps. i) First, we grew a $KCl:In^+$ or $KCl:Ga^+$ crystal with a concentration of about 10^{18} ions/cm³ in the following manner: a mixture of dry KCl salts, $InCl_3$ or $GaCl_3$ salts and indium or gallium metal was put in a quartz ampoule and sealed under argon and CCl_4 atmosphere.

ii) From these highly concentrated crystals, we drew the crystals with impurity concentrations mentioned above, by dilution from crystal as first step.

3.2 Electrolytical colouring

In this paper we have used both versions of the electrolytical colouring mentioned above but the non-standard version was used as a rule, because in this method it is not necessary to remove the F-centres from the samples. Thus the absorption spectra of the formed samples are more intense and well resolved. This method as it is mentioned in [16] takes place apparently without F-centres and besides isolated NMI⁻ ions appear also aggregates of NMI⁻ ions which are destroyed at colouring temperature of standard version. More details about the electrolytical colouring device and the technique of this colouring are reported in [20].

3.3 Absorption and emission spectra

For the coloured and uncoloured samples, the absorption spectra were recorded by a VARIAN 17D spectrophotometer. Emission and excitation spectra of the same KCl:In⁺ and KCl:Ga⁺ samples at room temperature were recorded using Perkin Elmer 50L spectrofluorimeter. For emission spectra at room temperature and at 4.2 K in the NIR range we used the experimental set-up of Laboratory of Prof. Clearjaud of University Pierre and Marie Curie from Paris, formed by an argon ionized laser, Ge-cooled detector and a cryostat for liquid helium.

3.4. RES measurements

This type of measurements were performed on coloured samples of KCl:In⁺ and KCl:Ga⁺ with a standard X-band spectrometer model ESP-300M from BRUKER equipped with gas-flow cryogenic system (EFR 910 for operation in 1.5-290 K temperature range) Oxford Instruments. No RES signal was detected.

3.5 Transmission electron microscopy (TEM) measurements and selected area electron diffraction (SAE)

The samples for transmission electron microscopy (TEM) have been prepared as follows: small pieces (2×2×1 mm³) of freshly cleaved coloured samples were placed on a microscope grid covered by a carbon film and carefully dissolved in distilled water. The amount of water was sufficient so that after drying of the grid no KCl crystals remained on.

TEM patterns were performed with a PHILIPS CM 30 transmission electron microscope equipped with a goniometer. In all our experiments we used an accelerating voltage of 200 kV.

4. Results

4.1 Migration in electrical field of non-standard coloured samples

The crystals of KCl:In⁺ or KCl:Ga⁺ were partially electrolytically coloured at 300 °C and, by cleavage, a slice of the sample with the trace of the pointed wire was removed (sometimes, during migration experiences F-centres appear). As electrodes we used platinum plates. At 550 °C an electrical field (~10³ V/cm) was applied and the electrical current which passes through the sample was monitored. Like in the case of a sample of pure KCl with F-centres, in experiments of migration of F-centres, the current, which passes through the sample decreases in time and reaches a stationary value (due to the electrical conductivity of the sample without F-centres). The current curve versus time, which we obtained, is practically the same as in the experiences of F-centres migration [11]. As we stated in 2.1 the absorption spectrum in the two parts of the samples after

migration shows only the band at 240 nm which belongs to the KCl:In sample, the absorption band of In-nanoclusters, as we demonstrated by TEM patterns in [9].

Careful measurements of the initially coloured samples and the surface values obtained after migration experiments prove that, they are the same within an error of $\pm 5\%$. By these results we prove that in our non-standard coloured samples all In^+ -ions are converted in In_a^- - species. The experiences with KCl:Ga⁺ samples lead to the same conclusions as for KCl:In⁺. The absorption spectra in the two parts of a migrated sample presented no absorption band because the absorption maximum of nanoclusters of Ga is situated below 200 nm as the calculation using improved Mie theory demonstrated [7], and our VARIAN 17 D spectrophotometer works only to 200 nm.

The presence of these Ga-nanoclusters was proved using TEM technique (see Fig. 9).

4.2 Absorption Spectra of KCl:In⁺ samples before and after nonstandard colouring

Absorption spectra of KCl:In⁺ before coloration presents (curve 1, Fig. 1) the well known absorption A₁, A₂, B and C bands characteristic for Sn²⁺, In⁺ and Ga⁺ all ions with ns² electronic configuration. After non-standard colouration as curve 2, Fig. 1 indicates the In⁺ ions do not exist any more in the sample.

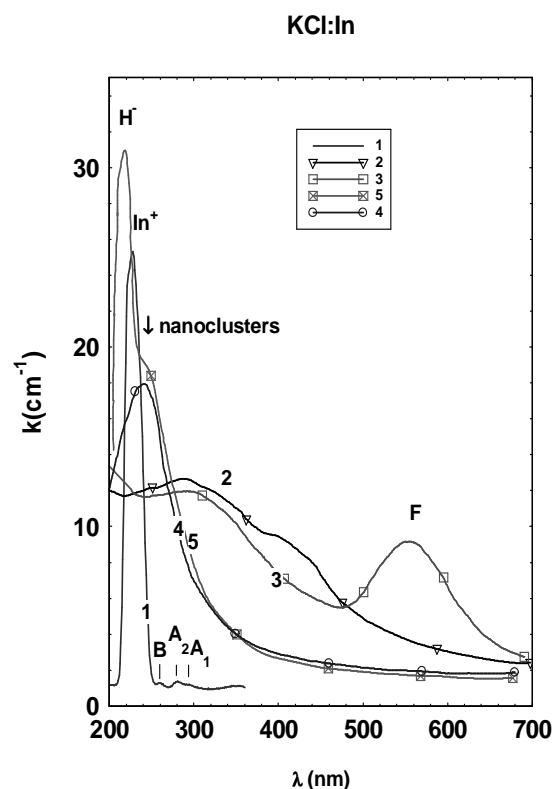
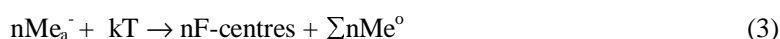


Fig. 1. Absorption spectra of KCl:In⁺; 1 uncoloured; 2 nonstandard coloured sample; 3 after thermal treatment and cooled in CCl₄; 4 after N₂-treatment; 5 after H₂-treatment

A new absorption range between 500 and 200 nm appears on the expense of initial In⁺-ions incorporated in the sample. If the coloured sample 2 is thermally annealed for 3 minutes at 700 °C, and suddenly cooled in CCl₄, the supplementary absorption band presents a small decrease, but a clear F absorption band appears (curve 3, Fig. 1) according to the solid state reaction



If two samples with the absorption described by curve 2, are subjected to a thermal treatment at 700 °C for 25 minute in dry N₂ flux (curve 4) and in H₂ flux (curve 5), the absorption spectra change drastically. These two curves prove that after electrolytical colouring the In⁺-ion are converted into In⁻-ions in anionic sites because: a) a thermal treatment leads to H⁻-ion band at 214 nm and nanoclusters of In are evidenced by the band of the 240 nm in concordance with the solid state reaction:



b) after the same thermal treatment in N₂ flux only the nanoclusters band is present in concordance with the solid state reaction:



It is important to mention that prolonged thermal treatment of the sample 5 (9h at 700 °C in N₂) produced partial recovery of In⁺-ions and the diminution of the nanoclusters band at 240 nm like in the case of Tl nanoclusters in KCl crystals [20].

4.3 Emission spectra of KCl:In⁺ samples before and after non-standard colouring

The emission and excitation spectra of KCl:In⁺-samples before electrolytical colouring show at room temperature a well resolved emission band situated at 420 nm and the excitation spectra are practically the same as the absorption one (A₁, A₂, B and C bands).

After electrolytical colouring, this emission and excitation spectra do not exist any more, what proves that all In⁺-ions are converted in new defects.

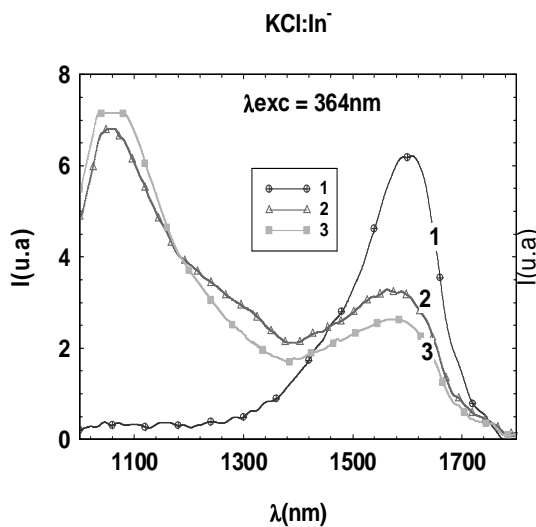


Fig. 2. Emission spectra at RT for KCl:In⁻ nonstandard coloured samples $\lambda_{exc}=364$ nm.

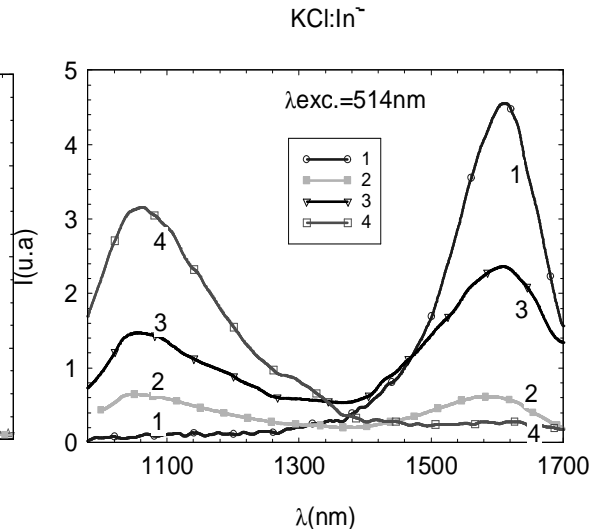


Fig. 3. Emission spectra at RT for KCl:In⁻. Different nonstandard coloured samples $\lambda_{exc}=514$ nm.

These new defects in NIR range, as the Fig. 2 shows, exhibit at room temperature with excitation $\lambda=364$ nm, at least two well resolved emission bands which appear at 1060 nm and 1600 nm. The same two excitation bands appear after the excitation with $\lambda=514$ nm (Fig. 3)

The results shown in Fig. 2 and Fig. 3 prove that by nonstandard electrolytical colouring of the samples present at least two different luminescent centres, because the two bands appear either

together (curve 2 and 3, Fig. 2 or curve 2 and 3 Fig. 3) or separated (curve 1 Fig. 2 and curve 1 and 4, Fig. 3).

Also is important to stress that excitation with $\lambda=514$ nm and $\lambda=364$ nm lead practically to the same emission bands. It is very interesting the experimental fact that the emission spectra of a sample only with the band at 1600 nm at room temperature at 4.2 K exhibit, as Fig. 4, a transfer energy spectra with several narrow vibronic but phonon lines excited with 364 nm. The emission spectra with $\lambda_{exc}=514$ nm are not represented.

Topa et al. [13] found in non-standard coloured KCl: Pb^{2+} similar transfer energy spectra at low temperature with several narrow vibronic lines due to aggregates of Pb^- -centres.

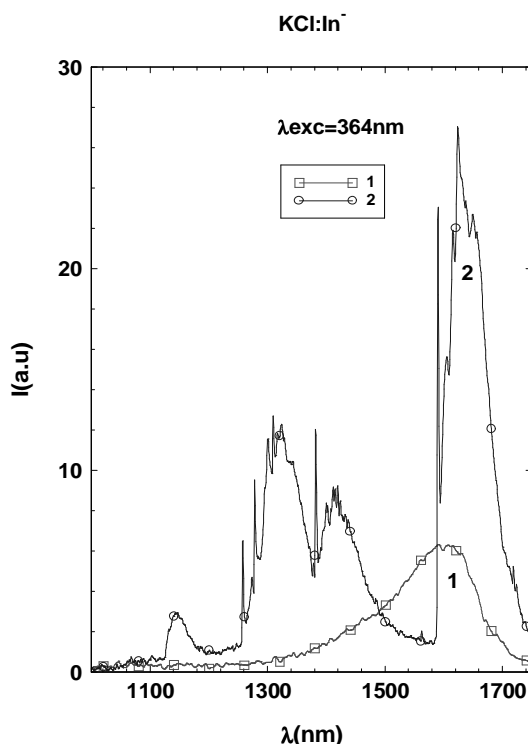


Fig. 4. Emission spectra of KCl:In⁻; 1, emission at RT; 2, emission at 4.2 K.

4.4. Absorption spectra of KCl:Ga⁺ samples after non-standard colouring

Absorption, emission and excitation spectra of the uncoloured samples proved that our KCl:Ga⁺ crystals contain only Ga⁺ -ions. If in the case of the oscillator strength we use the value $f=0.9$ for C absorption band in well known Smakula formula, the concentrations of Ga⁺ -ions are in the range $1 \times 10^{17} - 1 \times 10^{18}$ ions/cm³. As Jacobs stated [22], the ratio of the intensity of the C and A - band for Ga⁺ -ions is about a 400. Obviously, in the absorption spectra of our KCl:Ga⁺ samples, the A₁ and A₂ -bands are not observable (see curve 1, Fig. 7). The absorption spectra of non-standard coloured samples with above mentioned Ga⁺ -ions concentration as Fig. 5 shows - is completely different as initial ones. Curve 1 and 2 are typical for two samples with the same Ga⁺ -ions concentration ($\sim 1 \times 10^{17}$ -ions/cm³), but coloured with standard version with different number of F - centres. Surprisingly, as more is the number of F-centres as less is the intensity of absorption in the range 480 to 200 nm. These results indicate that in the standard electrolytical colouring, the new defects formed by nonstandard colouring are destroyed because of the relatively high temperature of the standard colouration. As seen from curves 4,5,6 and 7 in Fig. 5, the intensity of the new absorption bands increases with the concentration of the dopant and bands become more structured.

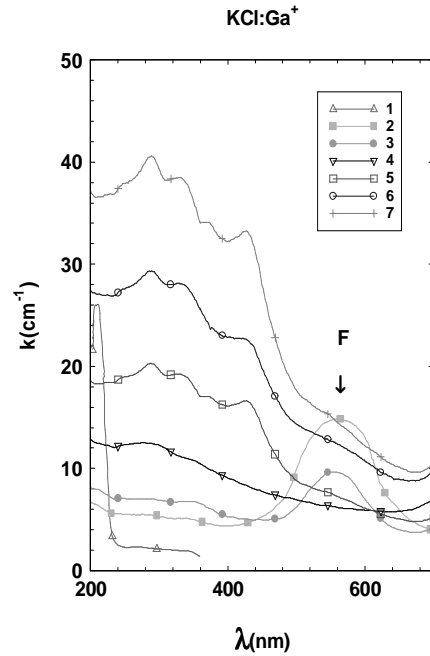


Fig. 5. Absorption spectra of KCl:Ga^+ crystals; 1 uncoloured; 2,3 coloured with F-centers; 4,5,6,7 non-standard coloured.

4.5 Emission spectra of KCl:Ga^+ samples before and after non-standard colouring

The emission and excitation spectra of uncoloured KCl:Ga^+ samples are the same as those reported in literature and prove again that only Ga^+ -ions are embedded in crystals. After nonstandard electrolytical colouring there are no traces of these ions detected which proves that all Ga^+ -ions are converted by this technique in new electronic defects. If the coloured samples exhibit no emission bands in UV and visible range, in NIR domain, as in the case of KCl:In^+ coloured sample, we found also two emission bands which belong to two different defects, because the intensities of these bands are changing even in the same sample and from sample to sample and sometimes appear only the band with low or high energy.

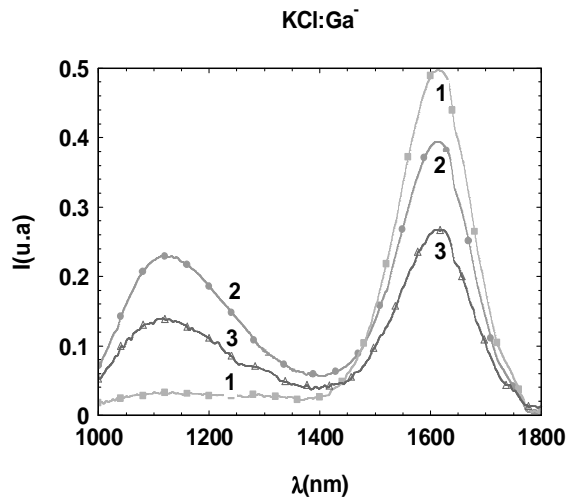


Fig. 6. Luminescence of KCl:Ga^- , in different points of the sample (non-standard electrolytical colouring) $\lambda_{\text{exc}}=514$ nm.

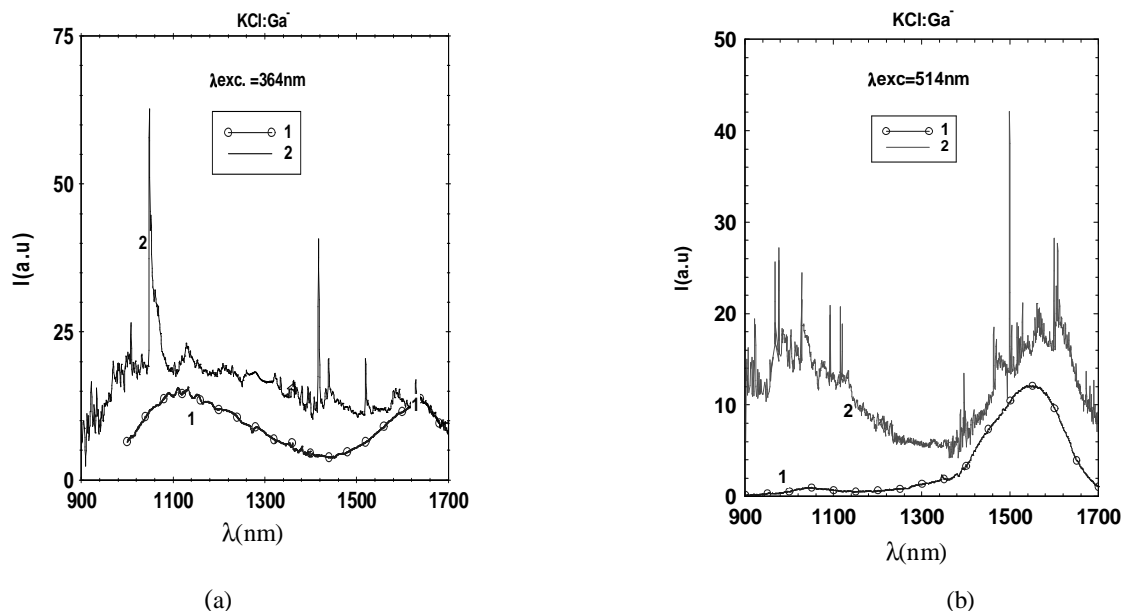


Fig. 7a. Luminescence of KCl:Ga⁻ crystals; excitation with $\lambda_{\text{exc}}=364$ nm.
 Fig. 7b. Luminescence of KCl:Ga⁻ crystals; excitation with $\lambda_{\text{exc}}=514$ nm.
 1. luminescence at RT; 2. luminescence at 4.2 K.

Fig. 6 shows the emission spectra of a KCl:Ga⁺ coloured sample with $\lambda_{\text{exc}}=514$ nm. If the excitation with 514 nm leads to two maxima at 1060 and 1600 nm, the excitation with 364 nm leads to slightly shifted maxima at 1120 nm and 1650 nm

The emission spectra are different when are excited with these two laser lines at 4.2 K as can be seen in Fig. 7a and 7b. Narrow vibronic lines are situated at different wavelengths, but the charge transfer character of emission spectra at low temperatures is the same as in the case of KCl:In⁺ coloured samples.

5. Discussion and conclusion

Taking into account all results presented above, we can not decide the structural model for the defects created by non-standard colouring. It is obvious that in our coloured samples Me_a⁻ -ions and/or aggregate of these Me_a⁻ -ions are created. These defects show all properties of NMI⁻ ions mentioned in introduction, which by experiences of migration in electric field prove, without doubt, that the non-standard electrolytical colouring convert all In⁺ and Ga⁺ - ions in In⁻ and Ga⁻ - ions in anionic sites by capturing two electrons from the F-centres and an anion vacancy. The In⁰, Ga⁰ and In⁰(1) and Ga⁰(1) centres are not formed by nonstandard electrolytical colouring because: a) no EPR signal of these defects is observed; b) absorption and emission spectra of our samples are totally different from the spectra of In⁰, Ga⁰, In⁰(1) and Ga⁰(1) ones published in [23,24].

A strong argument for the existence of NMI⁻ ions in our coloured samples is the conversion of new defects by thermal annealing in nanoclusters of In and Ga as the Figs. 8 and 9 show.

The presence of In_a⁻ and Ga_a⁻ dimers in the coloured samples is suggested by the appearance of narrow vibronic lines at low temperatures, a structure characteristic for aggregate colour centres [25].

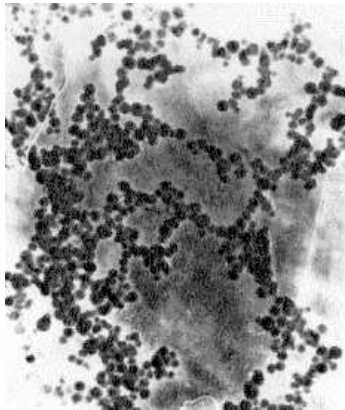


Fig. 8. TEM patterns of In-nanoclusters (1cm=144 nm).

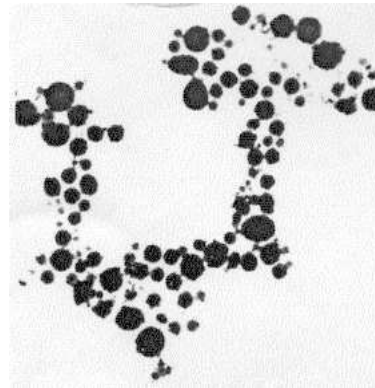


Fig. 9. TEM patterns of Ga-nanoclusters (1 cm=161 nm).

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