

Complex Centers in Wide-Gap Dielectrics

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Abstract – Spectra of absorption and luminescence of ammonium halide crystals doped with thallium in various concentrations are investigated. It is shown, that the long-wave bands quickly growing with growth of thallium concentration, belong to the dimer luminescent centers. The model of the dimer center is discussed.

1. Introduction

For spectra of absorption of ammonium halide crystals doped with s^2 ions three absorption bands are characteristic: A-, B- and C-bands [1]. Optical properties of s^2 centers of a luminescence in ammonium halide crystals are similar to those in alkali halide crystals. At increase of concentration of an impurity in spectra of a luminescence the contribution of the dimer centers consisting from two impurity ions in neighbour cation sites increases. The luminescence of these centers is shown already at small concentration of an impurity about 10-3 mol. %.

Spectra of absorption of the dimer centers are similar to spectra of absorption of the single centers [2]. It has allowed to carry out analogy between dimer and single centres and to designate absorption bands of the dimer centers in order energy growths as A', B', C'. Because of lower symmetry of the dimer center these bands are shown as multicomponent. For example, in spectra of excitation KI-(Tl^+)₂ are found out on three components A'- and C'-bands [3]. It corresponds to splitting three-componental 3P_1 and 1P_1 levels of thallium ion.

In emission spectra of the dimer centers in alkali halide crystals two bands are found out: long-wave and short-wave. Characteristics of short-wave emission are similar to characteristics of A-emission of the single centers that has resulted in the assumption that the electronic transitions corresponding to A-emission, occur from a level keeping substantially properties of an electronic A-level of a single ion of an impurity [4]. Long-wave emission is supposed similar to D-emission.

It represents the interest to investigate absorption spectra of ammonium halide crystals at various concentration of thallium. Unfortunately, samples with the large concentration of thallium to bring up from water solutions of ammonium halide salts difficultly, therefore we have taken advantage of a design procedure of absorption spectra from reflection spectra [5].

2. Experimental

We had been measured reflection spectra of polycrystalline samples at room temperature and at temperature of liquid nitrogen and in Kubelka-Munk ap-

proximation are counted on absorption spectra. In result four bands with maxima 4,75; 5,25; 5,4; 5,6 eV are received. The 5,25 eV band is the A-band of single Tl^+ -center and corresponds to transition $^1S_0 \rightarrow ^3P_1$. 5,4 and 5,6 eV bands grow with concentration of thallium.

The number of the centers responsible for 5,4 and 5,6 eV bands, is comparable to number of centers Tl^+ , whereas number of the dimer centers at concentration of thallium about 0,1 mol. % has the order 10-3 from number of single centers Tl^+ . 5,4 and 5,6 eV bands cannot be related to the dimer centers. At the same time the 4,75 eV band has such order (10-3) on intensity. Dependence of integral of a absorption band 4,75 eV from concentration of thallium is well approximated by a square-law parabola, i.e. this band can be connected to the dimer centers.

Similar bands are found out by us in spectra of excitation of crystals of ammonium chloride, bromide and iodide, activated by thallium. Long-wave bands of a luminescence belong to the dimer centers (Tl^+)₂.

3. Discussion

In ammonium halide crystals activated by high concentration of thallium (10-3 mol.% and higher) there are two groups of the centers of a luminescence. We categorize single Tl^+ ions with Oh environment symmetry as the first and ions Tl^+ with other environment symmetry which emission spectra coincide within the limits of experiment errors and integrals of absorption bands have one order of size. The centers of a luminescence concern to the second group with the excitation and emission bands shifted in the long-wave side which absorption band area is much less, than corresponding one of the single centers. The centers of the second group are the dimer centers.

There are two approaches in researches of the dimer center [3]. The first approach consists that the dimer center is considered as the ion of an impurity indignant of another neighboring ion. In the second approach the dimer center is considered as quasi-molecule. If for single s^2 centers there is well developed model in view of Jan-Teller effect [6] in case of the dimer centers of satisfactory model is not present.

If the role of the second components in the dimer center is reduced to perturbation of the first components electronic states which basically keeps properties of electronic states of a single ion this role the ion could play any distinct from Tl^+ ion. With the purpose of finding-out of a role of the second component of the dimer center we have measured luminescence spectra of system $NH_4Cl + 1 \text{ mol. \% } KCl + 0,005 \text{ mol. \% } TlCl$. The

contribution of the dimer centers is well seen in luminescence spectra of $\text{NH}_4\text{Cl-Tl}$ whereas in $\text{NH}_4\text{Cl-K,Tl}$ the single centers luminance only, and half width of excitation bands becomes less. It is possible to explain it to that presence of potassium in system stabilizes position of thallium and it does not allow the impurity "to be flown down" in aggregates. On the other hand, complexes Tl^+-K^+ can be formed instead of the dimer centers. However, we have not found out new bands in luminescence spectra and came to a conclusion, that systems such as Tl^+-K^+ can be related to the single centers because of very small influence neighboring K^+ ion on luminescence of Tl^+ ion. The similar result is received for a lot of other impurity. We activated crystals NH_4Cl in concentration 1 mol. % the following impurity: KCl , BaCl_2 , YCl_2 , TbCl_2 , CdCl_2 , SnCl_2 , MnCl_2 , SrCl_2 , MgCl_2 , NH_4Br , NH_4I , $(\text{NH}_4)_2\text{CrO}_4$. All these crystals contained TlCl in concentration 0,01 mol. % In excitation spectra of the investigated crystals the bands corresponding to the dimer centers have disappeared because of "fastening" single Tl^+ ions near to ions codopant. At the same time the centers similar to dimer were not shown.

Really, it is known, that already ions of the second coordination sphere weakly influence on spectral properties of cation impurity, the basic influence render environmental anions. In [7] it is shown, that overlapping integrals of none coupled electrons of Ga ions in relaxed excited state with wave functions of cations of the second coordination sphere are less than 5 %. It is necessary to expect the same result and for Tl^+ ion, having similar electronic structure. External similarity of absorption and emission spectra of the single and dimer centers is the basic argument for the benefit of the first approach. The role of the second components is reduced only to the perturbed factor.

The second approach was theoretically developed in [8, 9] where absorption bands of the dimer centers are interpreted. The basic difficulties of this approach are complexity of taking into account of anionic states though ones should play a significant role in interaction of ions – components of the dimer center, complexity of consideration of the nature of absorption bands. Satisfactory explanation for the single centers is available [10].

There are two models of the dimer center in crystals with structure of NaCl -type: with symmetry D_{4h} and with symmetry D_{2h} . The direction of an axis of the dimer centers in structure of CsCl -type in CsCl-Tl crystal is determined from azimuthal dependence of a luminescence as lengthways C_4 [11].

We had been measured a degree of polarization in bands of a luminescence of the dimer centers in crystals $\text{NH}_4\text{Cl-Tl}$ and $\text{NH}_4\text{I-Tl}$. Measurement was carried out under "excitation perpendicularly to emission" scheme at excitation of a crystal by the non-polarized light. The degree of polarization appeared in both cases weak $\sim 4\%$ in a direction $\langle 001 \rangle$ in $\text{NH}_4\text{I-Tl}$ and

$\langle 111 \rangle$ in $\text{NH}_4\text{Cl-Tl}$. Thus, symmetry of the dimer center in ammonium iodide is D_{4h} , and in ammonium chloride S_6 , i.e. in both cases an axis of the center is directed through anion.

At phase transition CsCl -type phase – NaCl -type phase the geometry of the dimer center can change. Sites where there are components of the dimer center in structure D_{4h} , pass in symmetry D_{2h} , sites with symmetry D_{2h} – in D_{2h} and D_{4h} , and sites with symmetry S_6 – in D_{2h} and D_{4h} . Half of neighboring sites of a cube leave on the distance exceeding a constant of a lattice in S_6 and D_{4h} symmetries, whereas sites with D_{4h} symmetry – only on $1/6$.

As, apparently, number of structures with ions of thallium on distances 2-3 E less average at phase transition the number of the dimer centers depending on symmetry of the centers should change essentially. Displacement of a maximum in the short-wave side and almost double growth of luminescence intensity in excitation spectra of $\text{NH}_4\text{I-Tl}$ crystal, measured in emission bands of the dimer centers, near to temperature (256 K) of phase transition CsCl-NaCl are appreciable.

Research of electron-phonon interactions on temperature broadening of luminescence bands of the thallium centers has enabled to estimate effective weight of the dimer center. It is known, that effective frequency of oscillators ω_{eff} is connected to effective weight m_{eff} a ratio (1):

$$\omega_{\text{eff}} = \sqrt{\frac{\alpha}{m_{\text{eff}}}} \quad (1)$$

In case of $\text{NH}_4\text{Cl-Tl}$ m_{eff} for bands of the dimer center approximately in 2 times it is more, than m_{eff} for Tl^+ . For crystals $\text{NH}_4\text{Br-Tl}$ and $\text{NH}_4\text{I-Tl}$ this ratio is equal 1.5. Thus, the size of effective weight shows that the dimer center has no more than two components.

The geometrical size of the dimer center can be estimated on trapping section of excitons. At research of energy transfer to the dimer centers at excitation of $\text{NH}_4\text{Br-Tl}$ crystal in exciton areas of a spectrum it is revealed, that the trapping section of excitons by the dimer centers approximately in 8 times exceeded trapping section of Tl^+ -centers. It speaks that the geometrical size of the dimer centers in 2-3 times exceeds a constant of a lattice, i.e. components of the dimer center are located in next cation sites.

4. Conclusion

Long-wave bands in absorption and excitation spectra of ammonium halide crystals, quickly growing with growth concentration of thallium belong to the dimer centers of a luminescence.

The distance between components of the dimer center does not exceed one constant of a lattice, i.e. they are in the nearest cation sites. Components of the dimer center are located through anion.

The second component of the dimer center plays the important role during excitation of the center.

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