Manifestation of the size effect in the optical and spectral properties of the \((\text{N(C}_2\text{H}_5)_4)_2\text{CoCl}_2\text{Br}_2\) nanoclusters incorporated into the polymer matrix

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Abstract. The spectral and non-linear properties of \((\text{N(C}_2\text{H}_5)_4)_2\text{CoCl}_2\text{Br}_2\) nanocrystallites incorporated into the polymer matrices were investigated. The temperature dependence of the photoinduced second harmonic generation (PISHG) demonstrates a remarkable dependence on temperature near the phase transitions. It has been found that the temperature of phase transition \(T_2\) in the nanostrustured ferroics could depend on host polymer matrix and is higher than those in the bulk material. It is suggested that this effect is connected with the surface tension coupled with polarization via electrostriction effect and the influence of the depolarization field arising around the surface of the nanocluster. The arising lateral pressure induces lowering of the symmetry of the metal-halogen complexes within the surface layer of the cluster. Their distortion is followed by more pronounced splitting of the degenerate energy levels due to the lower symmetry of the crystal field. The shift of the corresponding absorption bands as well as the suppression of the integral absorption in the region of the internal transition of \(\text{Co}^{2+}\) ion with diminishing of the nanocluster size is followed by considerable decreasing of PISHG intensity.

Keywords: nanocrystallites; phase transitions; tetraethylammonium tetrahalogeno-metallic compounds; photoinduced second harmonic generation; crystal field; surface tension; metal-halogen complexes

1. Introduction
Numerous crystals containing alkylammonium cations and inorganic anions are under detailed investigation of a great number of scientists due to the complicated sequences of different type phase transitions (PT), including transitions into the incommensurate phase, connected with dynamics of the organic cations and inorganic anions. Unfortunately, their technical application is restrained because of a high hygroscopicity, brittleness and damaging caused by overheating above 100 °C.

It was shown [1-4] that incorporation of the nanocrystallites (NC) into a polymer matrix may open a new opportunity for application of the semiconductor, oxide and dielectric NC as materials for photo-operated nonlinear optics, photorefractive devices as well as for optically operated modulators, Q-
switches, deflectors etc. Moreover, our preliminary dielectric study of the $(\text{N(C}_2\text{H}_5\text{)}_4\text{)_2CoCl}_3\text{Br}_2$ (TEACCB) nanocrystallites incorporated into a polymer matrix revealed the resonant type dielectric dispersion at comparatively high frequency of the measuring field (around 1.2 GHz) [4] that might find the effective technological application.

Recently the tetraethylammonium tetrahalogenometallic compounds $[\text{N(C}_2\text{H}_5\text{)}_4\text{)]_2\text{MeX}_4$ (abbreviately TEAMeX; Me = Co, Zn, Cu, Mn; X = Cl, Br) as well as TEACCB have been the subject of considerable attention [3, 5–7, 8]. According to [3] the bulk TEACCB crystal undergoes two structural phase transitions below room temperature:

$$T_2 \quad 224 \text{K (on cooling)} \quad T_2 \quad 249 \text{K}
\quad 232 \text{K (at heating)}$$

These crystals are of particular interest because they combine the organic cations with the inorganic anions. In this case the ethylene cations with the prevalingly covalence type of bonds coexist with the prevalingly ionic anionic tetrahedra. Moreover, due to availability of the transition metal complexes one can expect a substantial influence of the $p$-$d$ charge transfer playing important role in the optical properties as well as in the electron-phonon interactions.

The preliminary investigations of the nonlinear optics effects in TEACCB nanoclusters incorporated into oligoetheracrylate (OEA) matrix have shown that the intensity of the photoinduced second harmonic generation decreases with decreasing of crystallite sizes [3]. The choice of OEA as well as polymethylmethacrylate (PMMA) matrices allows to keep the nanocrystallites in the relatively low strained surrounding background contrary to the traditional high stiffness polymers. The observed size dependence of the photoinduced second harmonic generation is also followed by the high temperature shift of the phase transition point $T_2$. These phenomena were related to the quantum size effect, although, their nature is still not clear enough. This work is devoted to detailed study of the size effects manifestation in the optical and spectral properties of the nanoclusters of TEACCB embedded into the different polymer matrices.

2. Experimental

The samples of $[\text{N(C}_2\text{H}_5\text{)}_4\text{)]_2\text{CoCl}_3\text{Br}_2$ were grown from aqueous solutions of $\text{N(C}_2\text{H}_5\text{)}_4\text{Cl}$, $\text{N(C}_2\text{H}_5\text{)}_4\text{Br}$, CoCl$_2$ and CoBr$_2$ salts taken in the stoichiometric ratio. The absorption spectra were recorded using ZMR-3 monochromator. The optically-induced experiment was similar to that described in [9]. The 1.32 μm Nd:YAG laser as a fundamental ones and its second harmonic as pumping ones were used for the photoinduced second harmonic generation measurements.

For the investigations of the PISGH and absorption spectra in the region of internal transition of Co$^{2+}$ ion the synthesized samples were crushed using external acoustical focused field to the sizes within the 8-50 nm with dispersion of the sizes varied between the 3-14 nm. The powder-like NC specimens were dispersed in the liquid OEA photopolymer composition. The solidification process and electropolinig homogenization were performed by a method described in [1]. Nitrogen laser with $\lambda = 377$ nm and the photon energy power density about 65 W/cm$^2$ was used for the solidification.

The large size NC (70-80 nm) incorporated into the polymethylmethacrylate matrix were prepared for the optical absorption edge investigation. In this case the prepared nanoparticles were firstly mixed with polymethylmethacrylate in appropriate ratio and then dissolved in the organic solvent. After evaporating of the solvent the samples with 0.05–0.3 mm thickness and TEACCB nanoparticles concentrations of 3%, 5% and 7% were obtained.

3. Results and discussion

The absorption spectra corresponding to the internal transition of Co$^{2+}$ ion for the TEACCB bulk and nanocrystals of different sizes incorporated into olygoetheracrylate matrix reflect clearly the size effect...
(see Fig.1). In order to compare the data for the different samples, the spectra corresponding to the nanocrystals were normalised with accounting of the cobalt ion concentration in a sample. As it is clearly seen from Fig.1 the absorption spectra of the nanoclusters are characterised by the pronounced complex structure. Indeed, instead of the one intensive slightly asymmetric broad band for the bulk material, for the case of the nanoclusters one can observe the new bands arising at the high energy part of the spectra. Their energies are the higher the lower are the crystallite size. Besides, one can observe a clear splitting of the main intensive band that becomes the most pronounced for the case of the smallest nanoclusters.

![Absorption spectra](image)

**Fig. 1** Absorption spectra corresponding to the internal transition of Co^{2+} ion for the TEACCB bulk and nanocrystals of different sizes incorporated into oligoetheracrylate matrix

In order to perform an unambiguous assignment of the observed absorption band the spectra have to be approximated with the Gaussian line-shapes (Fig.2). The identification of the elementary bands was performed on the basis of corresponding spectroscopic study of the single crystals [8]. The $A$ and $B$ bands for the bulk material should be related to the spin allowed and spin forbidden electron transition on the degenerated energy levels respectively [8] (see Table 1). In the case of the absorption spectra of the nanoclusters the corresponding terms are splitted due to the lower symmetry of the crystal field. The degree of this splitting is the more pronounced the lower are the cluster sizes. On the basis of the obtained data one can conclude that such a splitting is connected with distortion of the metal-halogen complexes within the surface layers of the nanoclusters due to the surface tension. One can expect that the ratio of these distorted surface complexes increases with diminishing of the cluster sizes. It means that the most pronounced splitting of the two initial absorption bands have to be observed for the case of the smallest nanoclusters that is really observed in the experiment. It is also necessary to note that the oscillator strength of the two initial bands observed in the bulk crystal is “distributed” between the larger number of bands in the samples with nanoclusters that implies a noticeable decrease of absorption in the framework of 1.5-2.0 eV. This fact has to be taken into account in the nonlinear optics investigations since the wavelength of the light used for pumping also lies in the same region. At the same time, a clear blue shift of the high energy bands with decreasing of the cluster size would be considered as manifestation of the quantum size effect. Indeed, the confinement of the electrons and holes within the narrow potential well implies increase of their kinetic energy [10].
Fig. 2 Approximation of the absorption spectra corresponding to the internal transition of Co$^{2+}$ ion by Gaussian lineshapes for bulk and nanocrystals of the TEACCB incorporated into OEA-matrix.

Table 1
Parameters of the bands of the TEACCB bulk and nanocrystals incorporated into OEA-matrix

| Transition from $^4A_2$ ($^2F$) on | Bulk  | Nanocrystals |
|-------------------------------------|-------|--------------|
|                                     |       | 70 nm** | 50 nm | 12 nm | 8 nm |
| $^4T_1$ ($^4P$)                     | 1.67  |       | 1.71  |       | 1.67 |
|                                     | 1.75  | -      | 1.86  | 1.73  | 1.74 |
|                                     |       |       | 1.92  | 1.90  |       |
| $^2E$ ($^2G$)                       | 1.90  | -      | 2.33  | 2.49  | 2.71 |
| Charge transfer band* $Xnp \rightarrow Co3d$ | 4.20  | -      | -     | -     | -    |

(* $Xnp$: Cl$3p$ or Br$4p$)
(** incorporated into PMMA matrix)

Taking into account that absorption in the high energy region of the spectra corresponding to the charge transfer transitions was found to be very high for the TEACCB NC in the OEA-matrix, we have prepared the samples with nanoclusters incorporated into the polymethylmethacrylate matrix. This allowed us to identify clearly the complex charge transfer band in vicinity of 4.20 eV that cannot be observed in the bulk crystal due to the very large absorption in this spectral range (Fig. 3). In this case we take into account that the absorption edge of PMMA lies above 5 eV. Under such circumstances it is
possible to obtain more detailed information concerning the entire energy diagram for TEACCB. Moreover, it is possible to estimate the energies of the charge transfer transitions not only for the NC but also for the bulk crystals.

![Diagram](image)

Fig. 3. The high energy part of the absorption spectra of the TEACCB: bulk (pentagons), pure PMMA (squares), composite (PMMA+TEACCB) (triangles), nanocrystals (∼70 nm) (circles)

The investigations of the considered composites containing the NC offer possibility to study the first order phase transitions. They cannot be studied in a single crystal since the samples are cracked under the influence of internal tensions arising at the first order PT at $T_2$. The temperature dependences of absorption of TEACCB nanocrystals incorporated into PMMA-matrix at constant wavelengths in the region of the charge transfer band measured in a wide temperature region are presented at Fig. 4. It is worth to note, that such dependences possess the global hysteresis in the temperature region of 160-320 K, which could be connected with the electret properties of PMMA matrix [11]. As it is clearly seen, these dependences manifest anomalies at the temperatures of PTs close to those in a single crystal (see Table 2). However, below $T_2$ one can note an additional anomaly at $T_3$, which could be related to the previously unknown phase transition that could not be observed in a single crystal due to the above mentioned reason. It is worth to note that the phase transitions including those at $T_3$, were also observed in the temperature dependences of PISGH but at somewhat different temperatures. Under such circumstances one can conclude that the phase transition temperatures considerably depend on the type of polymer matrix used for preparing of such composites (see Table 2).
Fig. 4 Temperature dependences of absorption of the TEACCB nanocrystals incorporated into PMMA-matrix obtained at the constant wavelength $\lambda=350$ nm in a heating and cooling (insert) runs.

Table 2
The temperatures of the phase transitions in TEACCB - bulk and nanocrystals incorporated into a polymer matrix obtained at cooling (corresponding PT temperatures obtained for heating run are shown in parenthesis) on the basis of dielectric\textsuperscript{1} [3], optical spectroscopy\textsuperscript{2} and nonlinear optics\textsuperscript{3} data.

| Sample                        | $T_1$ (K) | $T_2$ (K) | $T_3$ (K) |
|-------------------------------|-----------|-----------|-----------|
| TEACCB bulk\textsuperscript{1} | 249       | 224 (232) | -         |
| TEACCB NC (70 nm) in PMMA-matrix\textsuperscript{2} | 247       | 219       | 202       |
| TEACCB NC (50 nm) in OEA-matrix\textsuperscript{3} | 238       | 225       | $\sim 210$ |
| TEACCB NC (12 nm) in OEA-matrix\textsuperscript{3} | 238       | 225       | $\sim 210$ |
| TEACCB NC (8 nm) in OEA-matrix\textsuperscript{3} | 237       | 230       | 223       |

On the basis of the performed spectroscopic study one can make the conclusion concerning the nonlinear optics properties of the TEACCB nanocrystals incorporated into OEA-matrix. The temperature dependence of the PISHG demonstrates a remarkable dependence on temperature near the PTs (see Fig. 5). Indeed, for the samples with larger nanocrystallites the clear jumps are observed at the temperatures $T_f=238$ K and $T_f=225$ K (at cooling), close to the PT points in the bulk solid solution. The low temperature jump for the sample with the smallest nanocrystallites is clearly shifted toward higher temperatures: $T_f=230$ K. One can also note the lower values of the PISHG in the latter case. On the basis of the performed investigations one can conclude that the temperature of phase transition $T_2$ in the samples with the smallest nanoclusters is higher than the one of the bulk material. The low temperature maxima on the corresponding dependences could be related to the phase transition at $T_3$. This PT is also shifted toward higher temperatures with diminishing of the NC sizes. Taking into account the supposed improper
ferroelectric origin of the phase lying in the framework of $T_2^0-T_3^0$ one can suggest that this effect is connected with the surface tension coupled with polarization (and order parameter) via electrostriction effect and the influence of the depolarization field arising around the surface of the nanocluster [12]. As a result the improper ferroelectric phase is suppressed with decreasing of the nanocrystallite size. Such a quantum size effect should be considered as a characteristic feature of the nanostructured ferroelectrics [12]. The shift of the corresponding absorption bands due to the lowering of the crystal field symmetry as well as the suppression of the intensity of the band $A$ with diminishing of the nanocluster size is followed by considerable decreasing of PISHG intensity in all crystal phases.

![Graph showing Photoinduced SHG versus temperature for the TEACCB nanocrystallites of different sizes incorporated into the OEA-matrix](image)

Fig. 5 Photoinduced SHG versus temperature for the TEACCB nanocrystallites of different sizes incorporated into the OEA-matrix

The temperature $T_1$ of the high temperature phase transition for the TEACCB nanocrystallites is also shifted in respect to the case of a bulk crystal. But this effect does not show clear size dependence and mostly is connected with the influence of the matrix type.

4. Conclusions:
On the basis of performed investigations it has been found that the temperatures $T_2$ and $T_3$ of phase transitions increase with decreasing of the TEACCB cluster size and are higher than those in the bulk material (at least for $T_2$). Taking into account the supposed improper ferroelectric origin of the phase lying below $T_2$ one can suggest that this effect is connected with the surface tension coupled with polarization via electrostriction effect and the influence of the depolarization field arising around the surface of the nanocluster [12]. As a result the improper ferroelectric phase is suppressed. Besides, the arising lateral pressure induces lowering of the symmetry of the metal-halogen complexes within the surface layer of the cluster. Their distortion is followed by more pronounced splitting of the degenerate energy levels due to the lower symmetry of the crystal field. At the same time the blue shift of the high energy elementary bands with decreasing of the cluster size is supposed to be due to the quantum confinement effect. The
shift of the corresponding absorption bands as well as the suppression of the intensity of the integral absorption in the region of the internal transition of Co$^{2+}$ ion with diminishing of the nanocluster size is followed by considerable decreasing of PISHG intensity.

This work was supported by Ministry of Education and Science of Ukraine.

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