

## Effect of polymer matrix on the structure and luminescence properties of barium zirconate nanocrystals

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**The influence of polymer environment on the luminescent properties of barium zirconate nanocrystals has been studied by cathodoluminescence (CL) spectroscopy. It was found that a polystyrene (PS) shell around the BaZrO<sub>3</sub> nanocrystals significantly modifies the CL spectra. This phenomenon can be explained by interaction between the PS matrix and the BaZrO<sub>3</sub> particles, changing the surface states of the nanocrystals. This conclusion is confirmed by complementary experimental studies including X-ray diffraction, FTIR spectroscopy and scanning electron microscopy.**

**BaZrO<sub>3</sub> nanocrystals / Polystyrene / Hybrid composite / Perovskites / Cathodoluminescence spectroscopy**

### Introduction

The synthesis of polymeric composites with inclusions of semiconductor nanoparticles is a new method of preparation of materials for electro-optics, sensor devices and alternative energy sources (solar cells), using simple, safe, energy-efficient technology [1-4]. Organic-inorganic hybrid systems are among the most promising for flexible solar cells, since they have a large interface surface, where effective dissociation of excitons (bound electron-hole pairs) can occur, and two separate channels for efficient transport of electrons and holes [4]. Inorganic/organic nanosystems based on semiconductor nanocrystals and conductive polymer matrices (polyaniline, polythiophene [3,4]), or thermoplastic polymer matrices such as polymethyl methacrylate (PMMA) and polystyrene (PS) [1,2], are nowadays being actively investigated. Thermoplastic polymers are useful for optical applications, due to complete transparency in the visible range of the spectrum and relatively high stability. For the preparation of nanocomposites based on polymers and semiconductors, inorganic nanocrystals such as CdTe, CdSe, ZnS, CdS, and GaSe are used [1-4]. The interesting physical properties of perovskites, in particular of barium zirconate, offer a possibility to

obtain new hybrid materials with useful functions. Despite this, polymer composites with perovskites remain almost unexplored.

In general, barium zirconate BaZrO<sub>3</sub>, due to its high thermal resistance, may be applied in manufacturing of electroceramics and refractories [5-10]. The BaZrO<sub>3</sub> perovskite has found several applications as substrate for the synthesis of superconductors and high-temperature microwave dielectrics; it can be used in fuel cells and in proton conductors. Recently BaZrO<sub>3</sub> attracted great attention as a fluorescent material [5-7]. We may note that many ABO<sub>3</sub> perovskites can reveal characteristic luminescence in the visible range (sometimes called "green" luminescence) peaking at 2.2-2.6 eV. The origin of this luminescence has been widely discussed and several mechanisms have been proposed [11-15].

It has been shown that the luminescent characteristics of BaZrO<sub>3</sub> significantly depend on the fabrication technology of the nanocrystals [14-16]. However, the effect of a polymeric environment on the structure and physical properties of luminescent nanocrystals has been little studied. In the present work we have studied the luminescent properties of hybrid composites based on different polymer matrices and nanocrystals of BaZrO<sub>3</sub>.

## Experimental

### Materials and compounds

Commercial BaZrO<sub>3</sub> powder (grain size  $d < 50$  nm) from ALDRICH was used for the preparation of hybrid composites. Conductive polymers: polyphenyl acetylene (PPA), poly-3,4-ethylenedioxythiophene (PEDOT), and dielectric polymers: polyvinyl alcohol (PVA) and polystyrene (PS), were used as polymer matrices. PPA was synthesized by electrochemical polymerization [17], PVA used as commercial product (P/2 mark), PEDOT in the form of an 1.5% aqueous suspension of polymer stabilized by an anionic surfactant, polystyrene sulfonic acid from ALDRICH. Polystyrene was synthesized by suspension polymerization of styrene in the presence of peroxide initiators of polymerization: benzoyl peroxide and ammonium persulfate, with a stabilizer of suspension: starch, as described in [18].

The samples for the investigation were prepared by ultrasonication of 7-40 mg of BaZrO<sub>3</sub> nanopowder in a 0.1 M solution of toluene sulfonic acid (TSA) and then in a 5% solution of polymer matrix for 10 minutes to obtain a uniform dispersion. For solvent evaporation the samples were dried in dynamic vacuum at 60°C for 6-8 h to constant mass. All the investigated samples were prepared as pellets.

### Measurements

Optical and luminescent spectroscopy under electron beam excitation are powerful experimental methods for the study of electronic properties of wide band gap materials, as well as of nanocrystalline semiconductors [19,20], including perovskite materials [21-23]. In the current study, excitation of cathodoluminescence (CL) was provided by a pulse-mode electron gun with the following parameters: electron beam energy 10 keV at a current of 100  $\mu$ A, pulse duration 2  $\mu$ s at a frequency of 300 Hz. CL spectra were recorded in the range 1.0-5.0 eV at room temperature ( $T = 293$  K) and liquid nitrogen temperature ( $T = 80$  K), using a specially designed unit, as described in [24].

Investigation of the molecular structure of the polymer composites was carried out by Fourier Transform Infrared Spectroscopy (FTIR), using an AVATAR-320N spectrophotometer in the wave number range 400-4000  $\text{cm}^{-1}$  at room temperature. A FTIR spectrum of BaZrO<sub>3</sub> powder was obtained using the KBr pellet method. Samples of polymer matrix and hybrid composites were obtained as thin layers on the surface of KBr single crystals.

X-ray powder diffraction data were collected on an automatic diffractometer STOE STADI P with a linear PSD detector (transmission mode; Cu  $K\alpha_1$  radiation; curved germanium (111) monochromator),  $2\theta$ -range:  $4 \leq 2\theta \leq 110$ . Standard Reference

Materials NIST SRM 640b (Si) and NIST SRM 676 (Al<sub>2</sub>O<sub>3</sub>) were used for the calibration of the diffractometer.

X-ray phase analysis (XPD) was performed using the Powder Cell [25] and LATCON [26] codes. The average apparent size and average maximum strain of the grains were determined by simplified integral breadth methods, using the profile fitting procedure. Intrinsic broadening was taken into consideration in the calculations, using instrumental resolution files obtained by profile fitting of the primary beam and NIST SRM 676 (Al<sub>2</sub>O<sub>3</sub>).

The morphology of the hybrid composites was studied with a scanning electron microscope (SEM) REMMA-102-02. For the sample preparation, a dispersion of polymer-semiconductor was dropped onto the surface of a silicon single crystal (111) and then dried under vacuum to complete evaporation of the solvent.

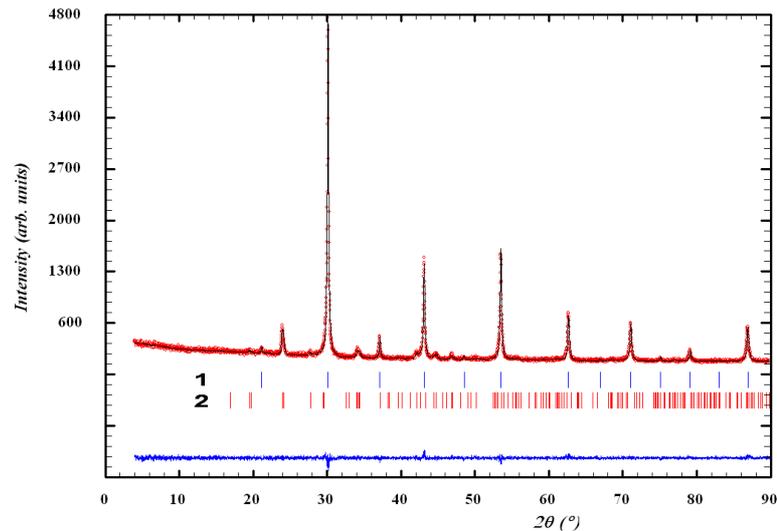
## Results and discussion

According to the results of the X-ray phase analysis (Fig. 1), the investigated commercial samples of barium zirconate powders contain two phases: the main phase is BaZrO<sub>3</sub> (structural type: perovskite CaTiO<sub>3</sub>, space group  $Pm-3m$ ), refined unit cell parameter  $a = 4.19083(6)$  Å, average size of coherent scattering domains (in approximation – average grain size of the phase) – 22.6 nm, average maximum internal stress in the grains –  $3.9 \times 10^{-3}$ . The additional phase is BaCO<sub>3</sub> (structural type: calcite CaCO<sub>3</sub>), representing 13.5 mass%, which is typically attributed to the method of synthesis of barium zirconate [5,7]. However, zirconium dioxide ZrO<sub>2</sub> was not detected in the tested samples.

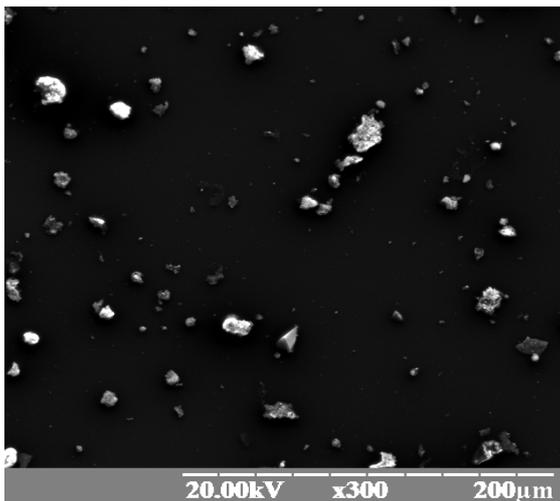
In the process of formation of BaZrO<sub>3</sub> composites with polymers of different nature (PPA, PEDOT, PVA, PS), the inorganic component is embedded in a polymer matrix (Fig. 2). Due to the excessive surface energy of nanocrystals, agglomeration can occur during the formation of the composites. Consequently, the size of the inorganic particles increases. On the other hand, the polymer matrix forms a shell around the inorganic nanoparticles and the sintering process is stabilized [2,3,27].

Although it is known that the luminescent characteristics of BaZrO<sub>3</sub> depend to a large extent on the method of preparation of the nanocrystals [7,8], there exists to our knowledge no investigation devoted to the modification of luminescence emissions in BaZrO<sub>3</sub> powders under the influence of a polymer matrix.

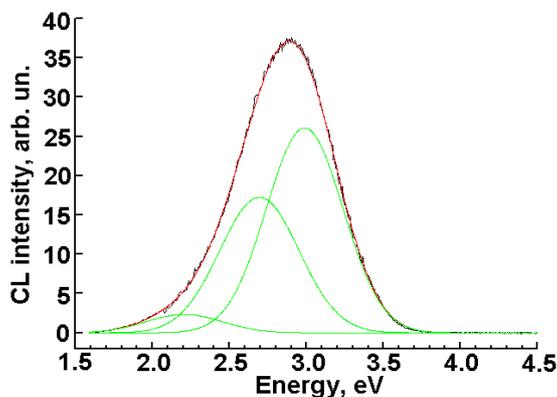
The CL spectrum of the nano-BaZrO<sub>3</sub> pellet presented in Fig. 3 can be decomposed into three bands with maxima at  $E = 2.99, 2.69$  and  $2.2$  eV. It is typical for a multiphonon and multilevel process in a system in which relaxation occurs *via* several paths.



**Fig. 1** Observed and calculated X-ray powder profiles for the sample of commercial BaZrO<sub>3</sub> powder. Experimental data (circles) and calculated profile (solid line through the circles) are presented together with the calculated Bragg positions (vertical ticks, 1 for BaZrO<sub>3</sub> and 2 for BaCO<sub>3</sub>) and difference curve (bottom solid line). Final reliability factors (in %):  $R_p = 5.74$ ,  $R_{wp} = 7.46$ ,  $R_1 = 2.56$  for BaZrO<sub>3</sub>.



**Fig. 2** SEM image of the surface of the PS-BaZrO<sub>3</sub> (10%) composite.



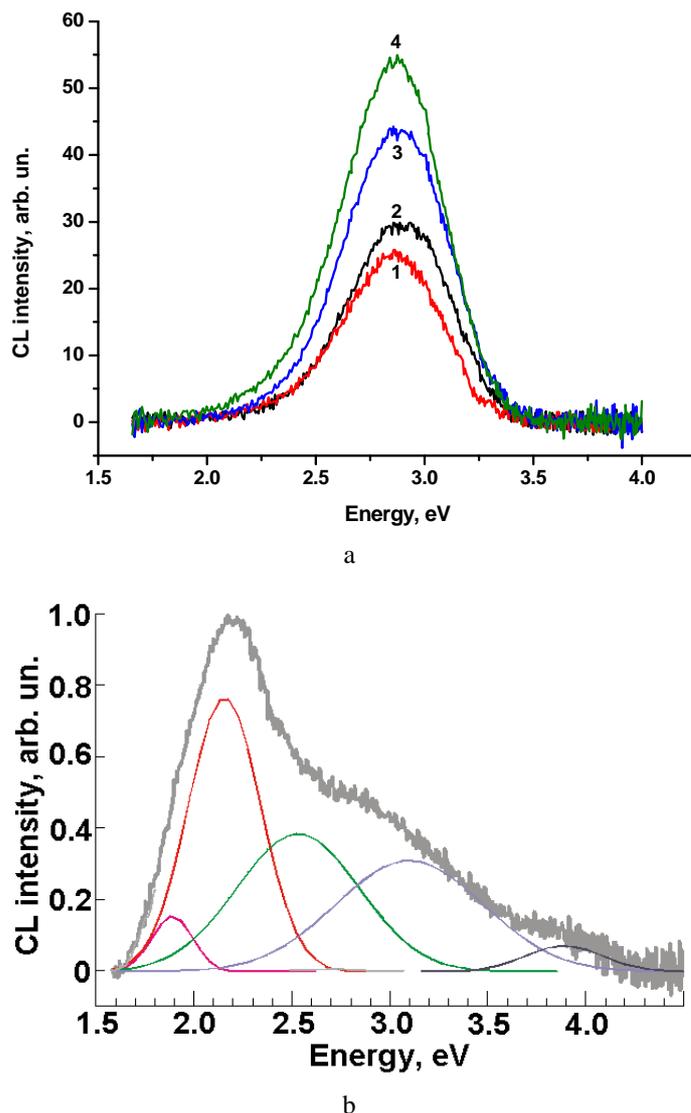
**Fig. 3** CL spectrum of BaZrO<sub>3</sub> nanocrystals at  $T = 293$  K.

This behavior is related to the structural disorder of BaZrO<sub>3</sub> and confirms the presence of additional electronic levels in the forbidden band gap controlled by  $[\text{ZrO}_5 \cdot \text{V}_\text{O}^*] - [\text{ZrO}_6]$  complex clusters [11-16].

It can be seen that entering the BaZrO<sub>3</sub> nanocrystals into a polymer matrix of PPA, PVA, PEDOT has no significant effect on the characteristics of the CL emission (Fig. 4,a). The position of the luminescence maximum ( $E = 2.83 \pm 0.02$  eV) and the shape of the line do not undergo significant changes. However, as expected, the intensity of CL of the composites depends on the content of inorganic phase and increases with increasing BaZrO<sub>3</sub> concentration, both at low and room temperatures (Fig. 4,a). This is in good agreement with the behavior of CdTe nanocrystals in a PS matrix [2], where no modification of the energy parameters of the emission was observed.

Among the hybrid polymer-BaZrO<sub>3</sub> composites, only the matrix of polystyrene caused strong modifications in the CL spectrum. The Gaussian decomposition of the CL curves shows energy bands at  $E = 1.9, 2.15, 2.45, 3.0,$  and  $3.96$  eV and significant reduction of the intensity (Fig. 4,b).

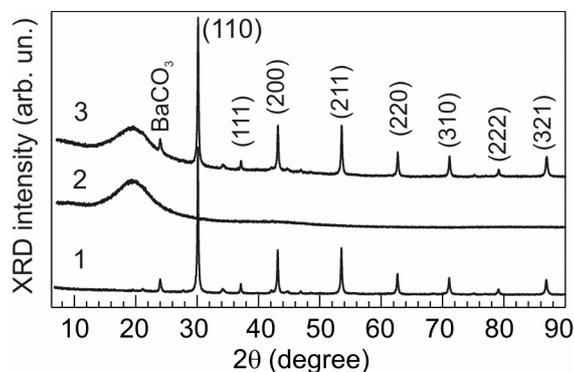
Suggesting that the changes in the CL emission for BaZrO<sub>3</sub> under electron beam excitation depend on the crystal lattice parameters, structure investigations were carried out. From the XRD analysis of BaZrO<sub>3</sub>, polymer and the PS-BaZrO<sub>3</sub> hybrid composites, it was found that, in contrast to the series of crystalline reflections from BaZrO<sub>3</sub> (Fig. 5, curve 1), for the polymer matrix only a broad peak is observed with a maximum at  $2\theta = 19.53^\circ$  (Fig. 5, curve 2). In the diffraction spectrum of the composite of PS and BaZrO<sub>3</sub>, coexistence of the broad peak of PS and sharp diffraction peaks of BaZrO<sub>3</sub> (Fig. 5, curve 3) is observed.



**Fig. 4** (a) CL spectra of nano-BaZrO<sub>3</sub>-PPA composites with a BaZrO<sub>3</sub> content of 80% (1), 90% (3) and 100% (4) and PEDOT-BaZrO<sub>3</sub> (60%) composites at  $T = 293$  K (2); (b) CL spectrum of a PS-BaZrO<sub>3</sub> (20%) composite.

In the composite the  $a$ -parameter of the unit cell of the BaZrO<sub>3</sub> phase decreases from  $a = 4.19083(6)$  Å to  $a = 4.1879(2)$  Å, while the microstructure parameters remain similar to those of pure BaZrO<sub>3</sub> (average grain size of the phase – 23.0 nm, average maximum internal stress in the grains –  $4.0 \times 10^{-3}$ ). Hence, for the BaZrO<sub>3</sub> phase in this composite, the  $a$ -parameter of the unit cell has decreased, indicating a change in the structure of the nanocrystals under the action of the PS matrix.

FTIR spectra of the BaZrO<sub>3</sub> nanocrystals, of the PS matrix and its composite with BaZrO<sub>3</sub>, are presented in Fig. 6. In the IR spectrum of the commercial BaZrO<sub>3</sub> nanopowder (Fig. 6, curve 1), the vibration band observed at  $1450 \text{ cm}^{-1}$  is attributed to the existence of carbonate CO<sub>3</sub><sup>2-</sup> groups in



**Fig. 5** X-ray powder diffraction pattern of BaZrO<sub>3</sub> nanocrystals (1), PS matrix (2) and PS-BaZrO<sub>3</sub> composite (3).

the nanopowder with small amounts of BaCO<sub>3</sub> [28,29]. The large vibration band appearing in the range 750-550 cm<sup>-1</sup> is due to Zr-O vibrations in the perovskite structure [29]. The maximum of this band is observed at 596 cm<sup>-1</sup>.

The FTIR spectra of the polymer matrix (Fig. 6, curve 2) and composite (Fig. 6, curve 3) exhibit almost identical spectral features, but different intensities. In both spectra, well-defined absorption peaks are observed at the following wave numbers: 3061, 3027, 2852, 1944, 1601, 1583, 1493, 1154, 1028, 908, 756, 698, and 602 cm<sup>-1</sup>, characteristic of PS [30,31]. In the spectrum of PS-BaZrO<sub>3</sub> some decrease of the intensity of the absorption bands of PS occurs in the whole spectral range, due to the lower concentration of PS in the composite. In the region of wave numbers 750-550 cm<sup>-1</sup>, the relative intensity of the absorption band at 602 cm<sup>-1</sup> for the composite is almost twice as high as the corresponding band for the PS matrix (Fig. 6, curve 3). This may be connected with overlap of the BaZrO<sub>3</sub> band with the absorption band of the polymer matrix.

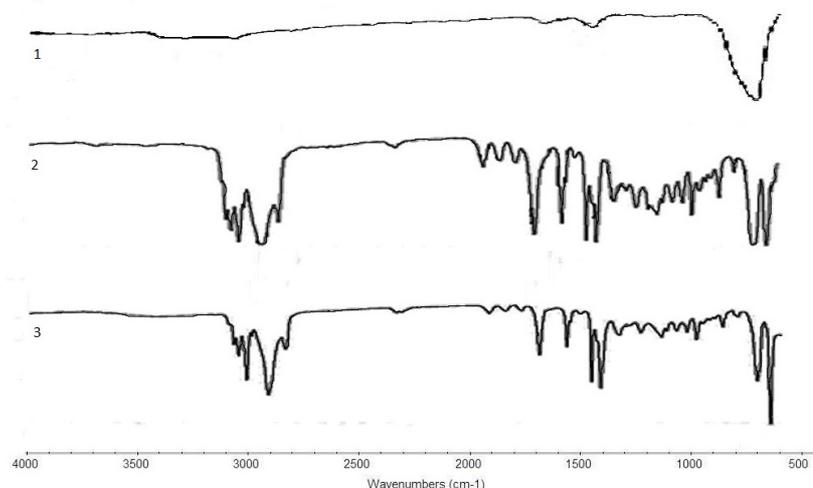
It is worth noting that, in the spectra of the matrix of PS suspension (Fig. 6, curve 2) and the composite based on it (Fig. 6, curve 3), quite intense absorption band with maximum at 1720 cm<sup>-1</sup> appears. A decrease of the normalized intensity of this band ( $I_{1720} / I_{1601}$ ), from 1.2 (PS) to 1.08 (composite), may also be noted. We suggest that the absorption band at 1720 cm<sup>-1</sup> may be attributed to a functional group responsible for interactions between the PS matrix and the surface of the BaZrO<sub>3</sub> nanocrystals. This absorption band corresponds to the stretching vibrations of the carbonyl group connected with residual hydrocarbon radicals in the PS matrix R'R''C=O [30]. This group probably appears during the polymerization process, as a result of oxidation of the polystyrene backbone by the peroxide initiator [31] with formation of compounds containing carbonyl groups.

The described modifications in the CL spectra of the BaZrO<sub>3</sub> phase in the composite can be connected with changes in the substructure of the BaZrO<sub>3</sub> surface under influence of the polystyrene matrix. It has been shown [27,32] that luminescence in hybrid composites based on an oxide (ceramic) core and a PMMA shell depends on the interface, where PMMA is connected via carboxylate bonding to the surface of the ceramic nanoparticles [32]. In this case, luminescence is likely to originate at the carbonyl group of the coating polymer.

Based on the obtained results, one can assume that adsorption of polystyrene on the surface of a semiconductor leads to changes in the surface states of the nanoparticles [27]. In this case fragments of PS directly touch the nanocrystal surface and are bound to the surface *via* an oxygen atom, as described in [32]. This creates new energy states of the interface, which, together with the decrease of the lattice parameter, lead to modifications of the CL spectra.

## Conclusion

We have studied the effect of different polymer matrices on the emission properties and structure of hybrid composites with barium zirconate nanocrystals. It was established that a matrix of polystyrene suspension has a clear influence on the cathodoluminescence spectra of nano-BaZrO<sub>3</sub>. In the spectra of the hybrid composite several additional emission bands were observed at  $E = 1.9$ , 2.15, 2.45 eV and a high-energy band near  $E = 4$  eV, absent in the spectra of BaZrO<sub>3</sub> nanocrystals. The modification of the CL spectra in the composites may be caused by changes in the substructure of the nanocrystals under the influence of the PS matrix. The decrease of the lattice parameter (from 4.19083(6) in BaZrO<sub>3</sub> to 4.1879(2) Å in the BaZrO<sub>3</sub>-PS composite)



**Fig. 6** FTIR spectra of commercial nanopowder BaZrO<sub>3</sub> (1), polystyrene matrix (2) and the polystyrene-BaZrO<sub>3</sub> (10%) composite (3).

and adsorption interactions between the PS matrix and the surface of the BaZrO<sub>3</sub> grains were confirmed by FTIR spectra. It was also found that the other studied polymers (PPA, PEDOT and PVA) did not have any significant effect on the luminescence spectra of the nanocrystals. The obtained results may be used to create hybrid composites with modified or non-modified CL spectrum for targeted production of new functional materials.

### Acknowledgments

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