



Research articles

Study of d0 magnetism of BaF₂ nanopowder after thermal and radiation exposureV.G. Ilves^{a,*}, S.Yu. Sokovnin^{a,b}, M.G. Zuev^{c,d}, A.M. Murzakaev^{a,e}^a Group of Electro-physical Technologies, Institute of Electrophysics Ural Branch Russian Academy of Sciences, Yekaterinburg 620016, Russia^b Institute of Physics and Technology, Ural Federal University, Yekaterinburg 620002, Russia^c Institute of Solids State Chemistry, Ural Branch Russian Academy of Sciences, Yekaterinburg 620990, Russia^d Department of Physical and Colloid Chemistry, Institute of Chemical Engineering, Ural Federal University, Yekaterinburg 620002, Russia^e Department of Fundamental and Applied Physics, Institute of Natural Sciences and Mathematics, Ural Federal University, Yekaterinburg 620002, Russia

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ABSTRACT

Mesoporous nanocrystal BaF₂ nanopowders (NPs) have been obtained with the pulsed electron beam evaporation (PEBE) technique. The transformation of the structure and morphology of BaF₂ nanoparticles (NPLEs) induced by thermal annealing in air at temperatures of 200, 400, and 900 °C has been monitored with the XRD, SEM, and HRTEM methods. The HRTEM analysis has shown the presence of three polymorph phases (cubic, octahedral, and hexagonal) in the unannealed NP. Upon the transition into the nanoscale, diamagnetic (DM) BaF₂ (in the volume state) has demonstrated both paramagnetic (PM) and ferromagnetic (FM) responses at room temperature. The thermal analysis (TA) has confirmed the strong adsorption of CO₂ while synthesizing the BaF₂ NP via PEBE method and adsorption of different NO_x oxides following irradiation of the BaF₂ NP (in air by 700 keV electrons). The appearance of the FM contribution in the diamagnetic BaF₂ NP after annealing at a temperature of 600–900 °C is likely associated with the achievement of the percolation threshold with an increase of the BaO oxide concentration. This is in agreement with the well-known theoretical predictions of d0 magnetism in N-doped (C-doped) BaO. The appearance and variations of the FM contribution to the BaF₂ NP irradiated by 700 keV electrons are likely connected with an increase of the NO_x oxide concentration (due to an increase of the time of electron irradiation), which confirms the hypothesis on the appearance of the FM response in solid-state N (C)-BaO solutions. The FM decrease with time is indicative of the surface character of d0 magnetism in the barium fluoride under study.

1. Introduction

D0 ferromagnetism is the ferromagnetic-like response to the applied magnetic field without participation of unpaired 3d-electrons, which are usually necessary for formation of high-temperature magnetic order [1]. Nowadays there is no commonly recognized explanation for D0 FM [2]. D0 FM was observed in many materials: oxides [3], sulfides [4], nitrides [5] and other inorganic compounds. However, magnetic properties of important class of materials such as fluorides of alkali and alkali-earth metals remain poorly studied. Nevertheless, in some experiments, room-temperature ferromagnetism (RTFM) was observed in NaCl [6,7], oxygen-doped CuCl [8], composite CeO₂/CeF₃ NPLEs [9], and pure CaF₂ [10]. Our recent studies also confirmed the unusual magnetic behavior of alkali-earth fluoride CaF₂ [11,12] and BaF₂ [11,13,14] NPLEs. In the literature, there are several reports on the magnetism of porous materials: nanoporous film Al₂O₃ [15,16], TiO₂

[17], and Cu₂O [18], as well as Cu₂O/porous anodic aluminum oxide [19].

Radiative defects are formed in NPLEs during the particle synthesis process by the PEBE method at the Nanobeam-2 setup [20]. In particular, in the process of deposition of BaF₂ NPLEs onto a substrate, the particles are subjected to pulsed X-ray irradiation. The X-ray irradiation is generated during the interaction of 40-keV electrons with the target material. As a result, a part of the target material evaporates, and a crater forms on the target surface (Fig. S1 in the Electronic Supplementary Material (ESM)). As NPLEs deposit on the cold substrate, they are quenching. As a result, the amorphous fraction is formed in the coating of NPLEs. Then, during the entire evaporation cycle, the coating is subject to X-rays, secondary electrons, light photons, and thermal heating from permanently depositing NPLEs. This combined action leads to formation of a large number of various structure defects in NPLEs generated the PEBE method.

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Essentially, no other known method for generation of NPles succeeds in providing such a complex, high-energy effect on the matter as the PEBE method does [20]. An interesting result was obtained in [21] with the use of BaF₂ NP generated by the method of plasma synthesis for sintering of transparent ceramics. The BaF₂ powder could be formed into an optically transparent pill when pressed uniaxially for 5 min at 370 MPa at room temperature. It should be noted that NPs generated by the PEBE method [20] have similar morphological and textural characteristics with NPs generated by the method of plasma synthesis and, in particular, with well-known Aerosil NPs [22]. This circumstance allows us to hope for obtaining transparent ceramics from NPs generated by the PEBE method.

In this study, we have obtained mesoporous crystalline NPs of pure BaF₂ with high specific surface area (SSA) up to 34.8 m²/g via evaporation by a pulsed electron beam in vacuum. The effects of the following thermal annealing in air (200–900 °C) and irradiation by high-energy electron beam on the size and morphology of BaF₂ NPles, as well as evolution of their magnetic, luminescent, textural, and thermal characteristics have been studied. Different ways of transforming d0 magnetism in samples annealed and irradiated by 700 keV electrons have been shown. The d0 magnetism in BaF₂ NP is found to have the surface nature due to the appearance of far order in the BaF₂-BaO oxide fluoride system co-doped by foreign carbon and nitrogen.

2. Experimental

2.1. Sample preparation

The BaF₂ NPs were generated through evaporation of a solid-state target by a pulsed PEBE in a vacuum [20]. The target material was micron-sized BaF₂ powder of optical purity. The evaporation conditions were the following: accelerating voltage of 38 kV, pulse duration of 100 μs, frequency of 50 Hz, beam current of 0.2 A, beam scanning area on the target surface of 8 cm², evaporation time of 50 min, and residual pressure in the evaporation chamber of 4 Pa. During the evaporation, NPles deposited onto the substrates of window glass spaced by 10–15 cm from the target center. Then, a part of obtained BaF₂ NP was annealed in alundum crucibles at a temperature of 200, 400, 600, and 900 °C. The annealing time was 10 min. From here on in the text, BaF₂ powder samples before and after annealing at temperatures of 200, 400, 600, and 900 °C are referred to as S0, S200, S400, S600, and S900, respectively. The sample of micron-sized powder is designated as S_{target}.

2.2. Sample characterization

The X-ray diffraction (XRD) was made using a diffractometer XRD 7000 Shimadzu (Japan). To analyze the textural characteristics of nano-oxides degassed at 373 K for several hours, low-temperature (77.4 K) nitrogen adsorption-desorption isotherms were recorded using a Micromeritics TriStar 3000 V6.03 A adsorption analyzer. The specific surface area was calculated according to the standard BET method. The total pore volume V_p was evaluated from the nitrogen adsorption at p/p₀ ≈ 0.99, where p and p₀ denote the equilibrium and saturation pressure of nitrogen at 77.4 K, respectively. The nitrogen desorption data were used to compute the pore size distributions. The morphology of the powders was determined with a LEO 980 scanning electron microscope (SEM). The method of SEM provided by built-in energy dispersive X-ray (EDX) microanalyzer was used to perform the elemental chemical analysis and the distribution of elements in the sample. The morphology and the phase composition of the powders were studied using a JEM-2100 transmission electron microscope (TEM).

Magnetic measurements were carried out using a Faraday balance at a temperature of 300 K. The pulsed cathodoluminescence (PCL) spectra were recorded at room temperature on a KLAVI 1 spectral analyzer [23]. The thermal analysis (TA) the BaF₂ NPs was performed on a NETZSCH STA-409 thermal analyzer. The PL and IR spectra were

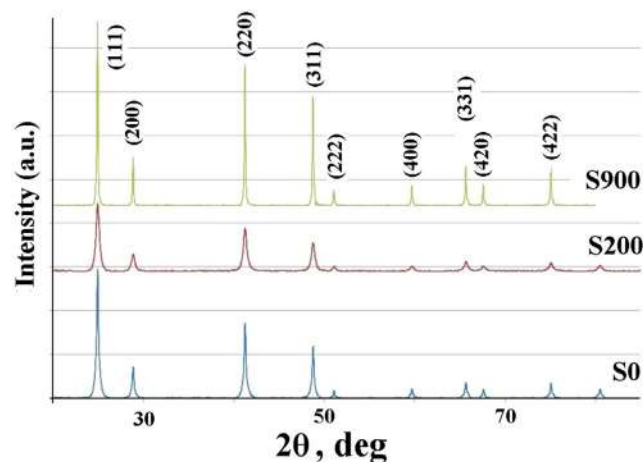


Fig. 1. XRD patterns of the S0, S200, and S900 specimens.

recorded on an MDR-204 monochromator and a Perkin Elmer Spectrum One FTIR spectrometer, respectively.

Powder samples were irradiated by a pulsed electron beam in air with the use of the URT-1 repetitively pulsed accelerator [24]. The absorbed doses were 31.5 MGy (1st series) and 63 MGy (2nd series). The pulse amplitude of the accelerating voltage was 700 kV, the pulse duration was 100 ns, and the pulse frequency was 35 Hz. The irradiation time was 15 min (1st series), then another 15 min (2nd series).

3. Results and discussion

3.1. XRD analysis

The results of XRD analysis are shown in Fig. 1.

The S0, S200, and S900 samples are single-phase, they include only barium fluoride (Frondicksonite, PDF-2 map No. 00-004-0452). Other possible phases (BaO, Ba(OH)₂, metal NPles of reduced Ba), which would be generated through electron evaporation in vacuum [25–28] were not found in the BaF₂ NP obtained by the PEBE method. The sensitivity of the XRD method is likely insufficient to detect possible low concentrations of additional nanophases distributed on the surface of BaF₂ NPles in the low concentration [29]. Nevertheless, the presence of oxygen atoms in the S200 sample was confirmed by the EDX method (see Section 3.6), which word order the possibility of formation of barium oxide and/or hydroxide considering that the solubility in water increases in the CaF₂ → SrF₂ → BaF₂ fluoride series [30].

The values of an elementary cell and peak half-width parameters are given in Table 1.

The parameters of the S0 and S200 samples coincide within the limits of experimental uncertainty. The parameter of the S900 sample is somewhat larger than those of the S0 and S200 samples. However, even a small increase of the parameter *a* in nanosized BaF₂ can lead to a considerable increase in the size of its NPles. As was shown in [31], the increase of the parameter *a* from 6.1656 to 6.1660 nm has led to the increase in the average size of BaF₂ NPles from 40 to 90 nm, respectively

Table 1

Lattice parameter and Full Width at Half-Maximum (FWHM) of the S0, S200, and S900 BaF₂ nanopowder samples.

Samples	<i>a</i> , (Å)	FWHM
S0	6,1917 (6)	0,22 (4)
S200	6,1914 (6)	0,35 (7)
S900	6,1933 (5)	0,108 (18)

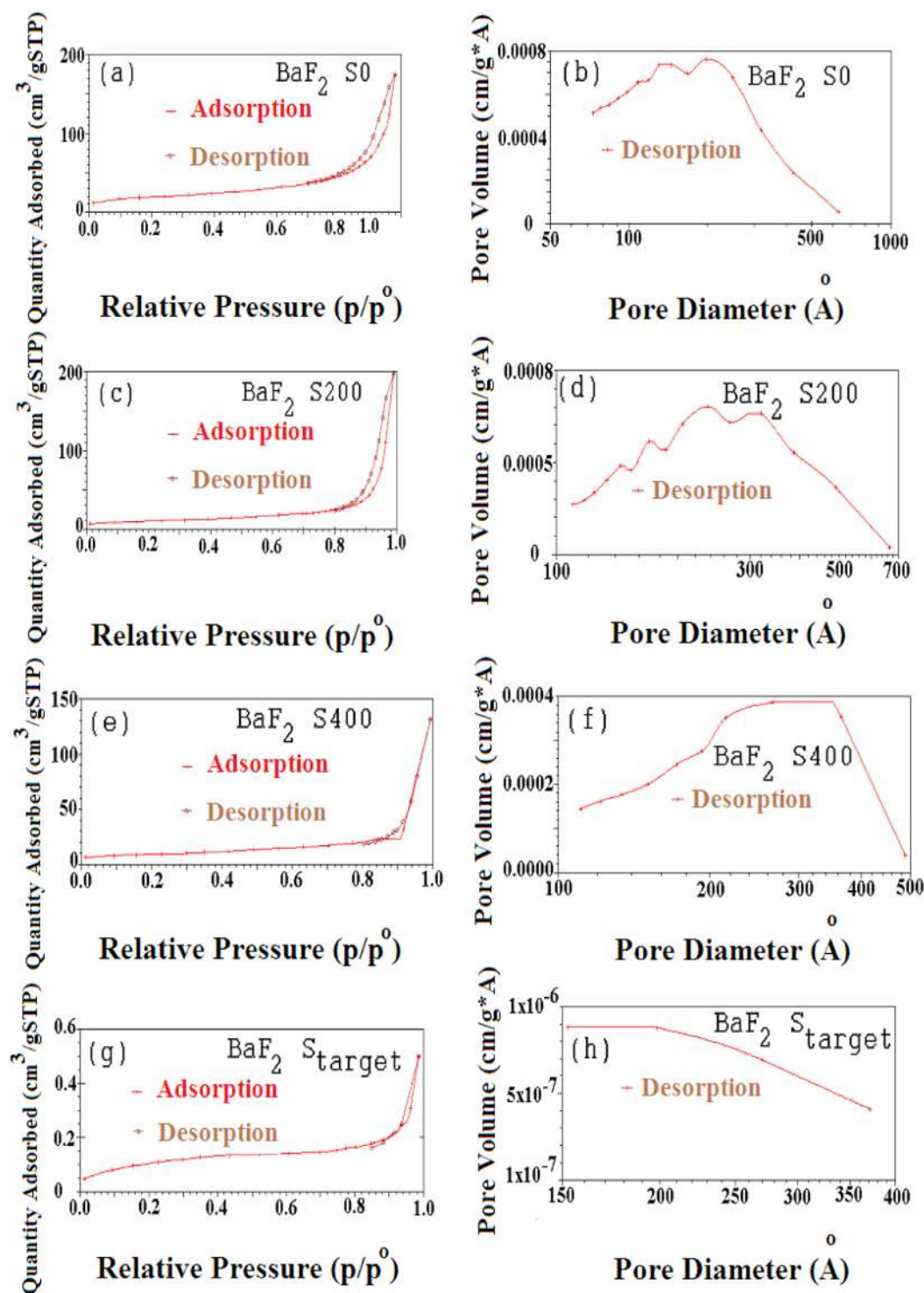


Fig. 2. (a,c,e,g) N_2 adsorption/desorption isotherms of the S0, S200, S400 and S900 (b,d,f,h) showing the corresponding pore size distribution.

3.2. Textural analysis

Fig. 2a,c,e,g show the nitrogen adsorption-desorption isotherms and pore size distribution curves (Fig. 2b,d,f,h) of the S0, S200, S400, and S_{target} samples.

The isotherms of the S0 and S200 samples fall in type IVa (for isotherms of type IVa, capillary condensation is accompanied by hysteresis), and hysteresis loops, according to the IUPAC classification [32], can be classified as Type H2b. (Type H2(b) loop is also associated with pore blocking, but the size distribution of neck widths is now much

larger. Examples of this type of hysteresis loops have been observed with mesocellular silica foams and certain mesoporous ordered silicas after hydrothermal treatment). The multimodal pore size distribution was observed in three samples: S0, S200, and S400 (Fig. 2b,d,f). The multimodal pore distribution is linked to the morphology of the obtained BaF_2 NP. NPs look like a spatial 3D-structure formed as a result of sintering of very fine nonporous NPles into aggregates and agglomerates, the spatial structure of which is very similar to that of Aerosil NPs. At the same time, a large volume of interparticle pores is observed. This volume is comparable with the pore volume in the well-known

Table 2

Textural properties of BaF₂ nanopowder samples before (S0) and after annealing (S200, S400).

Sample	SSA (m ² /g) ^a	V _{p-Total} (cm ³ /g) ^b	D _{BJH} (nm) ^c
S _{target}	0.38	0.00061	31.0
S0	19.01	0.46	29.3
S200	34.80	0.31	30.1
S400	30.88	0.20	32.3
S900	0.46	0.0092	15.9

^a BET surface area.

^b Total pore volume.

^c Pore diameter by BJH desorption.

representatives of mesoporous NPs, such as MCM-41 [33], SBA-15 [34], and others.

The measurements of textural properties of all BaF₂ NPs are given in Table 2.

To be noted is the sharp growth of the SSA of the initial NP after annealing at a temperature of 200 °C, which can be explained by the removal of water molecules (adsorbed from the ambient air) from the surface of NPles and interparticle pores. This is in agreement with the TG analysis data (see Section 3.3), in which the three-fold decrease of the water content in the annealed S200 sample in comparison with the initial S0 sample was observed. It should also be noted that a similar growth of the specific surface (~1.4 times) after annealing of CaF₂ NPs at a temperature of 200 °C: from 64.3 to 88.7 m²/g [11] we observed. Upon annealing at a temperature of 900 °C, the SSA of BaF₂ NPs decreased sharply (0.46 m²/g), which was indicative of the NP transformation into nonporous submicron powder. The data in Table 1 demonstrate that the other textural properties of the unannealed mesoporous BaF₂ NP (pore volume and diameter) change monotonically with an increase of the annealing temperature: the pore volume decreases, while the pore diameter increases. This behavior of the NP at annealing is quite predictable and can be explained by the regular growth of the particle size due to recrystallization.

3.3. Thermal analysis

Barium fluoride fall in class II of superionics. Fig. 3 shows the heating curves of differential scanning calorimetry (DSC) – thermogravimetry (TG) of the S0 and S200 samples [13].

The behavior of the DSC curves of the both samples in the

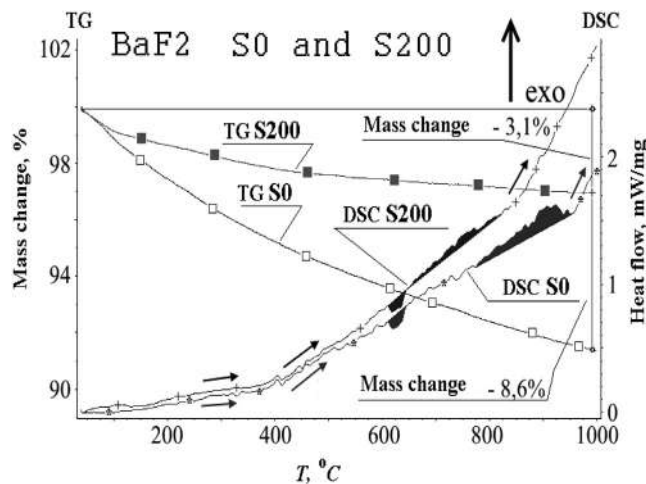


Fig. 3. DSC-TG curves of heating (air atmosphere, heating rate of 10 °C/min) of S0 and S200 BaF₂ NP samples. Arrows in the DSC curves show the change in the slope of basic line as a result of the change in heat capacity at the transition into the superionic state [20].

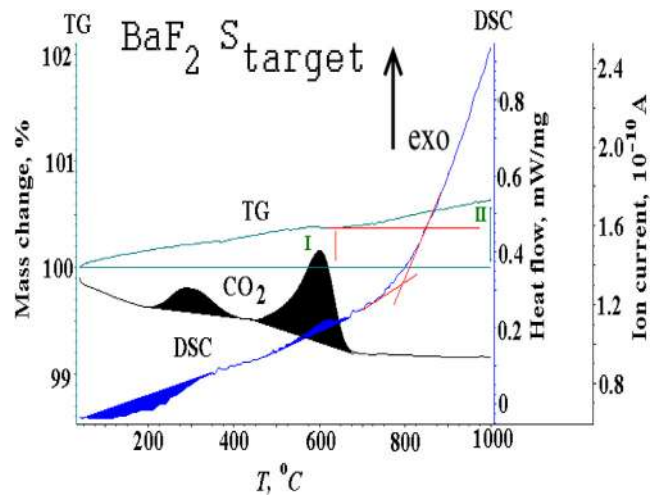


Fig. 4. DSC-TG curves of heating (air atmosphere, heating rate of 10 °C/min) and CO₂ mass-spectrum of the initial micron-sized BaF₂ powder (Target sample). Arrows in the DSC curves show the change in the slope of basic line as a result of the change in heat capacity at the transition into the superionic state.

temperature range of 40–650 °C is nearly synchronous. At a temperature of 400 °C, the slope of the basic line in the both DSC curves changes drastically. We showed [13], that the change in the slope of the basic line of the DSC curves of our samples at the temperatures above 400 °C is associated just with the start of generation of the Frenkel pairs only. Endothermic peak at a temperature of about 625 °C in the both DSC curves may be caused by melting of Ba nanoparticles reproduced at electron evaporation in vacuum. We have checked this assumption experimentally. We recorded the DSC-TG curves of the initial micron powder (Fig. 4) containing no reproduced Ba NPles, which is confirmed by the lack of endothermic peak at 625 °C in the DSC curve of the S_{target} sample. The generation of Frenkel pairs in the micron-sized sample starts at a temperature of about 750 °C, which is in a good agreement with the literature data [35,36].

Importantly, the change in the slope of the basic line at a temperature of 400 °C, which is characteristic of the S0 and S200 samples, was absent in the DSC curve of the S_{target} sample (Fig. 4). On our assumption, it is connected with the start of generation of Frenkel pairs in the BaF₂ NP samples. Therefore, we assumed that the start of generation of Frenkel pairs at a temperature of 400 °C was caused by the size factor, namely, the presence of metal Ba NPles in BaF₂ NPs. To confirm this hypothesis, we have irradiated the micron-sized BaF₂ powder by a high dose of radiation (31.5 MGy) to obtain Ba NPles from the interaction of the relativistic electron beam with the micron-sized BaF₂ powder. It is well-known that cation NPles are generated as a result of the interaction of different types of radiation (X-ray, laser, neural, gamma, ionic, and electronic radiation) inside alkali-earth fluorides (CaF₂, BaF₂, SrF₂, etc.) [37]. Therefore, according to our calculation the concentration of Ba NPles formed in the micron-sized powder under the exposure to a high radiation dose would be sufficient to observe the endothermic peak from the melting of formed Ba NPles. Our calculation was confirmed as follows from the DSC–TG curve of irradiated micron-sized sample in Fig. 5.

In the DSC curve, we can clearly see the endothermic peak from the melting of Ba NPles formed as a result of irradiation by an electron beam at a temperature of about 660 °C (insignificant excess of the melting temperature of Ba NPles in S_{target} (660 °C) as compared to the corresponding temperature in S0 and S200 (625 °C)) can be explained by the effect of the size factor on the melting temperature. However, the most important aspect is associated with the appearance of the slope of the basic line in the DSC curve of the irradiated S_{target} sample at a temperature of about 400 °C. This slope was absent in the DSC curve of the non irradiated micron-sized sample. The change in the slope of the

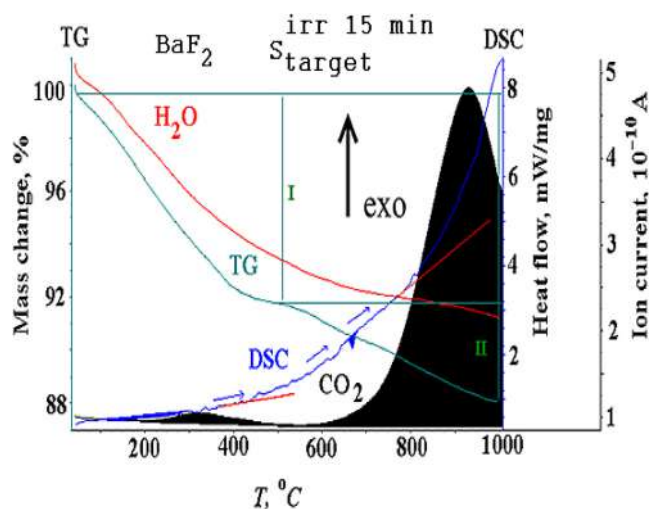
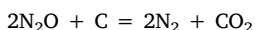


Fig. 5. DSC-TG curves of heating (air atmosphere, heating rate of 10 °C/min) and CO₂ mass-spectrum of electron-irradiated micron-sized BaF₂ powder (S_{target} sample after irradiation). Arrows in the DSC curves show the change in the slope of basic line as a result of the change in heat capacity at the transition into the superionic state.

basic line indicates clearly the appearance of ionic conductivity in the S_{target} sample at the low temperature as a result of formation of Ba NPles, which is indisputable. It is well-known that the irradiation by an electron beam with the electron energy of 150 keV in vacuum (10–7 mm Hg) leads not only to formation of metal Ba NPles (CaF₂ monocrystal was irradiated in [25–27], but also to the formation of BaO oxide and reverse transformation BaO ↔ Ba(OH)₂. Nevertheless, assuming the possibility of formation of barium oxide and hydroxide in our case, the endothermic peak at 660 °C cannot be assigned to the melting of Ba(OH)₂ hydroxide (the melting temperature of Ba(OH)₂ is much lower and equal to 400 °C or BaO oxide (the melting temperature of BaO is equal to 1368 °C). The absence of reflects from foreign phases in X-ray diffractograms (Fig. 1) and the lack of the endothermic peak at 408 °C from the melting of Ba(OH)₂ indicate the low possibility of the presence of Ba(OH)₂ NPles in the irradiated S_{target} sample. The results of transmission electron microscopy (TEM) (see Section 3.6) also confirmed the absence of the Ba(OH)₂ phase in the irradiated sample. With an increase of the heating temperature, the difference in the thermal behavior of the S0 and S200 samples became increasingly marked. The long exothermal peaks in the both DSC curves in the temperature range 650–950 °C were caused by desorption of volatile substances of unknown nature from the surface and/or volume of BaF₂ NPles. The irradiation of the micron-sized BaF₂ sample resulted in formation of Ba NPles in it and the appearance of superionic conductivity at 400 °C, which was lacking in the nonirradiated sample. The irradiation of the micron-sized BaF₂ sample resulted in formation of Ba NPles in the sample and the appearance of superionic conductivity at 400 °C, which was absent in the non-irradiated sample.

It is well-known that as an electron beam enters the air atmosphere, a large amount of gases represented mostly by the mixture of active forms of oxygen (including ozone) and nitrogen oxides NO_x is formed [38]. The ozone formed at the electron beam irradiation breaks down fast. Under normal conditions, NO₂ is chemically inert. However, at the heating, the following reaction proceeds:



This reaction is in agreement with EDX analysis data (see Section 3.5, Table 3), which has shown the three-fold increase in the carbon concentration in NPs after annealing at the low temperature of 200 °C. That is why we believe that the sharp emission of CO₂ upon the heating of the irradiated BaF₂ micron powder above 600 °C can be associated

Table 3

Results of elemental analysis of BaF₂ NPs by the EDX method.

Sample	The concentration of elements (at.%) in the samples				
	C	O	F	Ba	Total
S0	9.46	0.00	41.73	48.81	100.00
S200	29.7	3.52	36.52	30.26	100.00

with the reaction of nitrogen reduction reaction alone. In the experiments, we observed the very intense gas emission (see the mass-spectrum of CO₂ in Fig. 5), which led to the drop of a top of the aluminum crucible of NETZSCH STA-409 thermoanalyzer (heating was performed several times). It should be noted that the intense release of gaseous products at the high temperature was not observed at the heating of the S0 (Fig. 3) and of the chemically obtained S_{target} sample (Fig. 4). This observation supports the proposed interpretation of the gas emission process with participation of nitrogen oxide.

3.4. Scanning electron microscopy (SEM)

SEM images of the S0 and S200 samples are shown in Fig. S2 in the ESM. The initial S0 sample is the strongly agglomerated sample consisting of coral-like particles of irregular shape with the porous structure (Figs. S2a–e). The images in Fig. S2a–c show that the irregular-shape particles consist of agglomerates of two types. The first type is represented by nest-shaped agglomerates of larger (up to 13 μm) and smaller (about 3–5 μm) sizes. These agglomerates are constructed of very small NPles, the size of which cannot be estimated by the SEM method with the used instruments (the image blurs at x50,000 magnification). Another type of agglomerates that were observed is porous agglomerates with spongy, undefined shape. They also consist of very small NPles (Fig. S2d,e). The presence of nest-shaped agglomerates in the S0 sample is indicative of the tendency of NPles to self-organization, which is in agreement with the earlier observations of the phenomenon of self-organization NPles [39,40].

From the photos of the S200 sample in Fig. S2f–j, we can see that the morphology of NPles after annealing at 200 °C changes somewhat. The nest-shaped NPles disappear, and the majority of particles look like spongy coral-like agglomerates consisting of very small NPles. To be noted is the significant number of large pores in the S200 sample, which is consistent with the textural analysis estimate of the pore diameter in the S0 and S200 samples by the textural analysis. Hollow nest-like BaF₂ nanostructures synthesized in [41] with the simple sonochemical method from the aqueous solution with EDTA as a complexing reagent and CTAB as a surfactant have demonstrated the morphological similarity to our BaF₂ NPles. These hollow structures have shown a more intense PL in comparison with solid structures. The morphological difference between S0 and S200 could affect some physical-chemical characteristics of BaF₂ NPs and lead to a significant difference to the characteristics of S_{target}.

3.5. EDX and mapping

Figs. S3 and S4 in the ESM depict the EDX spectra and element maps of the S0 and S200 samples, respectively. The EDX analysis was carried out at three sections in every sample.

The analysis has shown the absence of possible magnetic impurities from 3 d elements (Fe, Co, and Ni) in the S0 and S200 samples. In both samples, the foreign carbon, which could adsorb on the developed surface of NPles in the process of their synthesis and/or storage, was detected.

From the maps shown in Figs. S3 and S4 in the ESM, one can see the uniform distribution of elements over the analyzed sections of the both can be seen. Results of the element analysis of the S0 and S200 samples

are given in Table 3.

From the data of Table 3, we can see the strong distortion of stoichiometry in the S0 and S200 samples. The excess of Ba was observed in each of the three analyzed sections in both samples. This observation is in agreement with the results of the above TA, in which the DSC curves of the S0 and S200 samples (Fig. 3) include endothermic peaks from the melting of metal Ba NPles. It should be emphasized that the concentration of foreign oxygen in the S0 sample is close to zero. This fact suggests that the relatively high pressure of residual gases in the evaporation chamber of the Nanobeam-2 setup (4 Pa), which is several orders of magnitude higher than the pressure of residual gases in the TEM column (10–5 Pa [25–27]), nevertheless does not lead to a considerable increase in the concentration of foreign oxygen in the BaF₂ NP. At least, we can assert univocally that the concentration of foreign oxygen is below its detection limit in Leo 980 TEM [42]. It is also obvious that the pre-annealing of the target of micron-sized BaF₂ powder in air at 900 °C, during which the powder could be saturated with oxygen from the ambient air, had no effect on the oxygen concentration in the end product – BaF₂ NP.

3.6. TEM-HRTEM

3.6.1. Morphology of NPles

Fig. 6 depicts the TEM and HR-TEM images of the S0 and S200 samples.

The S0 and S200 samples are the agglomerated NPs with the agglomerate size of up to several hundreds of nanometers. In Fig. 6a, an agglomerate of BaF₂ NP – S0 sample is shown as an example. Agglomerates look like mesoporous spatial 3D nanostructures formed by aggregation of crystalline nonporous NPles (inset in Fig. 6b). In the TEM images (Fig. 6c,d) we can clearly see irregular V-shaped mesopores. NPles of the both samples have a quasi-spherical shape. It is difficult to estimate the average size of NPles because of the spatial structure of agglomerates and relatively strong sintering of NPles in aggregates (inset in Fig. 6b). In the HRTEM image of the S0 sample (Fig. 6e), one can clearly see NPles of rectangular shape with rounded angles about 5 nm in size. In the HR-TEM image of the S200 sample (Fig. 6f), we can see several perfect NPles with non-rounded angles. It is obvious that the annealing at the relatively low temperature resulted in the much higher crystallinity of the S200 sample. It can be clearly seen in the HR-TEM images in Fig. 6e, f that BaF₂ NPles have a plate-like shape. The plate size exceeds 5 nm and can achieve 15–20 nm. Various structure defects (Fig. 6g,h) are present in a large number in aggregated NPles. Fig. 6h shows the dislocation.

3.6.2. Analysis of the phase composition from selected area electron diffraction

The structure and phase composition of BaF₂ NPles was determined by the SAED (selected area electron diffraction) method. The electronograms of the both samples (in Insets in Fig. 6c,d) have a point-ring shape, which is indicative of the polycrystalline structure of the S0 and S200 samples. All NPles are crystalline, no amorphous NPles were detected. The assignment of SAED patterns has confirmed the crystal structure of particles, which is indexed as orthorhombic (Pnam) and cubic (Fm3m) structures of BaF₂. In some electronograms of selected areas (Fig. 7), in addition to the main diffraction rings and points corresponding to the orthorhombic and cubic structures of BaF₂, we have revealed high-intensity points corresponding to the interplanar distance of 0.29 nm.

In the available database, there is no such value ($d = 0.29$ nm) of the interplanar distance for BaF₂. Within the experimental uncertainty (± 0.01 nm), this value of interplanar distance can correspond to Ba in the hexagonal phase (Hexagonal S.G. P6₃/mmc) or BaO in the tetragonal and cubic phases. The exact determination of the phase composition is possible from analysis of HRTEM patterns of separate NPles.

3.6.3. Analysis of phase composition and defects of BaF₂ NPles with HRTEM

The processing and analysis of the images were performed using the of the Gatan Digital Micrograph version 3.9.3 software, which allowed us to calibrate images, to apply masks and filters, to perform Fast Fourier Transformations (FFT) of both the image as a whole and its selected areas, to conduct measurements, and to save data in various formats. The interplanar distances of the BaF₂ and Ba phases were taken from the Powder Diffraction File. The processing of 100 TEM images of unannealed BaF₂ NPles (S0 sample) revealed the presence of the cubic phase in 53 images and the orthorhombic phase of BaF₂ in 67 images. Fig. 8 depicts a typical TEM image of BaF₂ NPles and its Fourier transform with the cubic and orthorhombic phases. Once Fourier transforms were obtained, the table including the interplanar distances and the supposed corresponding phases was compiled (see Table S1 in the ESM). The Gatan Digital Micrograph software allows us to examine Fourier transforms of any selected area of the image of interest (see Fig. 8).

In Fig. 8b,c, we can clearly see that the arrangement of atoms in the Fourier transforms corresponding to the top and bottom areas (shown by squares) of the TEM image of BaF₂ NPles in Fig. 8a corresponds to a hexagonal shape. In other words, BaF₂ NPles in the top and bottom areas of the TEM image in Fig. 8a have a hexagonal structure. In addition, Fig. 8d shows edge dislocations and the defect zone of the selected area in Fig. 8a. Fig. 8e depicts the perfect structure of a hexagonal NPle in the bottom selected area in Fig. 8a.

3.6.4. Study of phase peculiarities of F₂BaF₂ NPles after annealing at 200 °C

The processing of 100 TEM images of the S200 sample revealed the presence of the cubic phase in 54 images, the orthorhombic phase in 61 images, and the hexagonal phase of BaF₂ in 31 images (see Fig. 9).

It should be noted that the number of reflexes corresponding to the interplanar distance of 0.29 nm, that is, to the hexagonal phase of BaF₂, in the S200 sample is much larger than in the unannealed S0 sample. Thus, the data on the interplanar distances (see Table S2 in the ESM) and the data of assignment of the electronogram (see Table S3 in the ESM) suggest that the composition of BaF₂ NPles obtained by the PEBE method included three phases of barium fluoride (cubic, orthorhombic, and hexagonal), two phases of metal barium NPles (cubic and hexagonal), and tetragonal phase of BaO oxide. Three BaF₂ phases (cubic, orthorhombic, and hexagonal) were also detected in the composition of the annealed S200 sample. The issue of formation of metal Ba NPles in BaF₂, CaF₂, SrF₂ fluorides under the irradiation by electrons with different energy is extensively covered in the literature [25–27,37]. The effect of electron irradiation on fluorides of alkali-earth elements CaF₂, SrF₂, and BaF₂ in a TEM column was studied in [26]. It was shown that the excess of the e-beam current density above the threshold value favors the fluorine desorption and binding of released metal ions by residual oxygen into the oxide phase MeO (Me = Ca, Sr, Ba) which has the structure of rock salt NaCl. It is interesting that as the electron irradiation terminated, the transition of BaO into Ba(OH)₂ was observed in BaF₂ samples. The renewal of irradiation is accompanied by the reverse transition of Ba(OH)₂ into BaO. It is well-known that under normal conditions barium fluoride crystallizes into the cubic phase (α -phase) with the spatial group Fm3m. It was shown in [43] that under the effect of high pressure (about 3–5 GPa), a phase transition of the α -phase into the orthorhombic phase (β -phase, Pnma spatial group) occurs [43,44].

Thus, all the phases (except for the sulfide phase BaS₃) detected in the composition of the S0 sample were obtained earlier through the action of either high pressure or an electron beam on BaF₂ in different forms (monocrystals, films, powders). In this paper, we do not consider the results of action of other types of radiation (gamma, neutrons, laser radiation, etc.) on fluorides of alkali-earth metals.

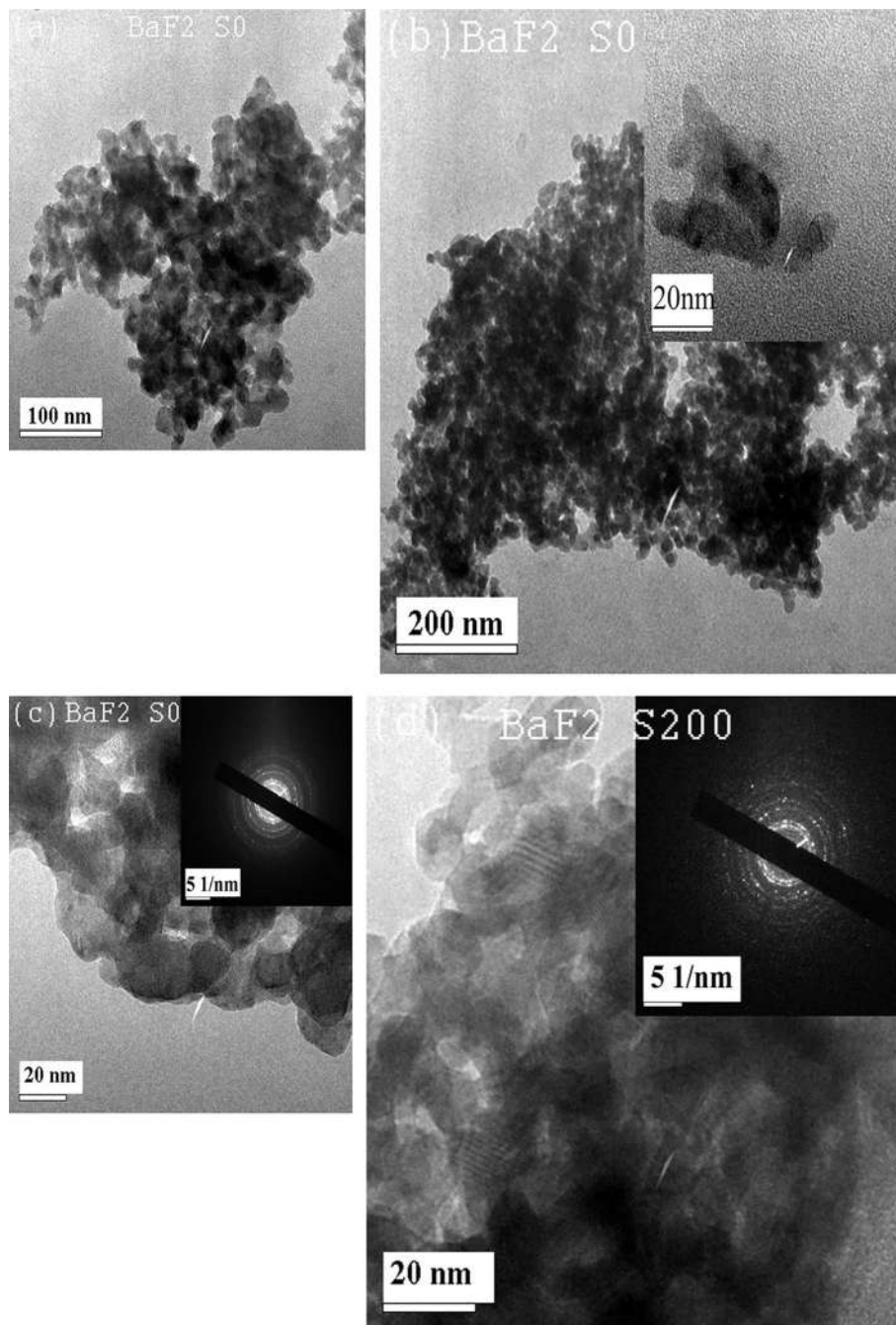


Fig. 6. TEM and HR-TEM images of BaF_2 NPLs: a) BaF_2 NP – S0 agglomerate, b) BaF_2 NP – S200 agglomerate. In Inset: NPLs aggregate, c,d) V-shaped mesopores and electronograms of the S0 and S200 samples, e,f) plate-like NPLs with rounded angles in the S0 sample and nonrounded angles in the S200 sample, g,h) Various structure defects in aggregated BaF_2 NPLs. White square show the area of construction of Fourier transforms (top right). The white arrows shows the edge dislocations in sample S200.

3.7. Pulsed cathodoluminescence (PCL) spectra

PCL spectra of the target and the S0-S900 samples in the ultraviolet (UV) and visible (VIS) spectral ranges are shown in Fig. 10.

Some information on cathodoluminescence properties of BaF_2 can be found in [45–48]. In [45], the cathodoluminescence a single crystal of BaF_2 was studied at the room temperature with the accelerating voltage varying from 2 to 15 kV. Two processes were observed: ordinary interband luminescence between the conducting and valent bands and cross-luminescence (5.6 eV (221.4 nm)) between the valent and outermost-core bands. Cathodoluminescence measurements of cross-luminescence induced by an electron beam at the fixed voltage of,

for example, 7 kV were carried out in [46,47]. In [49], it was reported that no high-energy bands were observed at the X-ray excitation of pure BaF_2 crystals at 77 and 300 K. However, a high-energy emission band with a peak nearby 7.5 eV (165 nm) was found at the e-beam (6 keV) excitation [50] or synchrotron irradiation [51] of pure BaF_2 crystals. It was shown in [52] that under irradiation by a nanosecond pulsed electron beam, the PCL spectra of the main oxide matrices (ZrO_2 , CeO_2 , etc.) give one emission peak centered around 500 nm. It is interesting that in the VIS region of the PCL spectra, the barium fluoride (see Fig. S5f–j in the ESM) and calcium fluoride (see Fig. 2a in [11]) NPs also had one wide peak around 500 nm. The results of deconvolution of the PCL spectra of all the BaF_2 samples (Table S4 in the ESM) by two Gaussians

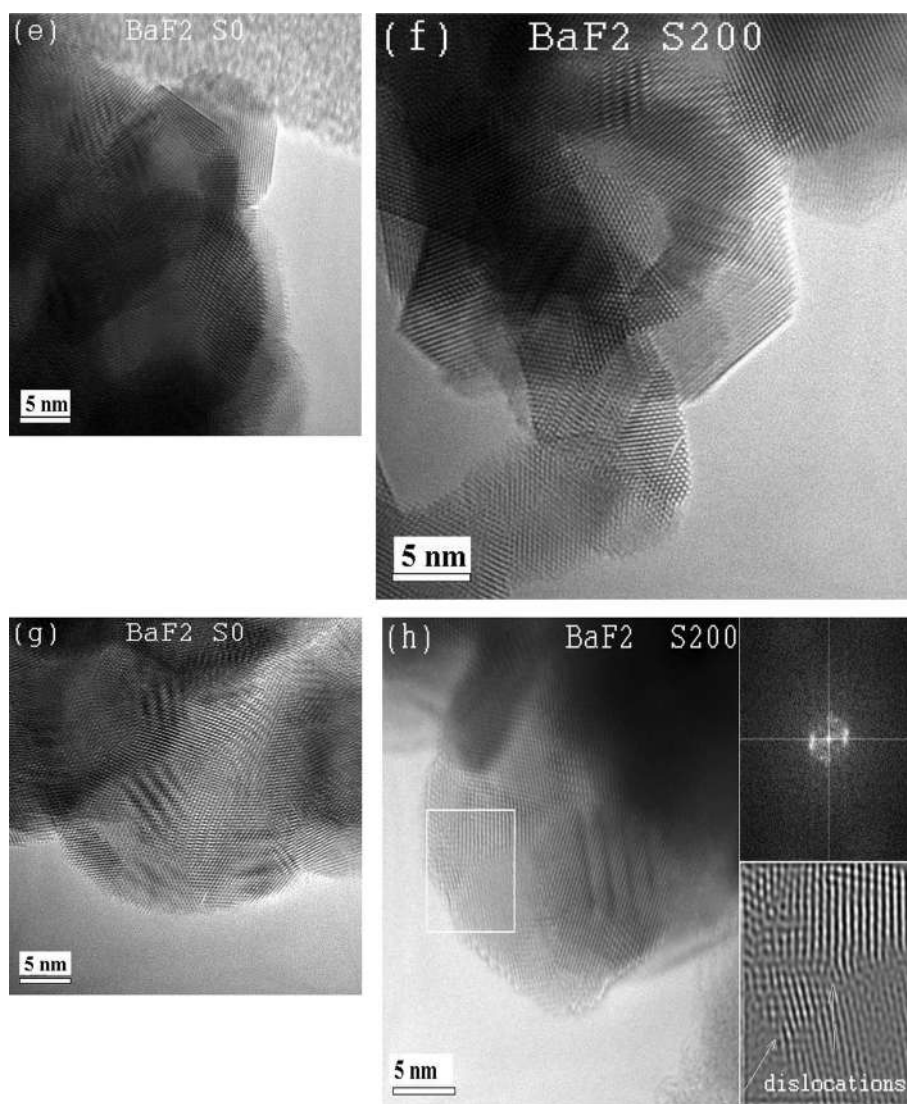


Fig. 6. (continued)

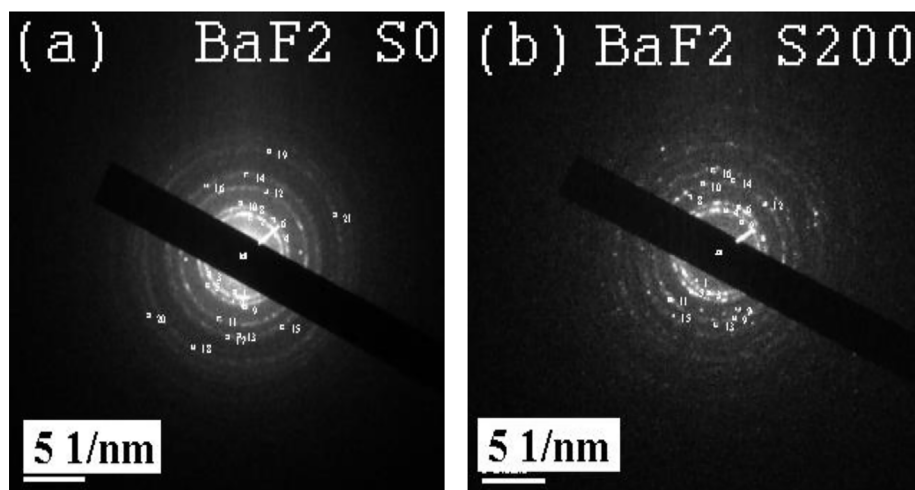


Fig. 7. Electronograms of the S0 (a) and S200 (b) samples.

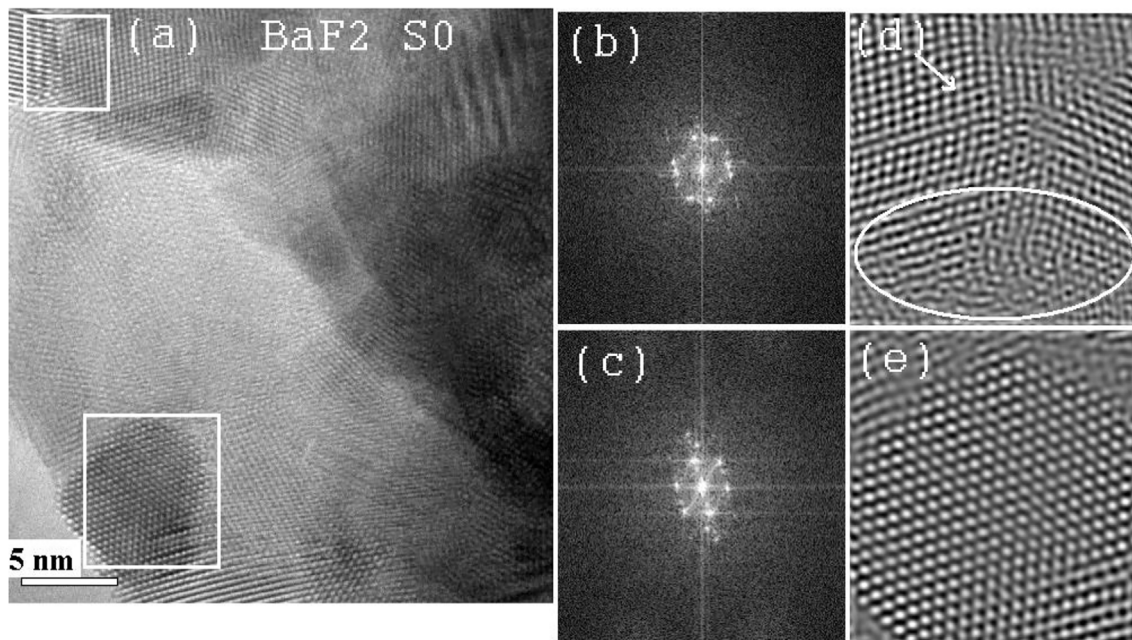


Fig. 8. TEM a) TEM image of BaF₂ NPLs (5-nm scale). White squares show the areas of construction of Fourier transforms, b,c) Fourier transforms of the top and bottom zones in Fig. 8a, d) Twinning (shown by the arrow) and defect zone (oval) in the top area of BaF₂ NPLs in Fig. 8a, e).

have shown that in the S0 sample with the minimal concentration of foreign oxygen, which is close to zero by the data of EDX analysis (Table 3), peak I lies in the blue spectral range and can be assigned to the luminescence of foreign BaO oxide. In [50], two PL bands in the BaF₂ monocrystal containing an oxygen impurity of 10000 ppm were explained in the following way: “The luminescence band at 2.83 eV (438 nm) (for an excitation energy of 5.17 eV) is due to an oxygen–vacancy complex with an oxygen on a fluorine site with a next-nearest fluorine vacancy along a $\langle 110 \rangle$ direction. The luminescence band at 2.25 eV (551 nm) is probably associated with oxygen–vacancy complexes with a nearest fluorine vacancy along a $\langle 100 \rangle$ direction.”

However, in the annealed S200 and S400 samples, which do include foreign oxygen, this oxygen most probably is a part of luminescence centers responsible for peaks I. Furthermore, peaks I in the S200 and S400 samples were shifted to the long-wavelength spectral range, toward 500 nm. The reverse shift of peak I in the PCL spectrum of S900 sample to the blue spectral range (442 nm) is attributed to the further

increase of the oxygen concentration in the S900 sample due to inevitable formation of the secondary phase BaO, the emission peak of which is known [50,53,54] to lie in the blue spectral range. The positions of PCL peaks I and II in the S_{target} and S900 samples nearly coincide. It should be noted that at PEBE a part of the target surface (outside the crater in the evaporation zone) luminesced blue, which was seen visually through the observation window of the evaporation chamber of the NANOBEAM-2 setup (see the photo of the target at the time of evaporation in the inset of Fig. 10b). It should be emphasized that the position of peak II changed monotonically from 554 to 595 nm with an increase of the annealing temperature, which indirectly indicates the involvement of oxygen into the formation of luminescent centers responsible for peaks II in nano-sized S0-S400 samples. It must be mentioned what the S900 sample annealed at the high temperature does not fall in the class of nano-sized samples. Therefore, the majority of defects of this sample were likely annealed, and both emission bands I and II in the S900 sample coincided with the corresponding emission

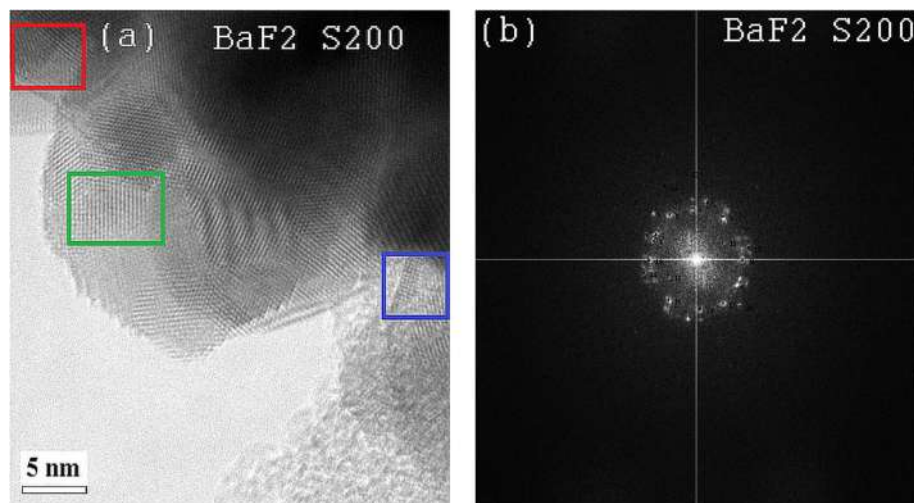


Fig. 9. TEM-image of BaF₂ NPLs (S200) (a) and its Fourier transform (b). The marked zones in Fig. 9a correspond to different phases of BaF₂: cubic (top), orthorhombic (center), and hexagonal (bottom).

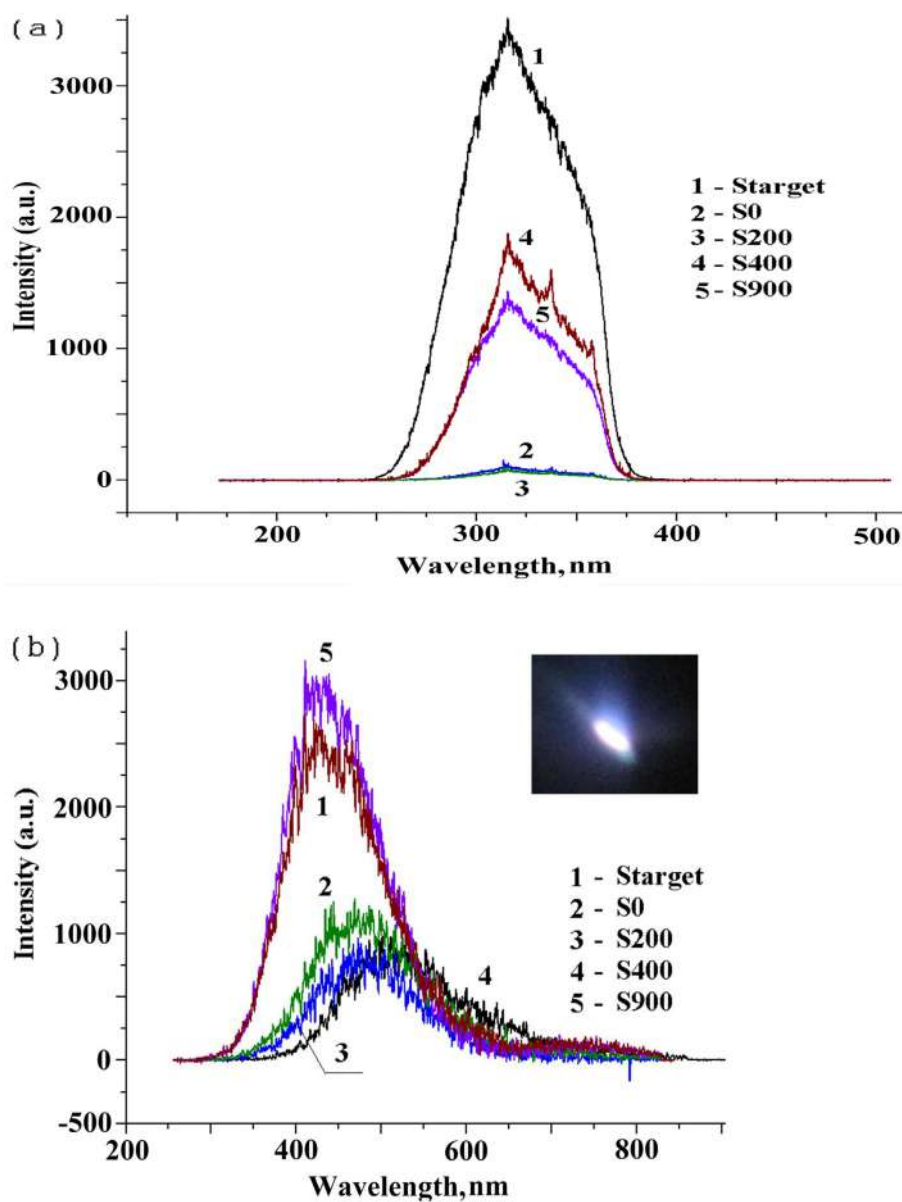


Fig. 10. (a) PCL spectra of the S_{target} , S0, S200, S400, and S900 samples in the UV spectral range; (b) PCL spectra of the S_{target} , S0, S200, S400 and S900 samples in the VIS spectral range. In Inset: blue color of target emission (S_{target}) in the PEBE process. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

bands I and II in the S_{target} sample.

3.8. Photoluminescence (PL) spectra

PL spectra of the samples are shown in Fig. 11.

The results of deconvolution of PL spectra of the target and BaF_2 NPs by Gaussians are shown in Table S5 in the ESM. The analysis of PL spectra has shown that: The spectra of the S0 and S200 samples were similar and looked like a wide band in the wavelength range 575–780 nm. The emission intensity of the S200 sample was nearly three times higher than that of the S0 sample, which is associated with the desorption of water molecules from S200 at the annealing. The peak in the near-IR range at $\lambda \sim 700$ nm (A4, Table S5 in the ESM) was observed in the PL spectra of all annealed S200–S900 samples, and it changed its position very smoothly at the annealing. As the annealing temperature increased, the red dominant peak (A3, Table S5 in the ESM) shifted monotonically toward shorter wavelengths from 653 nm (S0) to 608 (S900). The blue peak (464 nm) was present in the micron-

sized powder (S_{target} sample) and the S900 sample (454 nm); the intensity of the peak nearby 454 nm was much lower than that of the peak at 464 nm. The luminescence in the blue spectral range may be attributed to the emission of the BaO oxide [50], which may be present in both the micron powder and the annealed S900 NP. PL spectra of the S_{target} , S400, and S900 samples had a similar characteristic shape formed by three main emission peaks centered at (559–564 nm), (608–611 nm), and (670–701 nm). It should be noted that in all the three samples the predominant peak lied at $\lambda \sim 611$ nm. It is most interesting that the PL intensity of the nano-sized S400 sample was nearly three times as high as that of the micron-sized S0 powder and the S900 sample annealed at the high temperature (Fig. 11a). The decrease of the PL emission in the S900 sample can be explained by the formation of the considerable amount of BaO particles at the surface of BaF_2 NPles at the high-temperature annealing, which resulted in the decrease of luminescence in the samples annealed at the temperature higher than 400 °C. The PL spectra of the diamagnetic target (S_{target} sample) and annealed FM sample S900 each included four peaks corresponding to

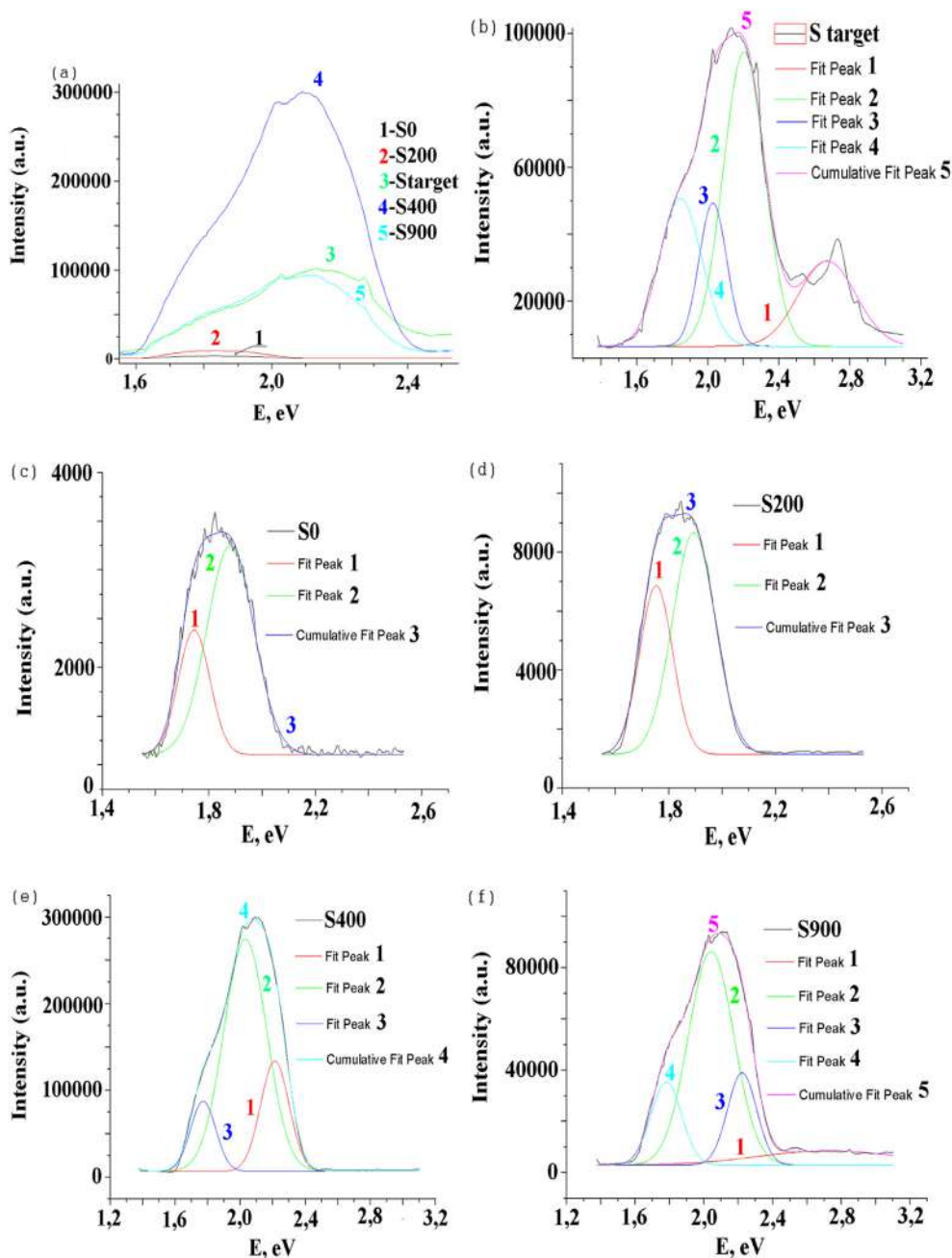


Fig. 11. a) PL spectra of the S_{target} , S0, S200, S400, and S900 samples; b-f) deconvolution of PL spectra of the S_{target} , S0, S200, S400, and S900 samples by Gaussians.

the same emission centers from the blue spectral range to the NIS one. Consequently, the corresponding luminescent centers cannot be responsible for the FM response in the S900 sample (see Section 3.10). The comparison of the PL and PCL spectra in Figs. 11a and 10a has shown that the intensity of the both types of luminescence in the S0 and S200 samples is very low in comparison with the emission intensity of the other samples, which is indicative of the significant hydration of these samples and insufficient temperature-time treatment of the S200 sample for the removal of all water adsorbed in the NP. This result is in agreement with the data in [55], where it was shown that the X-ray luminescence at 320 nm in the BaF_2 powder (obtained by the chemical method) appeared only after annealing of the sample in air at a temperature of 550 °C for one hour. The intensity of cathode- and photoemission of the S900 sample appeared to be comparable with the corresponding emission intensity of the S_{target} sample.

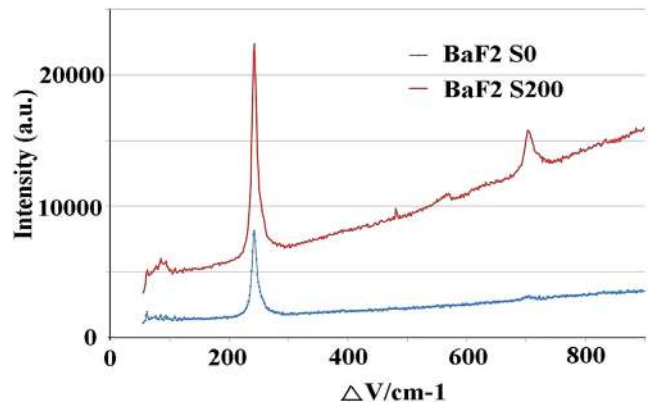


Fig. 12. Raman spectra of BaF_2 NPs [20].

3.9. Raman spectra

Raman spectra of the samples S0 and S200 are shown in Fig. 12.

The spectrum of sample S200 contains two low-intensity lines (473 and 567 cm^{-1}) and a line of moderate intensity (704 cm^{-1}). The line at 704 cm^{-1} is probably due to an oxygen vacancy [56]. The above lines are indicators of the process of disordering of fluorine ions over the crystal volume during annealing.

3.10. Magnetic analysis

The analysis of the above mentioned physical-chemical characteristics of the micron- and nano-sized BaF_2 powders and well-known theoretical prediction of magnetic properties of N-doped CaO, N-doped BaO, carbon-doped CaO, and carbon-doped BaO [57–63] has allowed us to put forward the hypothesis about the possible nature of appearance and transformation of d0 magnetism in the BaF_2 NP obtained by the PEBE method. The hypothesis consists in the following: the appearance of RTFM is connected with the presence of foreign carbon in BaF_2 NPs obtained by the PEBE method. The appearance and transformation of RTFM in the samples irradiated by relativistic electrons is associated with the simultaneous presence of gaseous molecules of various nitrogen oxides NO_x with the foreign carbon (in the form of CO_2). Essentially, the irradiated samples were the co-doped (N, C)-BaO system, in which carbon and nitrogen (the latter mostly in the gaseous state) were adsorbed on the surface of BaO oxide and BaF_2 fluoride particles. The hypothesis is confirmed by the fact that the desorption of the gaseous components at the long storage under normal conditions influenced the magnetic response (the response decreased), which counts in favor of the surface nature (in this particular case) of RTFM with participation of gaseous molecules, atoms, and defects on the surface of a solid body. We do not consider F-centers (fluorine vacancies) in the anion-deficient BaF_2 matrix as a main source of RTF, although we do not exclude the possibility that F-centers can favor in some way the appearance of RTFM by analogy with RTFM of NPles, with participation of oxygen vacancies in oxide systems [64].

Next we consider in what state the components of the N-BaO and (N,C)-BaO systems were present in annealed and irradiated samples. The BaO concentration in the initial S0 sample was negligibly low, which was confirmed by the results of EDX method analysis (zero oxygen concentration in the sample) (Table 3) and the XRD method (no foreign phases) (Fig. 1). Therefore, the main impurity in the unannealed S0 sample was carbon (9 at %, Table 3) in the presence of water

molecules and fluorine vacancies (strong nonstoichiometry has shown the deficit of fluorine, see Table 3).

In the freshly obtained S0 sample, the PM response was observed (curve 1, Fig. 13).

This response decreased significantly in the S200 sample (curve 2, Fig. 13) as a result of dehydration at the annealing (see TG curves in Fig. 3). In particular, a sharp increase of the carbon concentration in the S200 sample (Table 3) can be readily explained as a result of CO_2 adsorption by BaO crystals free of water molecules. Additionally, despite the growth of the carbon concentration in the S200 sample, the PM response in the sample decreased, which allows us to attribute the presence and transformation of the PM response in the S0 and S200 samples to the evaporation of water molecules adsorbed in mesopores and on the surface of small 3D particle agglomerates. However, the annealed S200 sample included oxygen (Table 3), and the results of electron microscopy (Tables S2 and S3 in the ESM) also confirmed the presence of the oxide phase BaO in S0 and S200 samples.

The available theoretical calculations justifying the FM ordering in N-doped and C-doped BaO [57–61] are somewhat contradictory. In the opinion of the authors of [57], “the origin of magnetism is linked to the electronic structure. The FM (FM) and antiFM (AFM) coupling between the N atoms in BaO reveals that doping N atoms have a FM ground state, and the calculated transition temperature (T_C), within the Heisenberg mean field theory, theorizes possible room temperature FM in N-doped BaO. Nitrogen also induces ferromagnetism when doping occurs at surface O site and has smaller defect formation energy than the bulk N-doped BaO. The magnetism of N-doped BaO is also compared with Co-doped BaO.”

In [58], it was also shown that not only C (N)-doped CaO [59–61], but also carbon-doped BaO (MgO, SrO) show half-metallic and transparent ferromagnetism without any TM impurities based on our *ab initio* calculation. However, the calculations in [62] have shown that the calculated Curie temperature is lower than the room temperature, and RTFM cannot be achieved in N-doped BaO. The study of interaction of oxygen vacancies with N-impurities has shown that the presence of N leads to a sharp reduction in costs for generation of oxygen vacancies. Vacancies, in their turn, decrease the magnetic moment of N-additives, thus favoring a decrease in the concentration of magnetic admixtures. It was concluded in [63] that the increase of the Curie temperature in N-doped MgO from 30 K to RT is hard to achieve.

Taking into account the mesoporous type of the BaF_2 powder in the S0-S400 samples (Table 2), we assumed that as the dose of irradiation by 700-keV electrons increases, the concentration of gaseous nitrogen oxide NO_x formed as a result of e-beam interaction with the ambient air should increase and lead to the active adsorption of NO_x on the surface of NPles and in interparticle pores. As a result, the coupling of NO_x should be formed (essentially, the doping of the surface layer of BaF_2 NPles by nitrogen and oxygen atoms), which should result, according to theoretical predictions [57–61], in appearance of the FM response in irradiated samples. The experiment has confirmed this hypothesis. Fig. 14 depicts the variation of the specific magnetization of the mesoporous S0, S200, and S400 samples before and after the irradiation.

One can see from Fig. 14a that after 30 min of irradiation, the magnetization of the non-irradiated samples in the magnetic field of 12 kOe increased nearly five times (from 0.004 (Fig. S6 in the ESM) to 0.01 emu/g for S0, 3.3 times (from 0.003 to 0.010 emu/g) for S200, and nearly three times (from 0.001 to 0.003 emu/g) for S400. This confirms experimentally the theoretical prediction of the possibility of d0 FM in the N-BaO system [57–61] and does not coincide with the conclusions of [62,63]. The measurement of magnetization of the irradiated micron-sized powder (S900 sample), which contained no mesopores (Table 2), has also demonstrated (Fig. 15) the almost fourfold growth of magnetization in the magnetic field of 12 kOe after 30-min irradiation (from 0.004 (curve 3, Fig. 13) to 0.015 emu/g).

This behavior of S900 can be explained quite readily. It is well-known that layered structures are formed in fluorides of alkali-earth

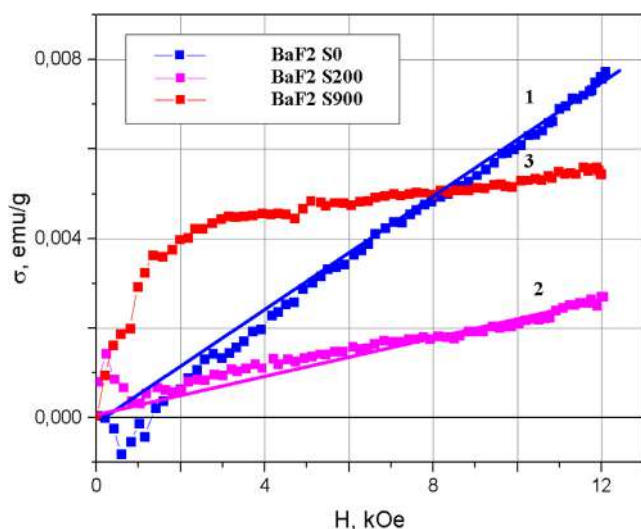


Fig. 13. Room-temperature magnetization curves of S0, S200 and S900 samples [21].

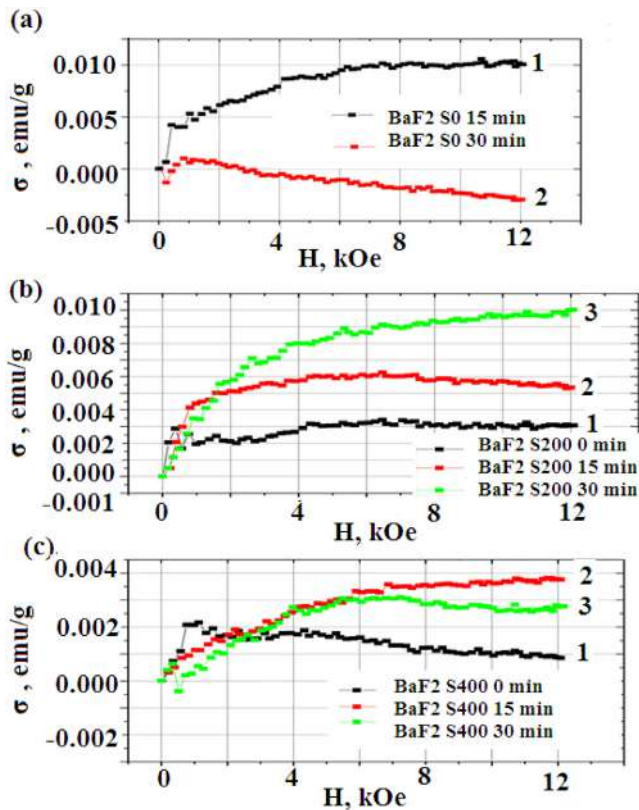


Fig. 14. (a) Magnetization curves of irradiated sample S0 for 15 min (curve 1) and 30 min (curve 2); (b,c) Magnetization curves of nonirradiated (curve 1) and irradiated samples S200 and S400 for 15 min (curve 2) and 30 min (curve 3).

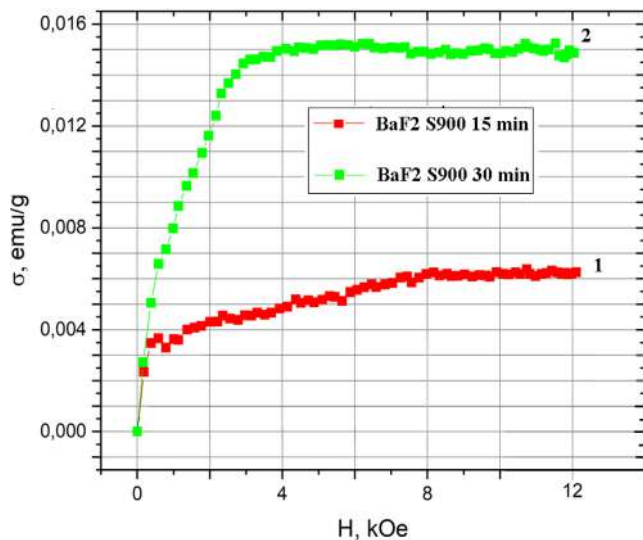


Fig. 15. Magnetization curves of S900 for different periods of irradiation by 700-keV electrons in air: curve 1–15-min irradiation; curve 2–30-min irradiation.

metals at the annealing temperature above 600 °C [64,65]. It is also known that BaO, which is generated at the annealing of fluorides, is used widely for purging of exhaust gases of car engines from the nitrogen oxides NO_x alone [66]. Nitrogen atoms are mostly captured at angles and edges of the BaO cubic structure [67]. Thus, in our case, the BaO concentration increases continuously at annealing, then BaO interacts with residual NO_x molecules stored in the mesoporous structure of the NP and with foreign carbon (the concentration of which is rather

high according to the EDX data), and this interaction leads to appearance of the surface FM response equal to 0.004 emu/g in N-doped BaO and C-doped BaO structures formed on the surface of the non-irradiated S900 sample (curve 3, Fig. 13).

The fact that magnetization of irradiated S200 and S900 samples exceeds three to four-fold that of the non-irradiated S200 и S900 samples proves unambiguously that the intensification of RTFM is linked to the effect of the ambient gas atmosphere formed in the process of irradiation by relativistic electrons on the powder samples. Under the irradiation by 700-keV electrons, the pollution of the samples with some foreign magnetic impurities is impossible. Therefore, we reject the impurity model of magnetism as the cause for RTFM.

Fig. 16a–d shows the transformation of specific magnetization of unannealed sample as a function of the annealing temperature.

One can see that:

With an increase of the annealing temperature, due to desorption of water, the smooth transformation of the PM response S0 and S200 samples (Fig. 13) to the FM response in (S400, S600, and S900) occurs (Fig. 16c–d), respectively). In the S400 sample, the magnetic response is a sum of the ferro- and diamagnetic-contributions (Fig. 16c). The FM contribution manifests itself in weak fields of about 1 kOe. The diamagnetic contribution becomes decisive in strong fields. This behavior is quite natural, since at the annealing temperature of 400 °C the sample contained the minimal concentration of structure defects in the matrix and was insufficiently oxidized to clear the percolation threshold between atoms of the fluorine matrix and nitrogen molecules adsorbed on its surface. In addition, the considerable part of carbon, capable of manifesting the d0 magnetism in the C-BaO system, was desorbed in the form of CO₂ from the sample as the annealing temperature increased up to 400 °C. The FM response in the S400 sample is very weak (below than $1 \cdot 10^{-3}$ emu/g), which is indicative of the insufficient BaO concentration in the S400 sample because of the short (10 min) annealing at the relatively low temperature. The change in the shape of the magnetization curves of the S400, S600, and S900 (Fig. 16c–e) samples indicates clearly the decrease of the contribution of diamagnetic fluorine matrix BaF₂ to the total magnetic response at the increase of the annealing temperature. The magnetization curve of the S600 sample (Fig. 16d) has shown a growth of the FM contribution due to an increase of the BaO concentration, as well as a reduction of the influence of diamagnetic fluorine matrix due to the further annealing of defects. In the S900 sample the BaO concentration is maximal and, similarly, the concentration of nitrogen and carbon absorbed from the air is maximal, which leads to considerable intensification of the magnetic response up to 0.004 emu/g (Fig. 16e).

The hypothesis was additionally checked through measurement of the magnetization of the initial and irradiated the micron-sized BaF₂ powder (Target sample) by 700-keV electrons. It was assumed that the electron irradiation of the micron-sized powder cannot lead to the appearance of the FM response in it because of the absence of the sufficient amount of BaO. This assumption has been confirmed. The experiment has shown the diamagnetic response in the Target sample (Fig. 16f). First, this proves its initial purity of magnetic purity from traces of magnetic additives. Second, the 15-min irradiation in the nitrogen-containing gas environment did not lead to the appearance of the FM response in the irradiated Target sample. This is also indicative of the lack of BaO oxide, the necessary component of the N-BaO system, in which the appearance of the d0 magnetism was predicted [57–61]. Fig. 17 shows the transformation of the magnetic response in the S0 BaF₂ sample as a function of the storage time.

It can be seen that the sample magnetization decreases with time, which indicates the absence of stability in the magnetic response due to desorption of NO_x gas molecules from the surface of interparticle pores of NP. A similar transformation of luminescent properties due to the decomposition of clusters was often observed in alkali fluorides [68,69]. In our case, no clusters formed, as can be seen from the element mapping data (Figs. S3 and S4 in the ESM).

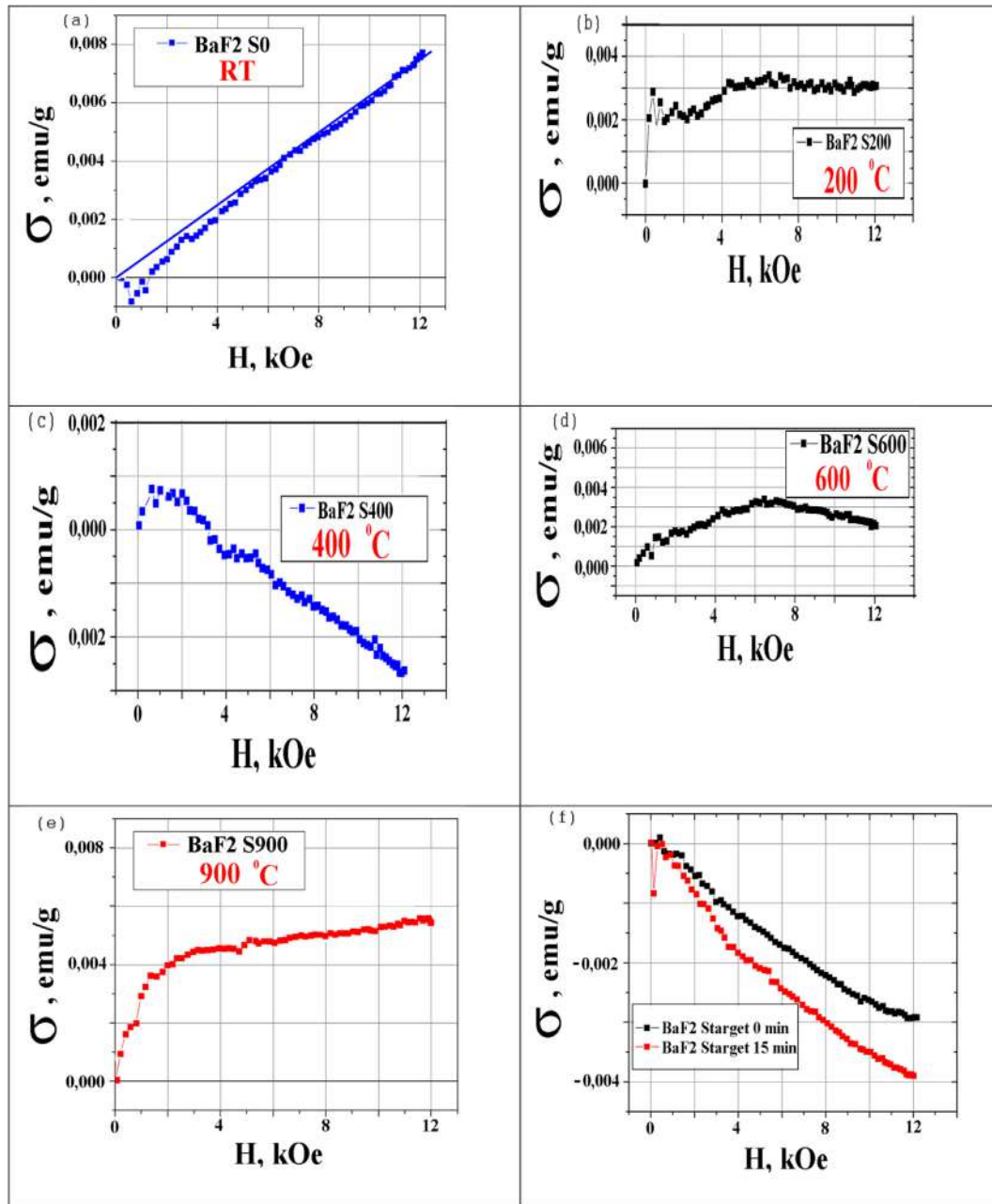


Fig. 16. (a)–(e) Specific magnetization as a function of annealing temperature in BaF₂ NP.; (f) Magnetization of Target sample before and after 15 min of electron beam irradiation.

4. Conclusion

The nano-crystalline mesoporous BaF₂ powder with the SSA up to 34.8 m²/g has been generated with the PEBE method in vacuum. With the thermal annealing and the action by a pulsed electron beam with the electron energy of 700 keV on BaF₂ samples, the alternation of the main physical-chemical characteristics of NPs has been demonstrated, namely.

The presence of d0 magnetism and the cause for its appearance in the BaF₂ NPs have been shown experimentally. The transformation of d0 magnetism at the annealing and irradiation by relativistic electrons in air has been demonstrated. With the TEM, DSC-TG, and EDX methods, the presence and mechanism of formation of foreign carbon- and nitrogen-containing phases in the BaF₂ samples at the annealing and e-beam irradiation have been shown. The hypothesis of appearance of d0 magnetism at the room temperature in the BaF₂ NP has been put

forward and confirmed experimentally. It has been shown experimentally that the nature of magnetism is different for the initial unannealed BaF₂ NP and that annealed in the air. In the samples annealed at the higher temperature, the FM response increases due to the appearance of the additional BaO oxide phase. The irradiation by relativistic electrons resulted in the growth of the FM contribution in each and every S0-S900 samples mostly due to an increase in the concentration of gaseous NO_x molecules in mesopores and on the surface of BaF₂ NPLs containing the BaO oxide. The magnetic measurements have shown the transformation of the magnetic response in the nonirradiated and irradiated samples with time due to desorption of gaseous impurities (NO_x, CO₂, etc.) from the mesoporous structure of BaF₂ NPs.

The analysis of possible correlation between magnetic and luminescent properties at different values of the annealing temperature in air revealed the absence of this correlation. Thus, in this study we observed, for the first time, the temporarily variable surface d0 magnetism

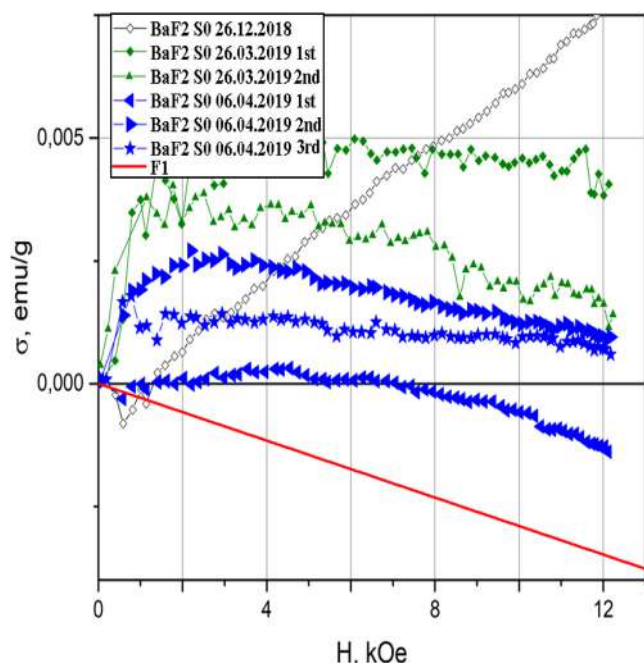


Fig. 17. The transformation of the magnetic response in the S0 BaF₂ sample as a function of the storage time. Dates of magnetization measurements are indicated. Curve F1—change in the magnetization of bulk BaF₂ in a magnetic field.

in the oxi-fluoride BaF₂-BaO system. It is shown that the d0 magnetism arises on the surface, rather than in the volume of BaF₂, therefore, the desirable stable N-BaF₂, C-BaF₂, and N(C)-BaF₂ solid solutions do not form. An important achievement of this study is the tentative demonstration of d0 magnetism in the BaF₂-BaO oxi-fluoride system co-doped by carbon and nitrogen.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jmmm.2020.166666>.

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