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V. I. Popkov, Facile combustion synthesis of TbFeO_3 nanocrystals with hexagonal
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Nanosystems: Physics, Chemistry, Mathematics, 2019, Volume 10, Issue 6, 694–700

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Facile combustion synthesis of TbFeO₃ nanocrystals with hexagonal and orthorhombic structure

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PACS 61.46.+w, 75.50.Bb, 75.60.-d

DOI 10.17586/2220-8054-2019-10-6-694-700

In this research, the formation process of nanocrystalline terbium orthoferrite (TbFeO₃) obtained via a solution combustion technique was studied using powder X-ray diffractometry, scanning electron microscopy, ⁵⁷Fe Mössbauer spectroscopy, N₂ adsorption analysis, and FTIR spectroscopy. It was shown that glycine-nitrate combustion method permits one to obtain TbFeO₃ of three different modifications: orthorhombic o-TbFeO₃ (Pbnm), hexagonal h-TbFeO₃ (P6₃/mmc) and amorphous am-TbFeO₃. It was found that the average crystallite sizes of orthorhombic and hexagonal TbFeO₃ were 29±3 and 15±2 nm, respectively. The formation mechanism of different structural forms of terbium orthoferrite was investigated on the basis of nanopowders morphology, specific surface areas, average pore sizes, and crystallite sizes.

Keywords: nanocrystals, rare earths, orthoferrites, terbium orthoferrite, TbFeO₃, phase formation, polymorphism.

Received: 12 October 2019

Revised: 4 December 2019

1. Introduction

During the last few decades, there has been an increased interest in the study of ferrites with various compositions due to a large number of areas of their practical application [1–3]. Unique structural and electromagnetic parameters allow the use of these type substances in the production of microwave ceramics, magnetically recoverable catalysts, magnetic devices, etc. [4–6]. Among a large number of rare-earth metal orthoferrites, terbium ferrite (TbFeO₃) stands out, due to its antiferromagnetic and ferroelectric properties [7]. Despite the fact that compounds of this class were actively studied for more than a decade, the discovery of new areas of use for nanostructured multiferroics in the case of which the electromagnetic properties differ significantly is an important and urgent task is to study the processes of their formation [8]. Furthermore, the discovery of the existence of metastable paramagnetic modification in a number of compounds of the type RFeO₃ leaves open the question of their controllable and phase-pure production [9].

Currently, terbium orthoferrite was successfully obtained in two different modifications with an orthorhombic and hexagonal structure. However, a metastable hexagonal structure was obtained only in the form of thin films and in this work, it was obtained for the first time in its bulk form via the solution combustion method. The complexity of its preparation lies in the nature of the polymorphism of terbium orthoferrite and related to the ratio of its ionic radii. According to the data presented in [10, 11], it is known that, under certain conditions, it is possible to obtain a metastable hexagonal modification of yttrium and holmium orthoferrites, due to a number of factors such as small crystallite size and inter-pore space.

The orthorhombic modification of terbium orthoferrite is a distorted perovskite-like structure Fe³⁺ cations, which are in an octahedral oxygen environment, and the Tb³⁺ cation is located in the distorted trigonal prism of O²⁻ anions. It is known from the literature that there are two types of directions of rotation of the oxygen octahedra of the rhombic structure of rare-earth metal orthoferrites that correspond to the space groups Pnma or Pbnm [12]. It should be noted that the latter type of structure is almost never encountered. The rhombic modification of o-TbFeO₃ is thermodynamically stable over the entire temperature range of the compound. The hexagonal modification of terbium orthoferrite corresponds to a more deformed perovskite-like structure and corresponds to the unit cell h-TbFeO₃ (P6₃/mmc) which consists of FeO₅ trigonal pyramids and yttrium Tb atom planes. Besides that, each terbium atom is in the octahedron, the structure of which is tightly packed oxygen atoms with four additional oxygen atoms along the axis c with a significant distance from the terbium atom. This explains the metastable nature of the hexagonal modification, in which case the Fe³⁺ cation is located in the center of a trigonal bipyramid.

In this work, terbium orthoferrite was obtained by the solution combustion method at various Red/Ox ratios using glycine as a fuel and a chelating agent (G/N = 0.2–1.4). The choice of this synthesis technique was made because the solution combustion method has already shown its effectiveness in obtaining metastable hexagonal modifications of

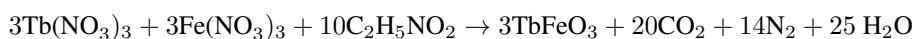
rare-earth element orthoferrites of the RFeO₃ type [10, 11]. All obtained terbium orthoferrite powders were investigated by a complex of physicochemical methods, including determination of chemical composition, morphology, and structure.

2. Experimental

Nanocrystalline terbium orthoferrite was obtained by the glycine-nitrate combustion method using glycine as fuel at different G/N ratios in the initial mixture (G/N = 0.2–1.4) using the technology described in detail in [13, 14]. The reaction solution was prepared using nitrates of terbium (Tb(NO₃)₃·6H₂O) (puris.), iron (Fe(NO₃)₃·9H₂O) (puris.) and glycine (C₂H₅NO₂) (puris.) dissolved in 40 ml of distilled water and heated to 50 °C. The redox ratio was calculated in such a way as to differ from the stoichiometry of the reaction in steps of 0.2:

$$G/N = \frac{n_{Gly}}{n_{NO_3^-}}$$

n_{Gly} – glycine amount of mole, $n_{NO_3^-}$ – nitrate groups amount of mole. It should be noted that in the case of a significant deviation from the stoichiometry of the reaction, a number of foreign substances (C, CO, N₂O, NO, NO₂) may form, in which case, it is difficult to accurately equalize the reaction. In this regard, the calculations were performed based on the formation of terbium orthoferrite with a stoichiometric ratio of glycine to nitrate-groups:



The reaction solution thus prepared was mixed until the starting components were completely dissolved and heated until the water was almost completely removed and the self-ignition point was reached and as a result, brown powders were formed. Obtained samples were thermally treated in a muffle furnace at a temperature of 500 °C for 2 hours to remove impurity organics and mechanically milled in a mortar.

The elemental analysis and morphology of the synthesized compositions were studied by scanning electron microscopy and energy dispersive x-ray analysis using a scanning electron microscope *Tescan Vega 3 SBH* equipped with an *Oxford INCA* x-act x-rat spectral microanalysis.

Powder X-ray diffraction analysis was performed using the method of powder x-ray diffraction on *Rigaku Smart-Lab 3* powder diffractometer using monochromatic CuK α radiation and *ICDD PDF-2* powder database. The average crystallite size (coherent scattering area) was determined from X-ray diffraction lines broadening using Scherrer equation:

$$D = \frac{k\lambda}{\beta \cos \theta}$$

where k is the crystal shape factor (assumed to be 0.94 in the isometric approximation), λ is the X-ray emission wavelength (CuK α , $\lambda = 0.15406$ nm), β is the diffraction maximum broadening with considering instrumental error (in radians), θ is the diffraction peak position (Bragg angle).

Absorption spectra of the samples and the presence of impurity organics were determined by FTIR spectroscopy on *Shimadzu IRTracer-100* in the range from 500 to 3800 cm⁻¹ in absorption mode.

The state of Fe atoms in obtained compositions has been studied using Mössbauer spectrometer *Wissel* (Germany). Measurements have been made in absorption geometry at room temperature. Isomer shift has been evaluated with respect to α -Fe. Information about phase composition has been obtained by comparing the Mössbauer parameters of iron atom state recorded in the experiment with the data of other studies presented within literature.

The specific surface of the obtained compositions was studied using a low-temperature nitrogen (N₂) sorption-desorption method. The isotherms of all synthesized samples were obtained at the temperature of liquid nitrogen (77 K) using a *Micrometrics ASAP 2020* analyzer after vacuum degassing at 300 °C for 5 h.

3. Results and discussion

According to energy-dispersive X-ray spectroscopy data the obtained samples correspond in their chemical composition to terbium orthoferrite (TbFeO₃) with a ratio of terbium atoms are close equal to 50%/50% (Fig. 1, a).

The largest deviation from the stoichiometric composition ($\approx 1\%$) is observed for the samples obtained at a ratio of G/N = 0.4 and 1.0, which lies within the error of the determination method used. The results of scanning electron microscopy demonstrate the effect of the Red/Ox ratio on the morphology of the synthesized TbFeO₃ powders (Fig. 1, b-h). The data obtained indicate that, with a slight deviation from stoichiometry (G/N = 0.4 and 0.8), agglomerates several microns in size consisting of nanometer-sized particles are formed. In their appearance, they resemble agglomerates of other orthoferrites obtained by solution combustion [15]. With a significant deficiency (G/N < 0.4) and excess glycine (G/N > 0.8), the formation of amorphous structures without pronounced differences is observed.

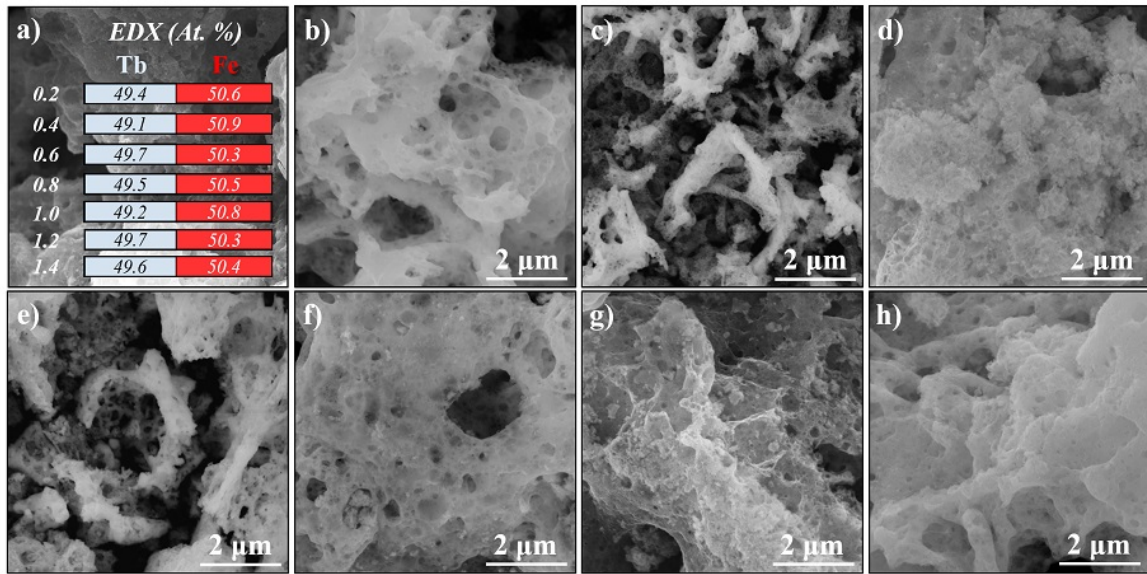


FIG. 1. EDX results (a) and SEM images of glycine-nitrate combustion products, synthesized at the following G/N ratio: 0.2 (b), 0.4 (c), 0.6 (d), 0.8 (e), 1.0 (f), 1.2 (g) and 1.4 (h)

The most unusual sample appears to be obtained with a stoichiometric ratio of glycine to nitrogen in nitrates ($G/N < 0.6$) in the agglomerates of which there are no large numbers of voids which are usually formed as a result of abundant gas evolution during the self-ignition process. In addition, the obtained images clearly demonstrate that this sample consists of loose nanostructured compositions. This feature is most likely related to the shift of the maximum point of the real combustion temperature, which was repeatedly mentioned in a number of other works [16, 17].

The results of the X-ray powder diffraction analysis show that the formation of terbium orthoferrite begins with a glycine-nitrate ratio of $G/N = 0.4$ (Fig. 2).

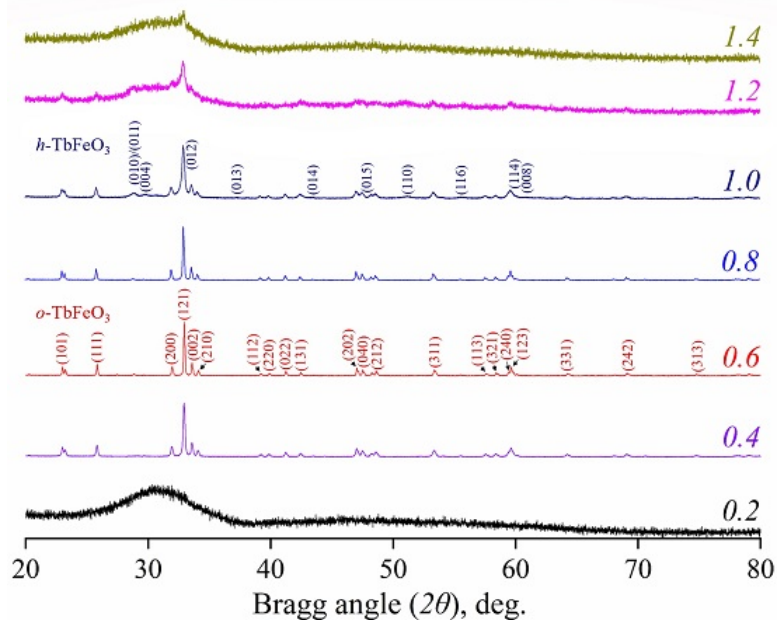


FIG. 2. PXRD pattern of $TbFeO_3$ -based nanopowders synthesized at different G/N ratio

It should be noted that the redox environment of the reaction solution significantly affects the phase composition of the resulting compositions. For example, the orthorhombic modification of terbium orthoferrite $o-TbFeO_3$ is formed in a wide range of G/N ratios from 0.4 to 1.2. In the case of a transition to the region of a significant excess of fuel

($G/N = 1.0$ – 1.4), the appearance of hexagonal terbium orthoferrite $h-TbFeO_3$ and amorphous terbium orthoferrite $am-TbFeO_3$ was observed. The appearance of metastable hexagonal modification is associated with the peculiarities of the process of its formation, namely, the thickness of the inter-pore space, the size of the resulting particles, and the combustion mode. All these factors are directly affected by the selected glycine to nitrate ratio, which was described in detail in [10, 12]. In this case, a similar situation is observed and the formation of metastable hexagonal modification occurs exclusively in areas of a significant excess of glycine, the conditions in which correspond to those necessary for its formation. In the region with a significant lack of fuel ($G/N = 0.2$), the formation of terbium hexagonal orthoferrite does not occur. The average crystallite sizes of orthorhombic and hexagonal $TbFeO_3$ are 29 ± 3 and $15 \pm$ nm, respectively.

The results of Mössbauer spectroscopy indicate the presence of three main components in the spectra of the synthesized samples – two doublets and one sextet (Fig. 3).

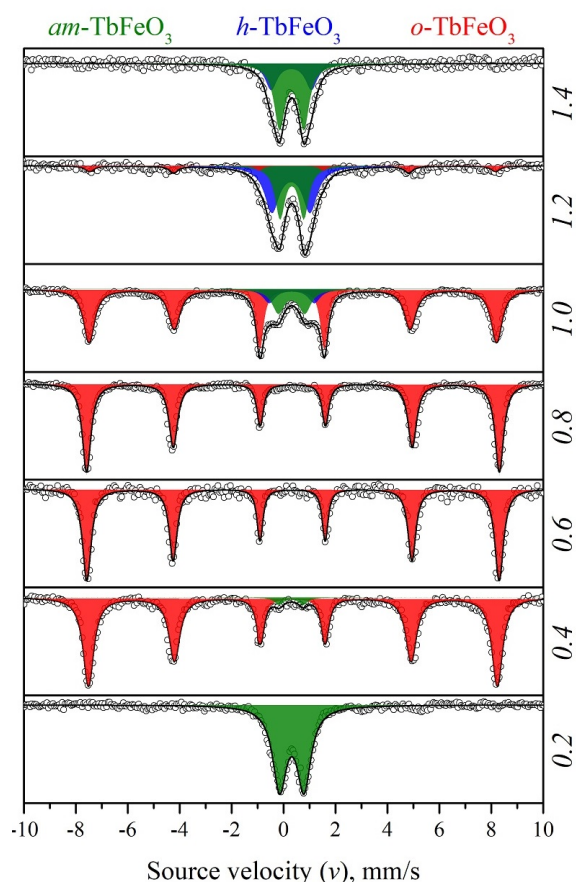


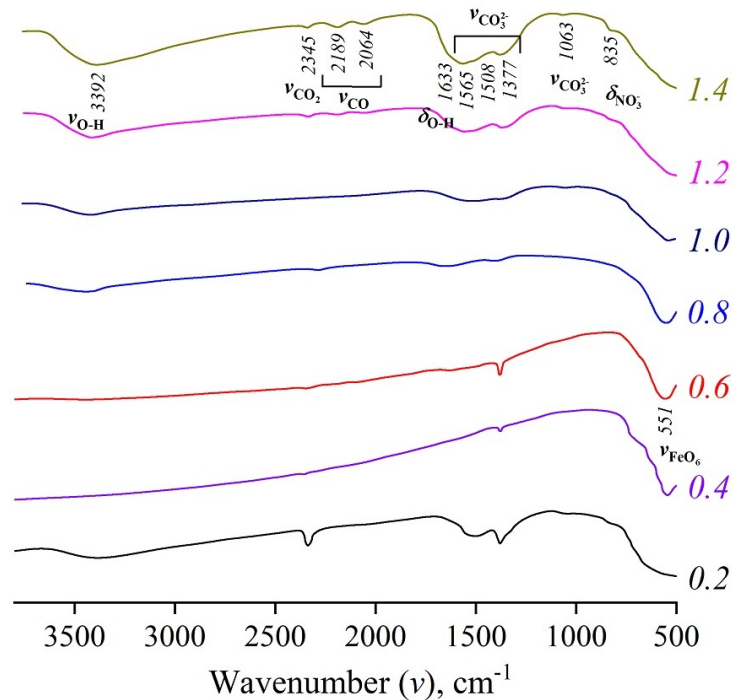
FIG. 3. ^{57}Fe Mössbauer spectra of $TbFeO_3$ -based nanopowders synthesized at different G/N ratio

These components according to the value of the isomeric shift ($IS = 0.306$ – 0.349 mm/s) correspond to the presence of iron atoms in the oxidation state of $3+$. A sextet with zero quadrupole splitting refers to the position of the Fe^{3+} cation in the oxygen octahedron $[FeO_6]$ in the perovskite-like structure of holmium orthoferrite and, according to the value of hyperfine magnetic splitting ($H_{eff} = 48.987$ T), agrees well with the results of other studies [18–20]. The remaining two doublets have close values of the isomeric shift – 0.313 and 0.306 mm/s, but differ greatly in the magnitude of the quadrupole splitting – 0.948 and 1.600 mm/s, correspondingly. In accordance with our previous study [10], these two components of the Mössbauer spectra can be attributed to the amorphous ($am-TbFeO_3$) and hexagonal ($h-TbFeO_3$) forms of terbium orthoferrite, correspondingly. The Mössbauer characteristics of various modifications of terbium orthoferrite are given in Table 1. Thus, the results of ^{57}Fe Mössbauer spectroscopy fully confirm the data of X-ray diffraction.

According to the results of FTIR spectroscopy of the synthesized samples (Fig. 4), the amount of substances adsorbed on the surface of terbium orthoferrite directly depends on the glycine to nitrate ratio.

TABLE 1. Mössbauer characteristics of the different TbFeO₃ modifications

Terbium orthoferrite modification	Isomer shift (<i>IS</i>), mm/s		Quadrupole splitting (<i>QS</i>), mm/s		Effective magnetic field (<i>H_{eff}</i>), T	
	This work	Literature	This work	Literature	This work	Literature
<i>am</i> -TbFeO ₃	0.313(19)	0.30 [19]	0.948(52)	1.18 [19]	—	—
<i>h</i> -TbFeO ₃	0.306(13)	0.29 [19]	1.600(86)	2.13 [19]	—	—
<i>o</i> -TbFeO ₃	0.349(11)	0.357 [20]	~ 0	0.007 [20]	48.987(91)	49.9 [18]

FIG. 4. FTIR spectra of TbFeO₃-based nanopowders synthesized at different G/N ratio

The samples obtained with a significant shortage and excess fuel ($G/N = 0.2$ and 0.4) are characterized by the presence of a large amount of sorbed water whose absorption bands are observed in the region of 3400 cm^{-1} and correspond to asymmetric vibrations of the O-H bond in H₂O molecules. Besides, several absorption bands in the region between 1500 and 1350 cm^{-1} correspond to symmetric and asymmetric stretching vibrations of the C–O bond in the carbonate group CO₃²⁻ and are most noticeable in the samples obtained with the ratio $G/N = 1.2$ and 1.4 , which, in turn, corresponds to the region of the presence of the maximum percentage of hexagonal modification. The presence of a large number of carbonate groups is most likely due to the active interaction of the obtained powders with carbon dioxide (CO₂), which is one of the main gaseous combustion products. It should also be noted the presence of absorption bands in the region from 2190 to 2060 cm^{-1} correspond to vibrations of the C–O bond in carbon monoxide, which is also a product obtained during combustion. In addition, the presence of the absorption band peaked at 550 cm^{-1} that corresponds to stretching vibrations of the Fe–O bond on the octahedron [FeO₆] of terbium orthoferrite confirms X-ray diffraction data.

The most important parameter that determines the possibility of forming a metastable hexagonal modification is the size of the inter-pore space and specific surface area. The determination of these parameters for terbium orthoferrite samples obtained at various glycine-nitrate ratios was carried out on the basis of the results of measuring the low-temperature (77 K) adsorption-desorption of nitrogen N₂ by the surface of the sample (Fig. 5).

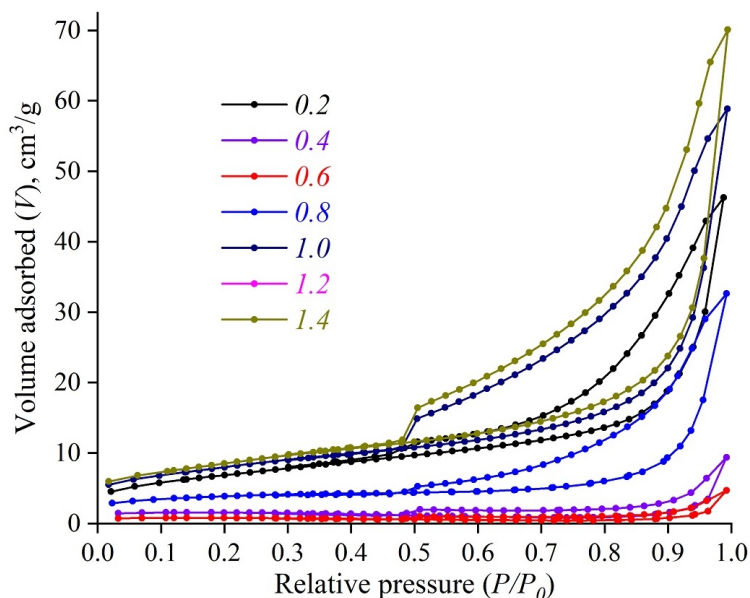


FIG. 5. N₂ adsorption-desorption isotherms of TbFeO₃-based nanopowders synthesized at different G/N ratio

An analysis of the data presented indicates that the obtained isotherms correspond to H2 type (with the exception of the sample synthesized at a ratio of $G/N = 0.6$) according to the IUPAC classification, which is typical for substances with a porous structure.

The specific surface value determined with the multi-point BET (Brunauer – Emmett – Teller) method is shown in Fig. 6.

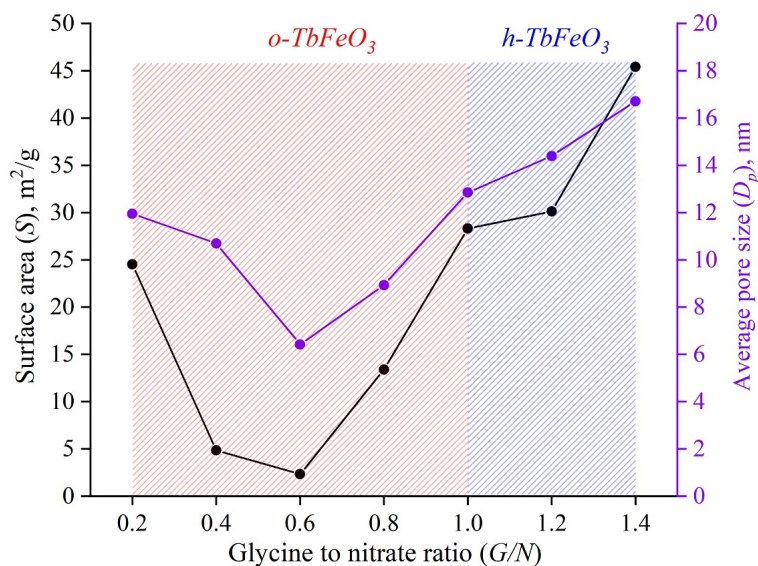


FIG. 6. Surface area vs average pore size of TbFeO₃-based nanopowders depending on the G/N ratio

According to the data obtained, the total porosity of the samples ranges from 0.073 cm³/g to 0.003 cm³/g and is due to the presence of pores with diameters of 6–17 nm depending on the glycine-nitrate ratio used (Fig. 6). These values are strictly correlated with crystallite sizes of terbium hexagonal orthoferrite, which may indicate the stabilization of this structural form due to the spatial limitations of inter-pore space. Thus the porous structure of the obtained compositions plays a decisive role in the formation of terbium orthoferrite nanocrystals with a hexagonal and orthorhombic structure, which is a distinctive feature of phase formation in systems based on rare-earth orthoferrites [10].

4. Conclusions

In the present paper, our investigation of the process for terbium orthoferrite formation under solution combustion conditions using glycine as a fuel has been completed. It has been shown that at glycine-nitrate G/N ratios ranging from 0.4 to 0.8, the orthorhombic terbium orthoferrite (o-TbFeO₃) is formed with a particle size of 29±3 nm. Upon reaching a point of a significant excess of glycine (G/N > 1.0) and, as a result, the appearance of a large number of carbonate groups from the combustion products and the average pore size about 13–17 nm, the formation of amorphous am-TbFeO₃ and hexagonal h-TbFeO₃ (P6₃/mmc) is observed. The maximum percentage of hexagonal modification is observed for the sample obtained at a ratio of G/N = 1.2 and is equal to 27%.

Acknowledgment

This study was financially supported by the Russian Foundation for Basic Research (project no. 18-03-00414) and partially performed using the equipment of the Engineering Center of St. Petersburg State Institute of Technology (Technical University).

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