

A new method of synthesis of BiFeO₃ prepared by thermal decomposition of Bi[Fe(CN)₆]·4H₂O

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Abstract In order to investigate the formation of the multiferroic BiFeO₃, the thermal decomposition of the inorganic complex Bismuth hexacyanoferrate (III) tetrahydrate, Bi[Fe(CN)₆]·4H₂O has been studied. The starting material and the decomposition products were characterized by IR spectroscopy, thermal analysis, laboratory powder X-ray diffraction, and microscopic electron scanning. The crystal structures of these compounds were refined by Rietveld analysis. BiFeO₃ were synthesized by the decomposition thermal method at temperature as low as 600 °C. There is a clear dependence of the type and amount of impurities that are present in the samples with the time and temperature of preparation.

Keywords Bi[Fe(CN)₆]·4H₂O · BiFeO₃ synthesis · Thermal decomposition

Introduction

The study of multiferroic materials is of great interest because they exhibit ferroelectricity and magnetic ordering in the same phase [1]. The application of an electric (magnetic) field to a multiferroic material is expected to control spontaneous magnetization (polarization) by means

of magnetoelectric interactions. Therefore, the study of multiferroic materials has been an interesting subject not only from the viewpoint of solid-state physics but also because of their possible applications in electric devices such as electric field induced magnetic memory effects, electro-optic transducer controlled by magnetic fields [2–4], etc. However, ferroelectricity and magnetism hardly coexist due to the structural competition. We can find many examples of these materials in the perovskite oxides family, e.g., BiFeO₃, BiMnO₃, and YMnO₃ [5–9]. BiFeO₃, one of the very few multiferroics with a simultaneous coexistence of ferroelectricity and antiferromagnetic order in perovskite oxides, has attracted much attention for many decades since the 60s. BiFeO₃ has a ferroelectric Curie temperature (T_C) of 1,103 K and antiferromagnetic Néel temperature (T_N) of 634 K [10]. It shows also a well saturated ferroelectric hysteresis loop with a large saturated polarization of approximately 24 mC/cm² [11]. Owing to this magnetoelectric coupling, BiFeO₃ based systems may be used to develop novel applications [12–16] in the field of radio, television, satellite communications, sensors, memory devices, and digital recording, etc.

Several ways for the preparation of BiFeO₃ were informed [17–21]. Most of them try to obtain the highest purity, to be obtained at the lowest possible temperature in order to reduce cost and volatility of Bi, or to obtain nanostructured materials. The most common impurities obtained during synthesis of BiFeO₃ are Bi₂Fe₄O₉ and Bi₂₅FeO₄₀, which are usually leached out by washing with nitric acid, but this is not a convenient procedure since it can change stoichiometry of BiFeO₃ by selectively dissolving some of the elements. The synthesis of oxides, particularly perovskites and related compounds from the decomposition of inorganic coordination compounds allows one to lower the reaction temperature and to obtain

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more homogeneous and finely divided powders [22–30] and highly stoichiometric oxides [31] as well as to reduce the number of oxygen vacancies. Lowering of the number of oxygen vacancies as well as decreasing the loss of stoichiometry is of great importance in order to decrease the leakage currents of ferroelectric materials, particularly for BiFeO₃ ceramics [6].

In this article, we propose the synthesis and the structural characterization of BiFeO₃ obtained by the thermal decomposition of the inorganic complex Bi[Fe(CN)₆]₄·4H₂O, a compound which is very easy to prepare and of low cost. The decomposition process was followed by infrared (IR) spectroscopy, thermogravimetric analysis (TG), differential thermal analysis (DTA), and laboratory powder X-ray diffraction (PXRD). We perform Rietveld analysis of all samples and quantified all impurities down to ~1%. The size and morphology of the particles were determined by scanning electron microscopy (SEM). We found the optimal conditions in order to obtain BiFeO₃ at the lowest temperature possible and with the lowest amount of impurities.

Experimental

Synthesis

The inorganic complex Bismuth hexacyanoferrate (III) tetrahydrate was prepared by a method already informed in [32]. A solution of 0.1 M Bi(NO₃)₃·5H₂O, reagent grade, was prepared in 0.3 M HNO₃ in order to prevent the hydrolysis of Bi³⁺ ion. The Bi(NO₃)₃·5H₂O solution was then added to an aqueous solution of 0.1 M K₃[Fe(CN)₆] which has previously been acidified with HNO₃ to a pH of 3.0. After the mixture was stirred, the orange precipitate obtained was collected by filtration, thoroughly washed with water, and finally stored in the dark in a dry box with silica gel. The potassium content of the bismuth complex was less than 0.05 wt% by atomic absorption analysis.

BiFeO₃ was prepared by heating Bi[Fe(CN)₆]₄·4H₂O at different times in air, at temperatures between 350 and 700 °C. Two different methods of synthesis were used. In method A, the sample was introduced into the furnace at room temperature and then heated to the desired temperature at 3 °C/min, maintained during the desired time and cooled to room temperature at 3 °C/min. In method B samples were introduced into the furnace already heated to the desired temperature, maintained at that temperature during the desired time and after that were air quenched. We have previously showed that these preparation methods produce different results when applied to the synthesis of mixed oxides from the decomposition of inorganic complexes [26].

Physical characterization

IR spectra in the region 400–4,000 cm⁻¹ were recorded with a FTIR Perkin Elmer 1600 spectrometer in the transmission mode using KBr pellets. TG and DTA measurements were performed in a Shimadzu TGA/DTA-50 (in the range from 20 to 800 °C), at 5 °C/min under flowing air. Laboratory PXRD were performed in a Philips X_pert Pro PANalitics with Cu K_α radiation λ = 1.5418 Å between 10° and 90° in 2θ, steps of 0.02° and counting time of 1 s. Crystal structures were refined by the Rietveld method [33] using the FULLPROF program [34]. The size and morphology of the particles were determined by scanning electron microscopy (SEM) in an electronic microscope JEOL JSM-35 CF.

Results and discussion

Bi[Fe(CN)₆]₄·4H₂O

In Fig. 1, we show TG and DTA results for the decomposition of Bi[Fe(CN)₆]₄·4H₂O in air. The TG curve indicates that the complex decomposes in four steps involving dehydration and decarboxylation to give BiFeO₃ as the final product. The sequence of decomposition steps could be expressed as:

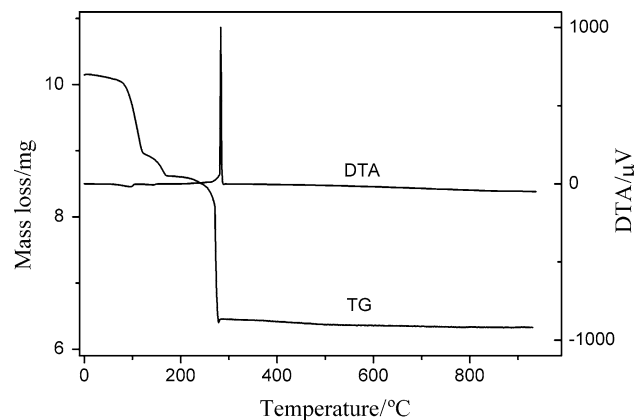
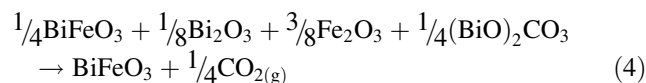
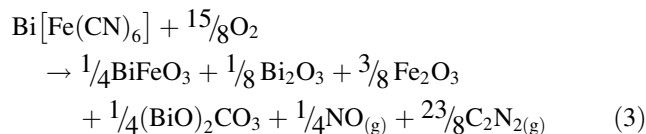
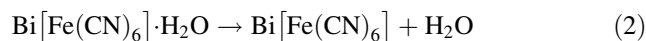
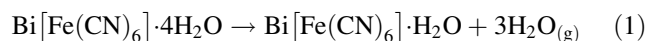
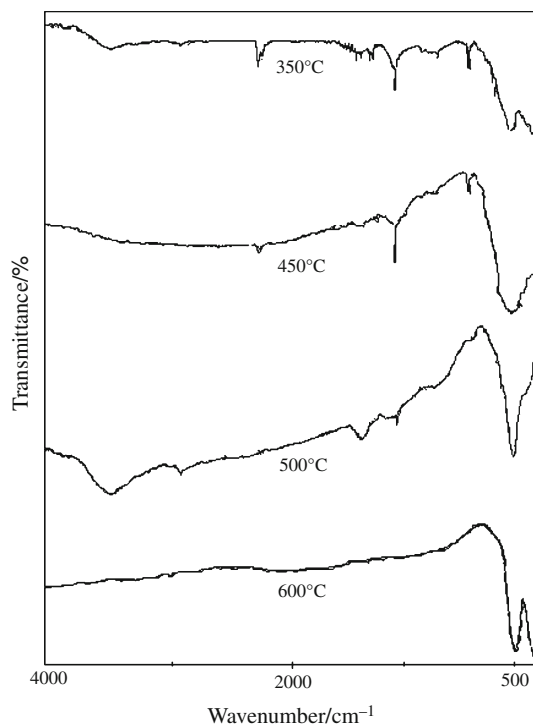


Fig. 1 TG and DTA for Bi[Fe(CN)₆]₄·4H₂O under flowing air

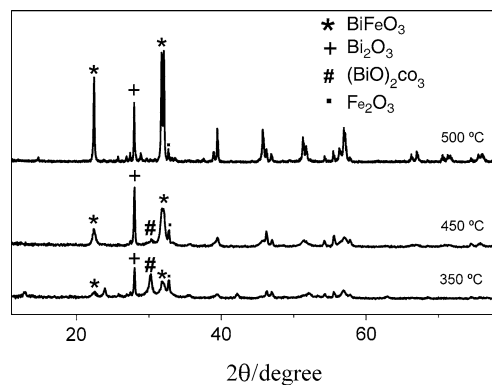
Table 1 Steps of the thermal decomposition and % mass loss

Steps	Temperature range/°C	Calculated mass loss/%	Observed mass loss/%
1	45–123	10.97	11.15
2	123–170	3.65	3.43
3	170–256	19.72	20.85
4	270–600	1.79	1.22

**Fig. 2** IR spectra of products obtained from thermal decomposition of Bi[Fe(CN)₆] \cdot 4H₂O at 350, 450, 500, and 600 °C by method A

The mass losses expected in each of the above decomposition step were in good agreement with those calculated from TG curve. These results were shown in Table 1. Solid residues obtained in the third step of the process have been confirmed from X-ray diffraction pattern and IR spectroscopy of the product isolated at different temperatures (see Figs. 2, 3).

At ca. 275 °C, 36.4% of the total mass has been lost (\approx 90% of the total volatile species). There is a large contrast with the lanthanide hexacyanoferrates (Ln[Fe(CN)₆] \cdot xH₂O) [27, 28], which in general lost their volatile compounds at larger temperatures. This could be assigned to the larger stability of carbonates of lanthanides compared to bismuth carbonate. At temperatures higher than 600 °C the mass loss remained constant.

**Fig. 3** X-ray diffraction data of products obtained from the thermal decomposition Bi[Fe(CN)₆] \cdot 4H₂O at 350, 450, and 500 °C by method A

The total mass loss from room temperature to approximately 500 °C is 37.6%. It is in agreement with the theoretical loss, calculated for the formation of BiFeO₃ from the complex.

The DTA curve shows two endothermic peaks, located at 117 and 163 °C, both due to dehydration. The third peak centered at 273 °C is exothermic and corresponds to the elimination and oxidation of the cyanide groups with the simultaneous formation of the simple oxides (Bi₂O₃, Fe₂O₃), oxycarbonate of bismuth (Bi₂O₂CO₃), and the mixed oxide (BiFeO₃).

Products obtained by heat treatment of Bi[Fe(CN)₆] \cdot 4H₂O

In Fig. 2, we show the FTIR spectra of products of calcinations obtained by method A heating at 350, 450, 500, and 600 °C for 10 h. At $T \leq 500$ °C there are bands corresponding to carbonate at 854 cm⁻¹, 1,083 cm⁻¹, and 1,380 cm⁻¹. At 552 cm⁻¹, a broad band for the stretching of M–O characteristic of oxides becomes to develop [35].

The PXRD data for the samples prepared by method A in the range 350–500 °C are shown in Fig. 3, and BiFeO₃, Bi₂O₃, (BiO)₂CO₃, Fe₂O₃ are indicated. We find that for all samples there are diffraction lines corresponding to trigonal–rhombohedral BiFeO₃ and Bi₂O₃, showing an incomplete reaction (at least for 10 h of heat treatment by method A). The main diffraction line for trigonal–rhombohedral BiFeO₃ increases at higher temperatures and this agrees with the results obtained by IR spectroscopy. Despite the fact that, Aono et al. reported the synthesis of hexagonal BiFeO₃ by the same method [36, 37].

Chamberlain et al. [38] and Raj et al. [39] have studied the thermal decomposition of hexacyanoferrates (II) and (III) using differential thermal analysis (DTA), dynamic gas evolution (DGE), and Mössbauer spectroscopic techniques. They suggest that cyanogen is a common product from all these thermal decompositions and is evolved as the

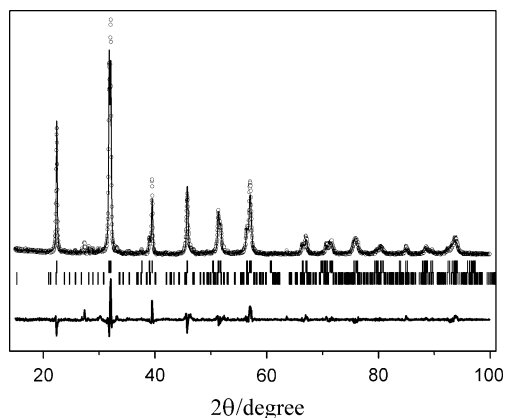


Fig. 4 Rietveld analysis of powder X-ray diffraction data of BiFeO_3 obtained at 600°C by method A from thermal decomposition of $\text{Bi}[\text{Fe}(\text{CN})_6] \cdot 4\text{H}_2\text{O}$. Circles experimental data, Continuous line Calculated diffractogram. Vertical lines correspond to Bragg reflections, upper ones BiFeO_3 , bottom ones $\text{Bi}_2\text{Fe}_4\text{O}_9$. Continuous line at the bottom Difference between experimental and calculated diffractogram

Table 2 Crystallographic parameters for trigonal–rhombohedral BiFeO_3 after Rietveld refinement of XRPD data at room temperature

Atom	Wyckoff site	x	y	z	B_{iso}
Bi	6 a	0	0	0	0.098 (5)
Fe	6 a	0	0	0.222 (1)	0.465 (3)
O	18 b	0.4707 (1)	0.0281 (1)	0.9474 (1)	1.147 (8)

SG: $R3c$; $a = 5.5798(5) \text{ \AA}$, $b = 5.5798(5) \text{ \AA}$, $c = 13.8370(2) \text{ \AA}$, $V = 373.09 \text{ \AA}^3$

Discrepancy factors: $R_{\text{wp}} = 20.1$; $R_{\text{exp}} = 13.30$; $\chi^2 = 2.28$; $R_{\text{Bragg}} = 3.32$; $R_p = 15.7$

result of an exothermic reaction. Since the formation of cyanogens from cyanide is an oxidation reaction, it seems reasonable to suggest that the metal is being reduced and that the compounds formed as thermal decomposition proceeds contain the metal in successively lower formal oxidation states.

In order to determine the composition of the residues at different temperatures, we used X'Pert HighScore program (version 2.1b, produced by PANalytical B.V. Almelo, The Netherlands). We have detected a very low percentage (less than 5%) of Fe_3O_4 but its more intense line ($2\theta = 29.73$, PDF#890951) is not observed because it is masked by another majority species.

When we increase the temperature at $T > 500^\circ\text{C}$, there is a clear definition of the structure of the trigonal–rhombohedral BiFeO_3 perovskite.

The refined PXRD data taken at room temperature for the sample prepared by method A at 600°C , using the structural model of trigonal–rhombohedral BiFeO_3 (SG $R3c$), are shown in Fig. 4. $\text{Bi}_2\text{Fe}_4\text{O}_9$ was included as

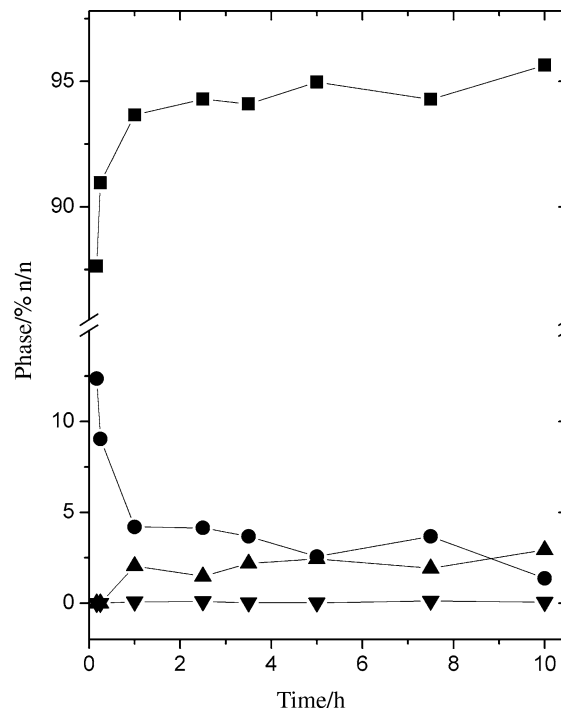


Fig. 5 Percentage (n/n) of products from thermal decomposition of $\text{Bi}[\text{Fe}(\text{CN})_6] \cdot 4\text{H}_2\text{O}$, obtained at 600°C and different times (from 10 min to 10 h) by method B. (filled square) BiFeO_3 , (filled circle) $\beta\text{-Bi}_2\text{O}_3$, (filled triangle) $\text{Bi}_2\text{Fe}_4\text{O}_9$, and (filled inverted triangle) $\text{Bi}_{25}\text{FeO}_{40}$

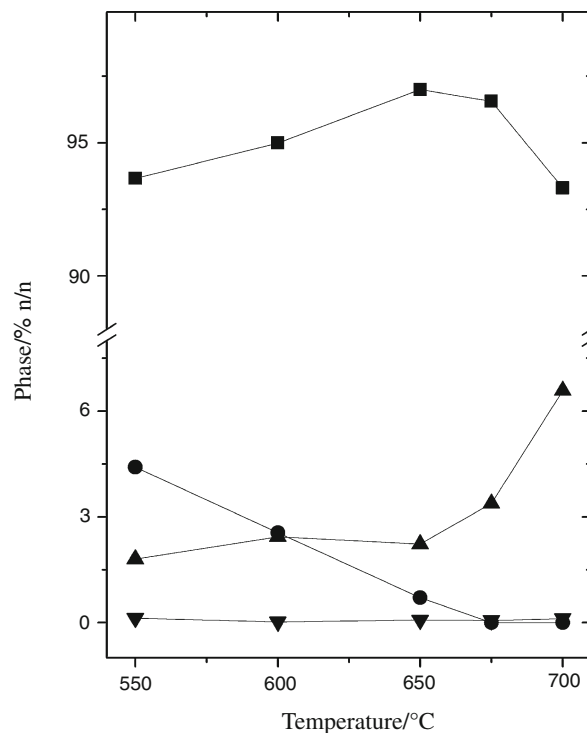


Fig. 6 Percentage (n/n) of products obtained at different T (550–700 $^\circ\text{C}$) and 5 h from thermal decomposition of $\text{Bi}[\text{Fe}(\text{CN})_6] \cdot 4\text{H}_2\text{O}$ by method B. (filled square) BiFeO_3 , (filled circle) $\beta\text{-Bi}_2\text{O}_3$, (filled triangle) $\text{Bi}_2\text{Fe}_4\text{O}_9$, and (filled inverted triangle) $\text{Bi}_{25}\text{FeO}_{40}$

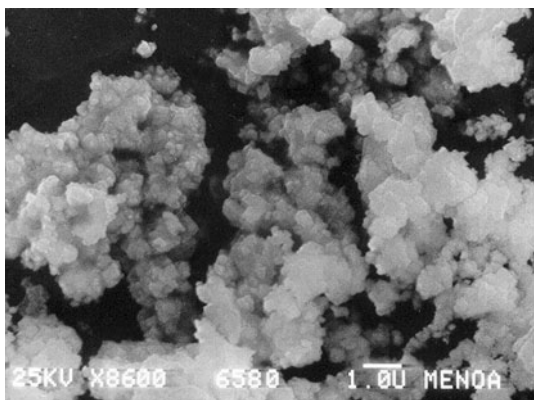


Fig. 7 Scanning electron microscopy of Bi[Fe(CN)₆] \cdot 4H₂O heat treated in air at 600 °C, during 10 h

impurity (1.1%). The final cell parameters, atomic coordinates, occupancies, thermal isotropic factors, and discrepancy factors are shown in Table 2. Data agree very well with previously informed structural data for BiFeO₃ prepared by other methods of synthesis [10, 40]. These results indicate that using this new method of synthesis we have obtained well crystallized almost pure (98.9%) BiFeO₃ at 600 °C. This low temperature of synthesis represents a considerable improvement in the preparation of BiFeO₃ compared to oxide-mixing methods, since they require up to 1,000 °C and extremely high pressures [3, 6]. In addition, the mixing of metal cations at the atomic levels and with the desired stoichiometry of the metals in the heteronuclear complex allows lowering the synthesis temperature. On the other hand, our method uses low cost reagents and a complex very easy to prepare, compared with other methods of synthesis such as thermal decomposition of precursors and sol–gel processes [19, 20].

Recently, Carvalho et al. [20] by a sol–gel combustion method showed that BiFeO₃ is a metastable phase that decomposes into Bi₂Fe₄O₉ and Bi₂₅FeO₃₉. In order to obtain pure BiFeO₃ with our synthetic method, we develop a different method (method B) in which we avoid the long heating and cooling times by steps of temperature. For example, in order to vary time, we select $T = 600$ °C and in order to vary temperature we fixed $t = 5$ h. The obtained phases with their respective molar fraction percentages, expressed as n/n, at 600 °C and different times are shown in Fig. 5. There is a strong increase in the amount of BiFeO₃ and the consequent decrease in β -Bi₂O₃ in the first hour, reaching the highest purity at $5 \leq t \leq 10$ h. Then we select $t = 5$ h and change temperature, the results are shown in Fig. 6. There is a clear increase in the amount of the impurity Bi₂Fe₄O₉ at $T \geq 650$ °C. Thus, if an increase of temperature seems to decrease the amount of unreacted β -Bi₂O₃, there is not a net increase in the percentage of BiFeO₃ because it starts to decompose to Bi₂Fe₄O₉.

In Fig. 7, we shown the SEM photograph for the decomposition product obtained at 600 °C from the Bi[Fe(CN)₆] \cdot 4H₂O. The average particle size was in the order of 0.1 μ m, agglomerates of small crystals with some pores between them are observed.

Conclusions

The thermal decomposition of the inorganic complex Bi[Fe(CN)₆] \cdot 4H₂O to prepare pure trigonal–rhombohedral BiFeO₃ at relatively low temperatures is a simple, non expensive, and efficient method.

The pyrolysis process was studied by thermal analysis, IR spectroscopy, and PXRD. Four decomposition steps were observed. The first two corresponded to the loss of water molecules, the third one to the elimination of cyanide, and the last step to the complete formation of the mixed oxide. Total mass loss ends at 500 °C, despite this; the sample at this temperature still is a multiphase (at least for 10 h of heat treatment). We found that the ideal conditions for the preparation of the purest possible BiFeO₃ are temperatures between 600 and 650 °C and times between 5 and 10 h. The only advantage, we found of method B over method A was that the former is using less time. Powdered samples with crystal sizes homogeneously distributed in the order of 0.1 μ m are obtained. Ferroelectric and magnetic properties are currently being investigated and will be published elsewhere.

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