



**Comment on “Structural, dielectric, and magnetic characteristics of  $\text{Bi}(\text{Ni}_{0.25}\text{Ti}_{0.25}\text{Fe}_{0.50})\text{O}_3$  ceramics” [J. Mater. Sci.: Mater. Electron. 27, 1209 (2016)]; “Structural and electrical characteristics of (Co, Ti)-modified  $\text{BiFeO}_3$ ” [J. Mater. Sci.: Mater. Electron. 27, 7115 (2016)]; “Structural, electrical, and magnetic characteristics of Ni/Ti-modified  $\text{BiFeO}_3$  lead-free multiferroic material” [J. Mater. Sci.: Mater. Electron. 28, 6673 (2017)]**

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## ABSTRACT

This comment on the above three papers argues that the crystals should be of sillenite type and the correct formula should be  $\text{Bi}_{25}\text{FeO}_{39}:\text{MTi}$  ( $M = \text{Co}$  or  $\text{Ni}$ ) instead of  $\text{BiFeO}_3$ . Due to the doping, a new type of unit cell, previously unknown, was proposed for such crystals. There is also about 15% of a secondary phase,  $\text{BiFeO}_3$ , in the sample. This part of the sample should be responsible for the magnetic properties recorded.

## 1 Results

The papers [1–3] present the results of studies on the different physical properties of  $\text{BiFeO}_3$  ceramics modified by two different dopants. It is clearly seen

that all the studied samples have nearly the same diffraction patterns with a characteristic set of diffraction peaks. Thus, it is obvious that the lattice parameters should be similar for all crystals. However, this is not a case. Table 1 presents all data which are totally different. As a result, it is not possible to

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accept such different unit cells. Moreover, none of the phases are consistent with those of perovskite structure contrary to the statement made by authors in [3]. Thus, it is necessary to find the source of the evident errors made in the interpretation of the diffraction patterns. Moreover, it is necessary to find the common unit cell for the studied crystals.

The authors of the commented papers supposed that they have synthesized the perovskite  $\text{BiFeO}_3$  compound doped by some supplementary ions. However, such a crystal should have the diffraction pattern as presented in Fig. 1 which does not agree with the patterns published in the commented papers. Thus, it is necessary to find an alternative structure, taking into account that the diffraction pattern is a kind of *fingerprint* of a given crystal.

The most simple diffraction pattern was presented in [2]—see below in Fig. 2. It will be a subject of the analysis shown below.

Fortunately, there is another crystal which has a diffraction pattern similar to that observed by authors of the commented papers. This is a sillenite  $\text{Bi}_{25}\text{FeO}_{39}$  [5]. Thus, the material in the commented papers should be  $\text{Bi}_{25}\text{FeO}_{39}$  crystals instead of assumed  $\text{BiFeO}_3$ . Note, that this compound frequently appears as an impurity phase when bismuth ferrite  $\text{BiFeO}_3$  is synthesized [6]. However, in the case of commented papers, the  $\text{BiFeO}_3$  phase exists only as an impurity [7].

A simple question arises: is it possible to index the diffraction patterns using the unit cell of this *sillenite*-type structure? First of all we must verify if the samples have only one phase. Then, it should be verified if the other diffraction peaks can be attributed to the main crystal which may be not strictly cubic. Such deviation from cubic symmetry may result in the appearance of new diffraction peaks as well as changes in the intensity of some peaks. Moreover, the intentional doping may also destroy the basic, parent structure. Unfortunately, the lack of

raw diffraction data excludes a more detailed analysis of structure. Thus, we try to estimate the possible solutions of structure using the published figure. Only in the case of crystal from [3] we can use the data furnished by authors (Table 1 in the commented paper).

Many sillenites with different compositions have been synthesised so far. Therefore, in the case of commented papers the general formula can be used as  $\text{Bi}_{25}\text{FeO}_{39}:\text{MTi}$  ( $M = \text{Co}$  or  $\text{Ni}$ ). The crystal structure of  $\text{Bi}_{25}\text{FeO}_{39}$  is described in cubic symmetry with space group I23 (No. 197) and lattice parameters  $a = b = c = 10.191 \text{ \AA}$  (ICSD#257493) [5, 8–11].

To verify the correctness of supposed existing of sillenite phase in the studied samples, the patterns calculated on the basis of ICSD data on corresponding crystals are presented in Figs. 1 and 3. To facilitate the direct comparison of all patterns, the  $2\theta$  range is the same ( $20^\circ < 2\theta < 70^\circ$ ).

Simple comparison of the patterns from Figs. 2 and 3 indicates that there are supplementary peaks at  $2\theta \approx 23.1$  and  $47.3^\circ$ , and we observe a lack of diffraction peaks at  $2\theta \approx 43.5$ ,  $48.9$ , and  $53.9^\circ$ . These supplementary peaks correspond well to those from  $\text{BiFeO}_3$  crystal (Fig. 1). Thus, it is clear that the studied sample is bi-phasic, i.e. contains  $\text{Bi}_{25}\text{FeO}_{39}$  and  $\text{BiFeO}_3$ . Note that the experimental pattern is a simple *sum* of the patterns corresponding to both compounds. One can assume that there is of about 15% of the parasite-phase  $\text{BiFeO}_3$ . Thus, it seems this part of the sample is responsible for the magnetic properties recorded. The reason for the lack of some diffraction peaks (but present in [1] and [3]) is not clear.

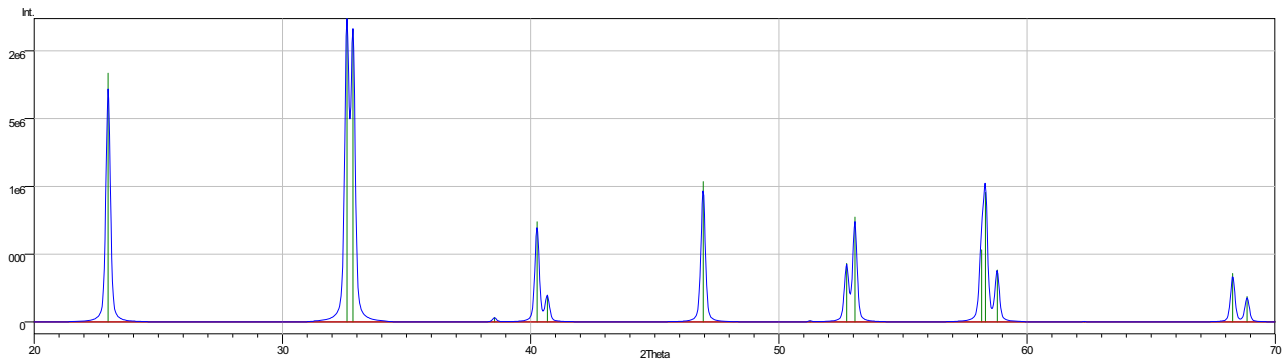
The diffraction patterns from papers [1, 3] are slightly more complicated but preserve the same main set of peaks characteristic for pure sillenite.

The attempt to index the main part of diffraction patterns was successful. There exists one common unit cell for all three crystals. The simple estimations of lattice parameters are presented in Table 2. The introduction of two different ions, Co and Ti or Ni and Ti, results in the deformation of the crystal structure and a creation of a new unit cell. The unit cell of prototype cubic phase,  $\text{Bi}_{25}\text{FeO}_{39}$ , calculated in the monoclinic system is presented for comparison. It is not known how the Co and Ni ions are distributed between both components of the sample studied.

Note, that the data from Table 2 concern the basic unit cell similar to that of well-known sillenite phase, but expressed in the monoclinic system which is fully

**Table 1** Lattice parameters of modified  $\text{BiFeO}_3$  crystals. Standard deviations are omitted for clarity

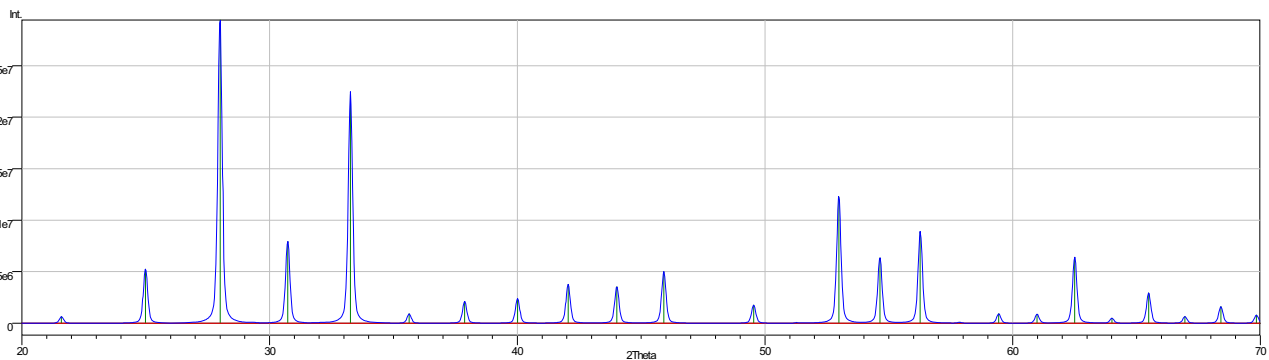
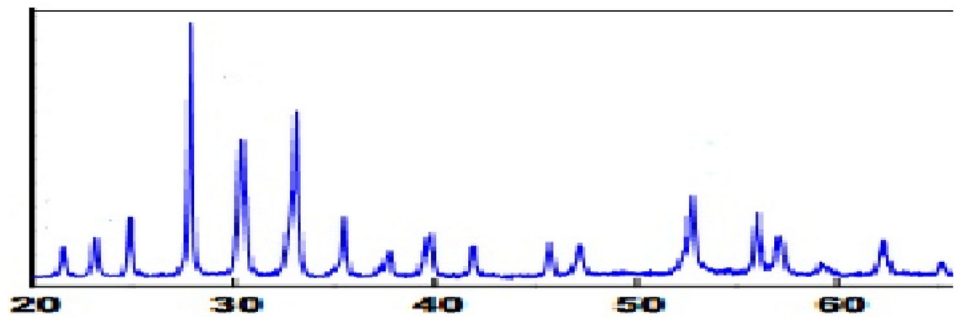
Dopant	$a$ [Å]	$b$ [Å]	$c$ [Å]	Ref.
Ni–Ti–25%	20.4677	4.1505	7.1446	[1]
Co–Ti–25%	38.1655	8.2514	3.8575	[2]
Ni–Ti–40%	21.5780	10.6767	4.5855	[3]



**Fig. 1** The diffraction pattern of  $\text{BiFeO}_3$  crystal according to the data from ICSD#29921 (R3c, No. 161,  $a = 5.5785(2)$  Å,  $c = 13.8696(5)$  Å, [4]) corrected to  $a \approx 5.49$  and  $c \approx 13.3$  Å to

show the similar  $2\theta$  position of some diffraction peaks in the published pattern

**Fig. 2** The diffraction pattern from the paper on  $\text{Bi}(\text{Co}_{1/4}\text{Ti}_{1/4}\text{Fe}_{1/2})\text{O}_3$  [2]. For clarity of comparison the original indexes  $hkl$  are removed

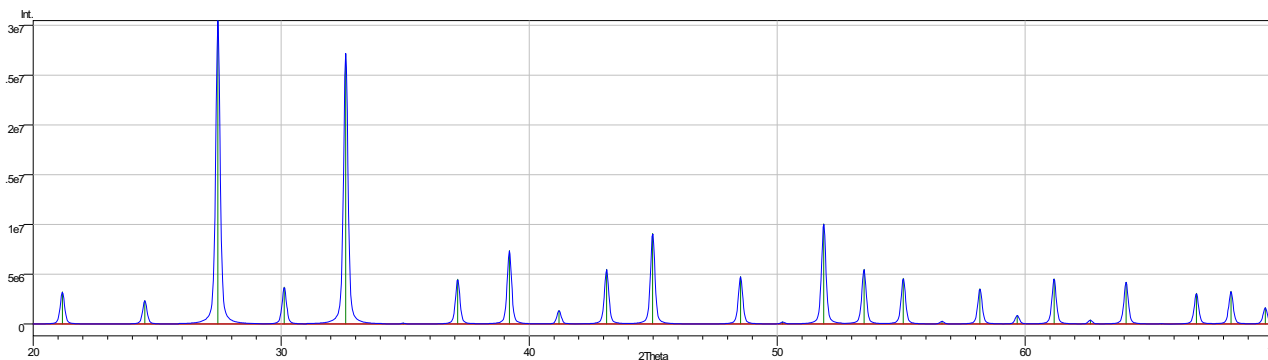


**Fig. 3** The diffraction pattern calculated according to the data from ICSD#257493 for pure  $\text{Bi}_{25}\text{FeO}_{39}$  crystal in the cubic phase, space group I23 (No. 197), and lattice parameter assumed as  $a = 10.07$  Å

equivalent to the cubic phase. Unfortunately, there was not possible to index the patterns in the cubic system. The main feature of this new unit cell is that the  $a$  and  $b$  axes are oriented along the face diagonal of parent cubic cell, thus  $a$  and  $b$  are equal to about  $\sqrt{2}a_{\text{cubic}}$ . It is interesting that the monoclinic axis is not the same as preserved  $c$ -axis. As I know, such unit cell was not observed until now. The preliminary estimation of the alleged space group for this phase

gives two possible symmetries: C1c1 (No. 9) or C12/c1 (No. 15).

It is also clear why the sillenite phase appears in all studied samples instead of assumed simple  $\text{BiFeO}_3$ . The starting compounds were annealed at the temperature corresponding to the creation of  $\gamma$ -phase of  $\text{Bi}_2\text{O}_3$ , the sillenite-type phase (Fig. 4). Thus, the final compound was based on this phase, i.e. sillenite-one.



**Fig. 4** The diffraction pattern calculated according to the data from ICSD#2376 for pure  $\gamma$ - $\text{Bi}_2\text{O}_3$  crystal in the cubic phase, space group I23 (No. 197), and lattice parameter  $a = 10.268(1) \text{ \AA}$

**Table 2** Lattice parameters of modified  $\text{Bi}_{25}\text{FeO}_{39}$  crystals doped by given amount of Co/Ni and Ti ions. Standard deviations are omitted for clarity

Dopant	$a$ [ $\text{\AA}$ ]	$b$ [ $\text{\AA}$ ]	$c$ [ $\text{\AA}$ ]	$\beta$
Ni–Ti—25%	14.645	14.288	10.027	90.42
Co–Ti—25%	14.359	14.140	10.085	90.49
Ni–Ti—40%	14.517	14.329	10.104	90.25
Prototype	<i>14.4124</i>	<i>14.4124</i>	<i>10.1910</i>	<i>90</i>

Italics indicate the comparison of the data on studied crystals with the data on “source” sillenite crystal expressed in the proposed monoclinic unit cell

Similar comments on the analysis of the data on other modified  $\text{BiFeO}_3$  crystals can be found in other journals [12–14].

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## Declarations

**Conflict of interest** The author has no conflicts of interest to declare that are relevant to the content of this article.

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