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Comments on the paper *Study of effect of Gd substitution at the Fe site on structural, dielectric and electrical characteristics of $BiFeO_3$* by L. Thansanga et al. (Appl. Phys. A. 125, 764 (2019))

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Abstract

My comments concern the severe errors in the crystallographic part of the commented paper. The correct formula is proposed to be $Bi_{1-x}Gd_xFeO_3$ instead of $BiFe_{0.95}Gd_{0.05}O_3$. Thus, the actual composition of the studied crystal is not known. Furthermore, it is evident that the sample contains at least three different phases. The subsequent studies do not present the properties of the title compound.

Keywords Bismuth ferrite · X-ray diffraction · Lattice parameters · Errors

1 Results

The commented papers [1] is one of 13 papers published by a team of Dr. Alok Shukla from the Department of Physics, National Institute of Technology Mizoram, Aizawl, India. It presents the results of studies on the different physical properties of $BiFeO_3$ ceramics modified by Gd dopant. However, the proposed unit cell (the set of lattice parameters) is not correct. Unfortunately, these papers are affected by the same or similar evident errors in their crystallographic parts. Furthermore, it is not clear if the subsequent results of studies are also affected by the errors.

1. The structural data (*i.e.* lattice parameters) published in this set of papers are completely different (see Table 1). The data from the commented paper are shown in bold characters. As a result, it is not possible to accept such different unit cells. It is hard to believe that so similar compounds (doped $BiFeO_3$) have such different lattice parameters. Thus, it is necessary to find the error(s) that can be a source of this phase situation, and some common unit cells for all the studied crystals. It is well known that the powder diffraction pattern of given crystal is its fingerprint. Therefore the supposed set of lattice parameters should be similar to that known for the high-temperature monoclinic phase of pure $BiFeO_3$ described by the space group $P12_1/m1$ (No. 11) [2, 3] (see the data at the bottom of the Table). It is well known that doping by small amounts of some ions can destroy the basic structure, inducing some small unit cell distortion. However, the general structure motif should be preserved, and the relation between unit cells must be well defined. Thus, we should find the lattice parameters of about: $a≈5.6$, $b≈5.7$, $c≈7.9$ Å, and $β≈90.5°$, as for other single-doped $BiFeO_3$. Moreover, all modified $BiFeO_3$ nanocrystals presented in the literature have similar unit cells.
2. First of all, it is necessary to verify if the sample contains only one phase. If not, the diffraction peaks should be attributed to each of the phases. Unfortunately, the lack of raw diffraction data excludes the more detailed analysis of structure.

   The comparison of the published diffraction pattern of several modifications of parent crystal indicates the same peak appearing independently of an amount of admixture; this is at about $2Θ=27.7°$; in the case of the studied sample, this peak was described as *070.* It indicates that this peak is not related to the supposed composition of the samples. It must be from another, parasite phase. More careful inspection reveals other peaks belonging to this parasite phase. This set of diffraction peaks corresponds well to $Bi_{25}FeO_{39}$ (see the

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Table 1 Lattice parameters of $BiFeO_3$ crystals with different amounts of admixtures studied by A. Shukla group

Dopant	Symmetry	*a* [Å]	*b* [Å]	*c* [Å]	β [°]	Refs
Y–“5%”	ortho	9.5490	8.6769	10.8778	–	[4]
Y–“10%”	ortho	12.4136	8.2908	11.2180	–	[5]
Y–“15%”	ortho	12.9661	8.3697	16.8618	–	[6]
La–“10%”	ortho	5.605	5.574	3.918	–	[7]
La–“50%”	ortho	17.9248	7.8209	6.8482	–	[8]
La–“40%”	ortho	24.3725	8.2605	4.2048	–	[9]
La–“60%”	ortho	30.9335	7.9078	7.0496	–	[9]
Nd–“5%”	ortho	5.5591	11.2167	11.7785	–	[10]
Nd–“10%”	ortho	9.8131	7.8894	15.9146	-	[10]
Nd–“15%”	ortho	3.9993	15.8562	22.1490	-	[10]
Gd–“5%”	**ortho**	**3.9297**	**22.2849**	**13.5115**	-	[1]
Gd–“10%”	ortho	4.5875	14.4751	11.5024	-	[5]
Dy–“5%”	ortho	6.4128	10.0403	23.3846	-	[11]
Dy–“15%”	ortho	4.0103	15.8409	29.3948	-	[12]
Pure	$P12_1/m1$	5.6148	5.6467	7.9725	$\beta=90.015$	[13]

The data from the commented paper are in bold. The basic set of data for the pure compound is also presented for comparison. Standard deviations are omitted

data from ICSD #257493), the parasite phase frequently observed when preparing the crystals of $BiFeO_3$. The highest diffraction peak at $2\Theta=29.1^\circ$ belongs to Gd_2O_3. The supposed phase, $BiFeO_3$:Gd, seems to be present in very small amount. There is also some amount of amorphous phase. The phase situation is similar to that published in [5]. Thus, the erroneous results in the commented paper come from using all peaks instead of those from the main phase. Moreover, such mixed character of the samples indicates that the method of synthesis is not sufficient to obtain the $BiFeO_3$:Gd crystals.

3. There is another erroneous assumption made by authors in all papers—all dopant atoms replace the Fe atom, *i.e.* enter at the position of B-site of the perovskite structure. As a result, the grave error appears in the used chemical formula of the studied crystals. Nature does not always realise the wishful thinking of scientists. Hence, the crystallo-chemical rules have to be considered. The detailed estimation of the real composition will be possible when one obtains access to the raw X-ray diffraction data. However, the simple analysis of atoms positions within the structure clearly shows that the correct position of doped atoms is that of Bi atom. If we look at the structure of $BiFeO_3$, it will be evident that the somewhat bigger ions, like Gd, must enter in the positions of Bi-atoms lying at the void in the framework composed by FeO_6 octahedra connected one to the other by the oxygen atoms. It is impossible to replace small iron atoms with greater dopants, especially inside rigid FeO_6 octahedron.

   Thus, the supposition that the Gd ions replace the Fe atoms is wrong, and the correct chemical formula must be written as $Bi_{1-x}Gd_xFeO_3$, contrary to the formula used by authors, $BiFe_{0.85}Y_{0.15}O_3$. Note that this incorrect chemical formula is used only by the concerned team of authors since 2015—all other people worldwide use the correct formula. As the formula must be different, it is impossible to indicate the valid nominal value of *x*. That is why we use the quote “ ” in Table 1 to underline that the correct composition is not known.
4. The suggestion on the “structural phase transition from rhombohedral to orthorhombic” is not correct within the framework of pure understanding of the term “phase transition”, *i.e.* transition under external parameters changes as temperature and pressure, provided the chemical composition of the sample is preserved. It is well known that some people use the composition as an equivalent of an external parameter, which is not entirely correct (the substitution-driven phase transition). In such a case, one change passes from one crystal to the other with different chemical composition. Thus, it is more correct to use the term “transformation” instead of “transition”.

There is another interesting problem. “Transition” from rhombohedral to other systems in the studied crystals seems to be not related to the admixture of ions but to the crystallite size change. We observe the so-called size-induced phase transition [14]. The structure of the nanocrystalline phase can be different from that of bulk crystal. It is well known that the bulk $BiFeO_3$ crystal exhibits a temperature-induced structural phase transitions from *R3c* symmetry at room temperature to *Pbnm* or metrically orthorhombic $P2_1/m$ above 1100 K [13, 15, 16]. Thus, it can be supposed that the phase diagram can be of the type B2 as described in [14], *i.e.* the high-temperature phase can be observed for the small-size crystallites. The main factor governing such transformation is not a change of calcination temperature but the change of crystallite size.

2 Conclusions

The commented paper presents wrong analyses of the structure of the studied samples. The authors did not correctly determine the composition of the sample (at least three phases were present) and consequently incorrectly indexed the diffraction patterns. The resulting lattice parameters (and symmetry, also) are wrong. Astonishingly, the authors overlooked the incompatibilities of the obtained results.

Declarations

I declare that I am a sole author of this original paper (Comment). Due to the character of this paper (comment to the given paper), it can be and was not published in any other journal. There is no conflict of interest. If accepted, this article will not be published elsewhere in the same form, in any language, without the written concent of the publisher.

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