

Does $\text{Ba}_3\text{Bi}_2\text{WO}_9$ exist?

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Abstract

The aim of this commentary is to bring attention of the scientific community to erroneous claims about the existence of a new compound, “ $\text{Ba}_3\text{Bi}_2\text{WO}_9$ ”, as reported in [Inorg. Chem. Commun. 1530 (2023) 110785]. In this commentary, it is shown that the absence of phase-analysis procedures and incorrect indexing led to erroneous claims. It is demonstrated that a so-called “ $\text{Ba}_3\text{Bi}_2\text{WO}_9$ ” was a mixture of four phases: $\text{BaBiO}_{3-\delta}$ (a cubic perovskite with $a = 4.3575 \text{ \AA}$), $\text{Ba}_3\text{W}_2\text{O}_9$, BaWO_4 , and a cubic perovskite with $a = 4.225 \text{ \AA}$.

Keywords: X-ray diffraction; phase analysis; lattice parameters; errors

A recent paper has claimed the synthesis of a new compound with a chemical composition of “Ba₃Bi₂WO₉” [1]. “Ba₃Bi₂WO₉” was prepared using a conventional solid-state method from a stoichiometric mixture of BaCO₃, WO₃, and Bi₂O₃ by annealing in air at 1123–1173 K. Reflections on a powder X-ray diffraction pattern of “Ba₃Bi₂WO₉” could be indexed by the authors with lattice parameters of $a = 8.4621$ Å, $b = 6.7358$ Å, $c = 6.9064$ Å, and $\beta = 109.94^\circ$. Therefore, the authors of Ref. [1] concluded that a new single-phase compound was prepared, and space group $P2_1$ was assigned to “Ba₃Bi₂WO₉”.

A powder X-ray diffraction pattern of “Ba₃Bi₂WO₉” contained reflections with very different widths as can be seen from Figure 1a of this commentary, where Figure 1b from Ref. [1] is reproduced. This is a strong indication that the sample in Ref. [1] was not single-phase, and at least two phases were present with different degrees of crystallinity, particle sizes, and/or defects. Our phase analysis could identify three previously known phases, whose reference powder X-ray diffraction patterns are reported in International Center for Diffraction Data (ICDD) database. These phases are BaBiO_{3- δ} with a simple cubic perovskite-type structure (ICDD Powder Diffraction File (PDF) record 86-0618, but with $a \approx 4.3575$ Å), Ba₃W₂O₉ (PDF 34-1479), and BaWO₄ (PDF 85-0588). There remained a few unidentified reflections, for example, the strongest reflection was at $2\theta = 30.0^\circ$ (with $d = 2.976$ Å), indexed as (021) on Figure 1a. These reflections did not match with any reference patterns in the ICDD database (of course, under the constraint that just Ba, Bi, W, and O elements should present). On the other hand, these reflections could be explained/indexed by another simple cubic perovskite-type phase with $a \approx 4.225$ Å. Therefore, all observed reflections in the sample in Ref. [1] could be explained by the presence of the four phases mentioned above.

Note that without the access to the raw sample and raw powder X-ray diffraction data chemical compositions of the proposed phases could only be assigned based on matches with reference powder X-ray diffraction patterns in the ICDD database. As there is no match for the cubic perovskite-type phase with $a \approx 4.225$ Å we did not assign a chemical composition to this phase. Note also that the nature of the BaBiO_{3- δ} phase allows wide variations in cation and oxygen stoichiometry, Ba_{1+x}Bi_{1-x}O_{3- δ} and Ba_{1-x}Bi_{1+x}O_{3- δ} (for example, PDF 85-1806, 48-0936, and 45-0292), depending on synthesis conditions and starting stoichiometry. Nonstoichiometry of the BaBiO_{3- δ} phase and the other perovskite phase (with $a \approx 4.225$ Å) could probably explain why the Ba₃W₂O₉ phase was formed in a majority amount in comparison with the BaWO₄ phase. In the case of a related “Ba₃Bi₂MoO₉” claim [2], a sample was showed to be mainly a mixture of 2BaBiO₃ + BaMoO₄ [3]. A small amount of a cubic perovskite phase (with $a \approx 4.20$ Å) was also found in “Ba₃Bi₂MoO₉” [3] similar to “Ba₃Bi₂WO₉”.

Note that powder X-ray diffraction patterns of the BaBiO_{3- δ} phase and a double perovskite Ba₃WO₆ phase (PDF 89-5178) are very similar to each other. It is basically impossible to distinguish them by a visual comparison of powder X-ray diffraction data (without a detailed analysis of raw powder X-ray diffraction data) as the fundamental perovskite lattice parameter of Ba₃WO₆ ($a_p = 4.31$ Å) is close to that of the BaBiO_{3- δ} phase. However, the formation of Ba₃WO₆ can be ruled out using different information. The preparation of Ba₃WO₆ requires annealing at 1473–1673 K [4, 5], which is much higher than

the annealing temperature used in Ref. [1], and Ba_3WO_6 is usually formed with a more complicated superstructure [4], for example, with a strong reflection near 26.94° (PDF 33-0182). The powder X-ray diffraction pattern of Ba_3WO_6 reported in PDF 89-5178 is a calculated pattern based on a simplified structural model, while the original paper [5] (from which PDF 89-5178 was obtained) reported a more complicated superstructure (Figure 1c in Ref. [5]) in agreement with PDF 33-0182. On the other hand, $\text{BaBiO}_{3-\delta}$ can be prepared at 973–1173 K [6], which is close to the annealing temperature used in Ref. [1]. Moreover, in the case of a related “ $\text{Ba}_3\text{Bi}_2\text{MoO}_9$ ” claim [2], the presence of $\text{BaBiO}_{3-\delta}$ was clearly shown [3], and a “ Ba_3MoO_6 ” compound is not known in comparison with Ba_3WO_6 .

Figure 1b shows a resultant powder X-ray diffraction pattern after summation of contributions from all four phases, whose individual contributions are shown on Figure 2. A very good match is observed between the experimental powder X-ray diffraction pattern and the calculated one. The calculated patterns were obtained using the RIETAN-2000 program [7] and Inorganic Crystal Structure Database (ICSD): $\text{BaBiO}_{3-\delta}$ (code 81316, but with $a \approx 4.3575 \text{ \AA}$), $\text{Ba}_3\text{W}_2\text{O}_9$ (code 100689), and BaWO_4 (code 291537). For the fourth, cubic perovskite-type phase, we used the same structural parameters as for $\text{BaBiO}_{3-\delta}$, only a lattice parameter was different. The intensity ratios for each phase were adjusted to match with the experimental powder X-ray diffraction pattern. We also used different profile parameters for each phase to reflect different widths on the experimental powder X-ray diffraction pattern of “ $\text{Ba}_3\text{Bi}_2\text{WO}_9$ ”, where broader reflections belong to $\text{BaBiO}_{3-\delta}$.

There are also other shortcomings in Ref. [1]. 1) The indexing results reported in Figure 1b of Ref. [1] could not be correct because it is basically impossible to correctly index a sample containing four phases with different symmetries and lattice parameters as a single-phase product even if only strong reflections of four phases are considered (and weaker reflections are omitted). Of course, this statement is true for a reasonable-size cell and acceptable figures of merit for powder pattern indexing (such as, M_{20} and F_N [8]). Such standard figures of merit were not reported in Ref. [1]. In other words, some reflections should show large difference between observed and calculated reflection positions meaning that they remain unindexed, and resulting in unacceptable M_{20} and F_N parameters. 2) Calculated patterns were reported on Figure 1a and Figure 1b of Ref. [1]; however, there were discrepancies between them as some calculated peaks of Figure 1a were missed on Figure 1b. 3) P–E hysteresis loop, reported in Figure 10 of Ref. [1], was only measured up to 1.5 kV/cm, and it just shows leaky dielectric behavior (not a proof of ferroelectric properties). 4) EDX results (Table 1 of Ref. [1]) were reported with very larger errors.

In conclusion, a mixture of four phases was investigated in Ref. [1] instead of a new compound, “ $\text{Ba}_3\text{Bi}_2\text{WO}_9$ ”. The authors in Ref. [1] did not perform any standard phase-analysis procedures, wrongly assumed that a new single-phase compound was obtained, and moved to indexing attempts resulting in erroneous conclusions. Therefore, all other results/measurements in Ref. [1] have little scientific values.

In the context of this conclusion, we mention that the claimed “ $\text{Ba}_3\text{Bi}_2\text{MoO}_9$ ” compound [2] was mainly a mixture of BaBiO_3 and BaMoO_4 [3] as mentioned before; “ $\text{Ba}_3\text{Bi}_2\text{Fe}_2\text{O}_9$ ” [9] was mainly a mixture of two cubic perovskite-type phases [9], which can be called BaFeO_3 -based and BaBiO_3 -based; our phase analysis of the claimed “ $\text{Ca}_3\text{Bi}_2\text{MoO}_9$ ”

compound [10] showed that the sample was mainly a mixture of CaMoO_4 (PDF 29-0351) and $\text{Bi}_{3.11}\text{Ca}_{0.89}\text{O}_{5.56}$ (PDF 40-0317) with the presence of some other phases; and “ $\text{Sr}_3\text{Bi}_2\text{MoO}_9$ ” [11] was experimentally shown to be mainly a mixture of $\text{Sr}_2\text{Bi}_2\text{O}_5$ and SrMoO_4 [12], when prepared at 1073–1123 K.

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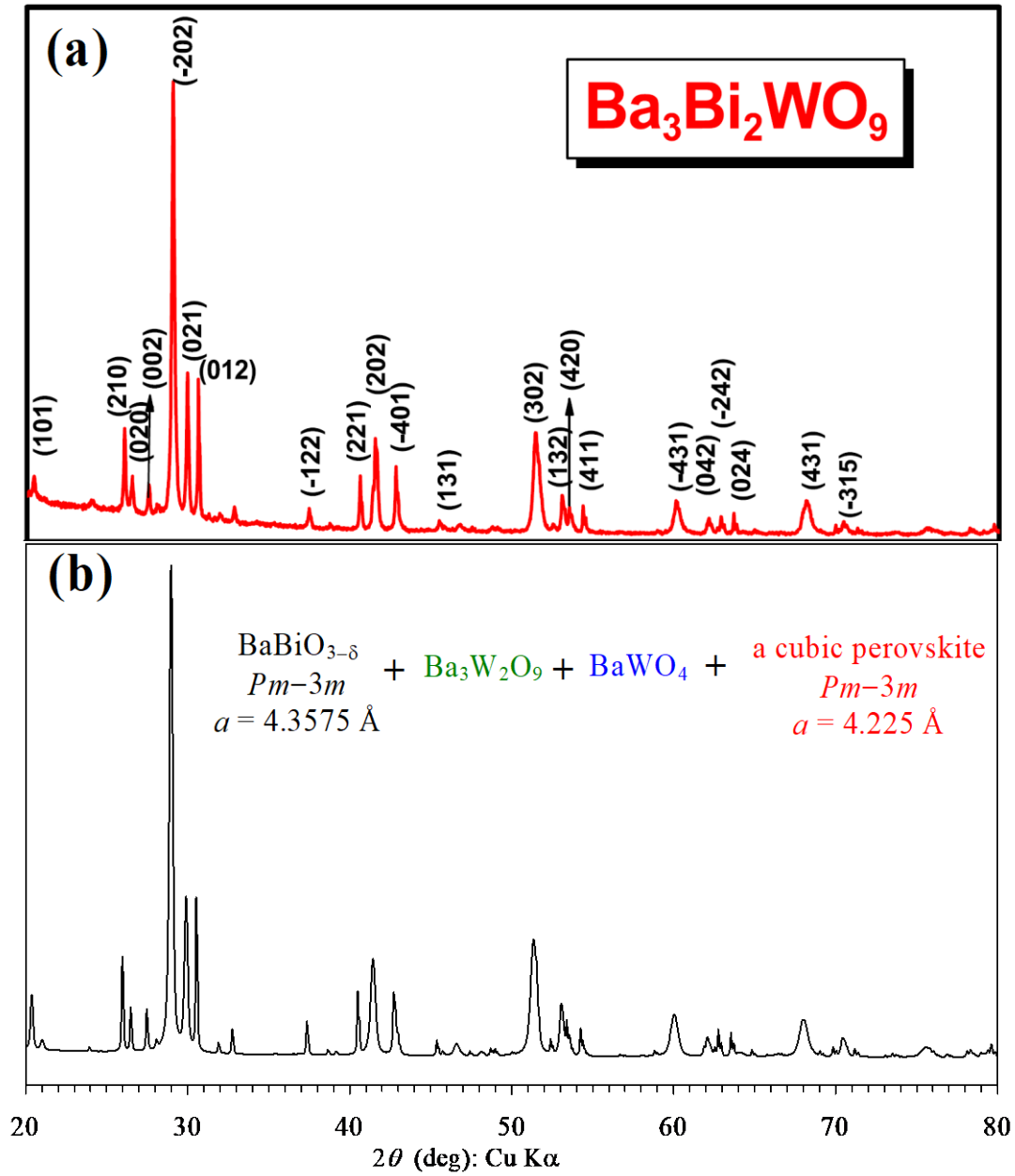


Figure 1. (a) An experimental X-ray powder diffraction pattern of a “ $\text{Ba}_3\text{Bi}_2\text{WO}_9$ ” sample from Figure 1b of Ref. [1]. (b) A calculated powder X-ray diffraction pattern of a mixture of $\text{BaBiO}_{3-\delta}$ (a cubic perovskite with $a = 4.3575 \text{ \AA}$), $\text{Ba}_3\text{W}_2\text{O}_9$, BaWO_4 , and a cubic perovskite with $a = 4.225 \text{ \AA}$ after summation (individual contributions are shown on Figure 2b). The calculated patterns for each phase (intensity ratios) were adjusted to match with the experimental X-ray powder diffraction pattern. Figure 1a is reproduced with the permission from Elsevier.

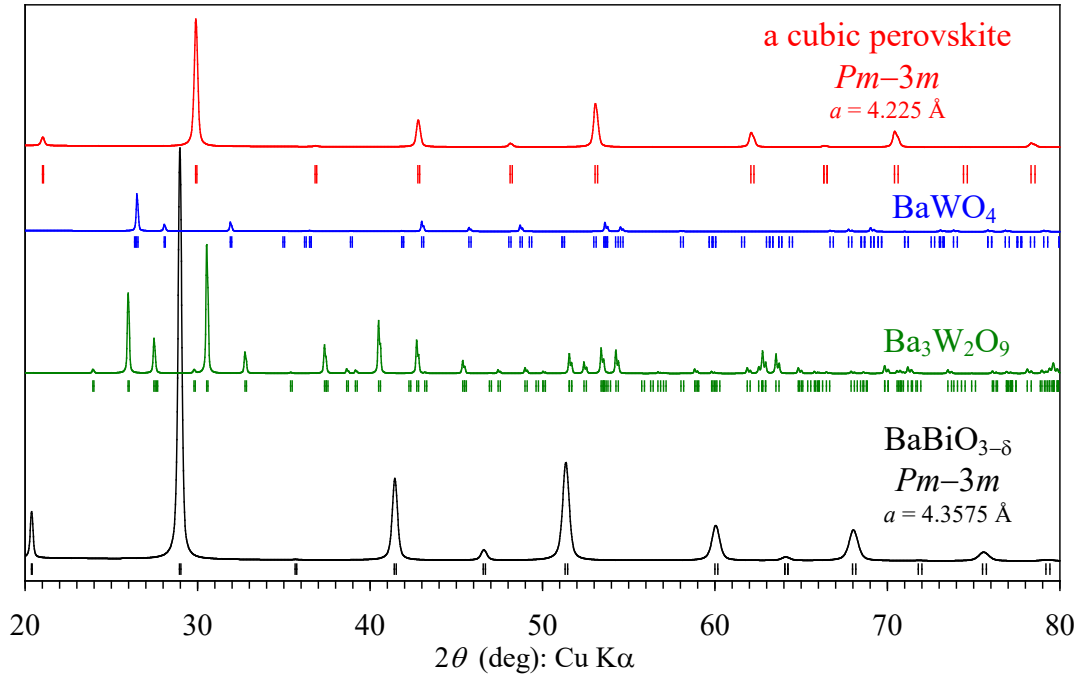


Figure 2. Calculated, individual powder X-ray diffraction patterns of $\text{BaBiO}_{3-\delta}$ (the black curve and the fourth row (from top) of black tick marks for possible Bragg reflection positions), $\text{Ba}_3\text{W}_2\text{O}_9$ (the green curve and the third row of green tick marks), BaWO_4 (the blue curve and the second row of blue tick marks), and a cubic perovskite with $a = 4.225 \text{ \AA}$ (the red curve and the first row of red tick marks). The calculated patterns (intensity ratios) were adjusted to match with the experimental X-ray powder diffraction pattern.