Structural and optical characterization of metal tungstates (MWO₄; M= Ni, Ba, Bi) synthesized by a sucrose-templated method

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Abstract

**Background:** Metal tungstates have attracted much attention due to their interesting structural and photoluminescence properties. Depending on the size of the bivalent cation present, the metal tungstates will adopt structures with different phases. In this work, three different phases of metal tungstates MWO₄ (M= Ba, Ni and Bi) were synthesized via the sucrose templated method.

**Results:** The powders of BaWO₄ (tetragonal), NiWO₄ (monoclinic) and Bi₂WO₆ (orthorhombic) formed after calcination temperatures of 750, 650 and 600°C for 4 h respectively are found to be crystalline and exist in their pure phase. Based on Scherrer estimation, their crystallite size are of nanosized. BET results showed NiWO₄ has the highest surface area. BaWO₄ exhibited less Raman vibrations than the NiWO₄ because of the increased lattice symmetry but Bi₂WO₆ showed almost the same Raman vibrations as BaWO₄. From the UV-vis spectra, the band gap transition of the metal tungstates are of the order of BaWO₄ > Bi₂WO₆ > NiWO₄. Broad blue-green emission peaks were detected in photoluminescence spectra and the results showed the great dependence on morphology, crystallinity and size of the metal tungstates.

**Conclusion:** Three different phases of metal tungstates of BaWO₄ (scheelite), NiWO₄ (wolframite) and Bi₂WO₆ (perovskite layer) in their pure phase were successfully prepared by the simple and economical sucrose-templated method. The highest surface area is exhibited by NiWO₄ while largest band gap is shown by BaWO₄. These materials showed promising optical properties.

**Keywords:** Metal tungstates, Sucrose, Optical

Introduction

Metal tungstates with formula MWO₄ have attracted much attention due to their interesting structural and photoluminescence properties [1-5]. These materials have found applications in scintillation counters, lasers and optical fibers [6,7]. Some of the divalent transition metal tungstates have also gained commercial interest in lasers and fluorescent lamps, while some are of special importance due to their electrical conductivity and magnetic properties. In addition, these materials also find applications as catalysts and humidity sensors [8,9].

In the MWO₄ compounds, if M²⁺ has small ionic radius < 0.77 Å (Ni = 0.69), it will belong to the wolframite-type monoclinic structure where the tungsten atom adopts an overall six-fold coordination [10]. However, if larger bivalent cations with ionic radius > 0.99 Å (Ba=1.35), they exist in the so-called scheelite-type tetragonal structure where the tungsten atom adopts tetrahedral coordination. Bismuth tungsten oxide belongs to the orthorhombic system, space group Pca₂₁, and crystallizes in a layered crystal structure including the corner-shared WO₆. The Bi atom layers are sandwiched between WO₆ octahedral layers [11]. It is the simplest member of the Aurivillius family from Bi₂Aₙ₋₁BₙO₃n+3 (A=Ca, Sr, Ba, Pb, Bi, Na, K and B=Ti, Nb, Ta, Mo, W, Fe) (when n=1) of layered perovskites, which structurally comprises of alternating perovskite-like slabs of WO₆ and [Bi₂O₂]³⁺ layers. Recently, many studies have been reported on the preparation and characterization of metal tungstates using various methods.

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preparation methods such as Czochralski [12], precipitation [13,14], hydrothermal [11,15], solid state [16], pulsed laser deposition [17]. Meanwhile the nanostructures of metal tungstates in different crystal structures including nanorods, nanoparticles, hollow clusters and others have been prepared by chemical and physical methods. For Bi$_2$WO$_6$, its nanometer sheet shaped was prepared by a molten flux reaction using alkali metal nitrates as the reaction media [19]. Nickel tungstate (NiWO$_4$) nanoparticles were successfully synthesized at low temperatures by a molten salt method at a temperature as low as 270°C, where the mixture of NaNO$_3$ and LiNO$_3$ was used as the molten salt medium with 6:1 mass ratio of the salt to the NiWO$_4$ precursor [20]. Generally, these methods require expensive and sophisticated equipment, high temperatures with long processing times, expensive precursors and high consumption of electric energy.

Prabhakaran et al. [21] had used a cheaper and simpler method of using sucrose in order to synthesize yttria-stabilized zirconia (YSZ) nanoparticles in both acidic and basic solutions. The analyses consistently reported to have fairly uniform nanoparticles with small size, containing both tetragonal and monoclinic phases with crystallite size between 10 and 30 nm. Due to its simplicity, the sucrose-template method has great potential for manufacturing high quality ultrafine ceramic oxides economically [22] and this creates a new approach for synthesis of the other ceramic materials. In this method, the -OH and -COOH groups of the decomposed sucrose products help in binding the metal ions in the homogeneous solution, which reduces the chances of precipitation. During the decomposition process, a voluminous, organic-based, black, fluffy mass of carbonaceous material is formed which upon heating will decompose further into carbon dioxide and water and a large amount of heat is generated. The outgoing gases prevent agglomeration, and form pores and fine particles with high surface area in the final products. The aim of this paper is to synthesize the different crystal structures of BaWO$_4$, NiWO$_4$ and Bi$_2$WO$_6$ by a sucrose templated method and to characterize the materials for their structural and optical property by X-ray diffraction (XRD) measurements using Siemen D5000 with a copper K$_\alpha$ radiation tube and wavelength $\lambda$ of 1.54 Å, operated at 40 kV and 40 mA. The X-ray powder diffraction patterns were obtained in the range 5-60°, with increments of 0.05°. The crystalline phases were identified by using the International Centre for Diffraction Data (ICDD). The full width at half maximum (FWHM) of the diffraction peaks obtained from the refinement have been used to calculate the crystallite size. Specific surface area (S$_{BET}$) measurements were made with a Quantachrome AUTOSORB-1 model by nitrogen adsorption at -196°C using the BET isotherm. Samples were degassed under flowing argon at 250°C for 9 h before being adsorbed by nitrogen. The surface morphology of the samples was analyzed using the Field Emission Scanning Electron Microscope, FESEM, Brunauer-Emmet-Teller (BET) and Raman spectroscopy while optical properties were investigated using UV-vis and photoluminescence spectroscopy.

**Experimental details**

**Preparation of powders**
The desired metal nitrates [Ba(NO$_3$)$_2$, Ni(NO$_3$)$_2$, 6H$_2$O, Bi(NO$_3$)$_3$] of 2.6135, 2.9081 and 4.8511 g were individually dissolved in distilled water before being mixed into an aqueous solution of sucrose. This is followed by addition of an equal volume of 2.4633 g of ammonium metatungstate to maintain stoichiometric ratio (1:1) with continuous stirring. Sucrose acts as a template and the ratio of sucrose to metal used was 3:1. Towards the end of the evaporation, the precursor solution (after further heating) gave rise to a fluffy black organic mass. The carbon rich mass was easily crushed to form the precursor powders. Precursor powders are denoted as MWO$_4$ (M= Ba, Ni, and Bi). Calcination treatment was applied in the next step because of the large amount of organic compounds present in the crunchy powders. The temperatures and durations for calcinations were derived from the results of the thermogravimetric analysis whereby processes such as dehydration and other volatilizations to go to completion before proceeding to higher temperatures.

The calcination treatment applied to the samples involved heating at the rate of 10°C/min and the temperature was held constant for 4 h for each thermal change as inferred from the thermal analysis to allow completion of each of the processes. The three powdered precursors, MWO$_4$ (M= Ba, Ni, and Bi) were subsequently calcined at 750, 650 and 600°C respectively for 4 h and the samples were denoted as MWO$_4$ (M= Ba, Ni, and Bi).

**Characterization**
The formation of oxides was monitored by X-ray diffraction (XRD) measurements using Siemen D5000 with a copper K$_\alpha$ radiation tube and wavelength $\lambda$ of 1.54 Å, operated at 40 kV and 40 mA. The X-ray powder diffraction patterns were obtained in the range 5-60°, with increments of 0.05°. The crystalline phases were identified by using the International Centre for Diffraction Data (ICDD). The full width at half maximum (FWHM) of the diffraction peaks obtained from the refinement have been used to calculate the crystallite size. Specific surface area (S$_{BET}$) measurements were made with a Quantachrome AUTOSORB-1 model by nitrogen adsorption at -196°C using the BET isotherm. Samples were degassed under flowing argon at 250°C for 9 h before being adsorbed by nitrogen. The surface morphology of the samples was analyzed using the Field Emission Scanning Electron Microscope, FESEM, Brunauer-Emmet-Teller (BET) and Raman spectroscopy while optical properties were investigated using UV-vis and photoluminescence spectroscopy.
UV lens set at \( \lambda_{UV} = 325 \) nm and equipped with 2,400 l/nm diffraction grating. The same equipment was also used for photoluminescence (PL) analysis by using a visible lens set and equipped with 1,200 l/nm diffraction grating.

**Results and discussion**

**XRD**

XRD pattern can reveal the phase purity and crystallinity of the powder sample. Figure 1 shows sharp diffraction peaks indicating that the oxide products are well crystallized and no peaks attributable to other impurities were observed. The pattern agrees well with the JCPDS file of NiWO\(_4\), BaWO\(_4\) and Bi\(_2\)WO\(_6\) (PDF card 72-0480, 72-0746 and 79-2381). The NiWO\(_4\) indexed in wolframite monoclinic structure (space group: \( P2_1/c \), with \( Z = 2 \)) is characterized by alternating layers of transition-metal and tungsten atoms parallel to the (100) plane. The oxygen atoms are hexagonally closely packed and the metal ions occupy a quarter of all the octahedral sites [23]. For BaWO\(_4\), the peaks from diffraction patterns are consistent with a body-center primitive tetragonal scheelite, space group I\(_4\)/a and has \( C_6^4 \) point group with two formula units per primitive cell. In an ideal scheelite type of ABO\(_4\) larger A (Ba\(^{2+}\)) cation shows eight-fold coordination and smaller B (W\(^{6+}\)) cation shows four-fold coordination. The tungstates reported have strong covalent bonds of W-O in [WO\(_4\)]\(^{2-}\) molecular ionic units and weak coupling between [WO\(_4\)]\(^{2-}\) anions and Ba\(^{2+}\) cations [24]. All the peaks of Bi\(_2\)WO\(_6\) are recognized with the crystal structure of orthorhombic symmetry crystal phase with space group \( Pca_2_1 \) and crystallized in a layered crystal structure including the corner-shared WO\(_6\). The Bi atom layers are sandwiched between WO\(_6\) octahedral layers [11].

Table 1 shows that crystallite sizes of all the samples calculated from Scherer’s equation are in nano-size range: NiWO\(_4\) at \( d_{100} \), \( d_{110} \) and \( d_{011} \) are 19.3, 19.3 and 17.2 nm, while those of BaWO\(_4\) at \( d_{112} \) and \( d_{004} \) are 18.9 and 17.4 nm. Smaller crystallite sizes of 15.5 and 14.9 nm are shown by Bi\(_2\)WO\(_6\) at \( d_{131} \) and \( d_{002} \), respectively. Dong Young et al. [18] have also synthesized similar compounds by commercial hydrothermal methods and obtained the crystallite size of 17-24 nm in same plane of \( d_{131} \). NiWO\(_4\) synthesized by reacting ammonium metatungstate and nickel nitrate as a function of temperature from 673 to 1073 K of 1 h reaction time has been reported by Quintana-Melgoza et al. [25] and average crystallite size as determined by Scherrer analysis obtained was from 55 to 112 nm, which is three times bigger than that reported in this work. In the case of BaWO\(_4\), calculated crystallite size synthesized by room temperature the metathetic reaction method has been reported to grow twofold in crystallite size (51 nm) along \( d_{112} \) [26]. The existence of sucrose in the solution of the metal cations will form a matrix in which the metal cations are distributed through the sucrose structure. The sucrose molecule is hydrolyzed into glucose and fructose and in this way sugar recrystallization is prevented. The complex mass is obtained by complexation via gel formation and the final particles are obtained upon decomposition in the calcination process. During heating, the metal ion complex is decomposed into CO\(_2\) and H\(_2\)O and a large amount of heat is generated. All these products are gaseous, preventing agglomeration and thus giving rise to pores and fine powders of smaller crystallite size (Table 1).

**FESEM and BET**

The FESEM results demonstrated that the morphology of BaWO\(_4\), NiWO\(_4\) and Bi\(_2\)WO\(_6\) samples strongly depend on size of particles while BET results showed the dependency of their surface areas on pore volume and pore distribution. All three samples show different morphologies:

| System       | X-ray phase | Crystal structure       | \( \theta \) (°) | hkl | t (nm) |
|--------------|-------------|-------------------------|------------------|-----|-------|
| NiWO\(_4\)   | Wolframite  | Monoclinic              | 23.89            | 100 | 19.3  |
|              |             |                         | 24.85            | 110 | 19.3  |
|              |             |                         | 30.87            | 011 | 17.2  |
| BaWO\(_4\)   | Scheelite   | Body cubic tetragonal   | 26.38            | 112 | 18.9  |
|              |             |                         | 27.99            | 004 | 17.4  |
| Bi\(_2\)WO\(_6\)| Orthorhombic| Orthorhombic         | 28.29            | 131 | 15.5  |
|              |             |                         | 32.83            | 002 | 14.9  |

![Figure 1](attachment:image.png)
BaWO₄ particles (Figure 2(a)) grow in large spherical grain sizes between ~0.8-0.9 µm. Samples NiWO₄ and Bi₂WO₆ in Figure 2(b & c) show smaller inter-connected grain sizes of 30-90 and 20-60 nm, respectively. From Figure 3, BaWO₄ shows mesoporous characteristics obtained from adsorption-desorption isothermal of type IV and the H3 and the hysteresis loop observed in the range of 0.70 – 0.95 P/Pₒ (according to the IUPAC classification) agrees reasonably well with the small pore volume (0.05 cm³g⁻¹) and low surface area (2.30 m²g⁻¹), as shown in Table 2. Both samples of NiWO₄ and Bi₂WO₆ show adsorption-desorption isotherms of a macroporous characteristic (type III) with absence of any hysteresis loop.

Even though the NiWO₄ sample has larger crystallite size (according XRD), its surface area is fivefold larger (20.06 m²g⁻¹) than Bi₂WO₆ (3.58 m²g⁻¹). This phenomenon is attributed to the higher pore distribution (Table 2) and less agglomeration of NiWO₄ itself (Figure 2(b)). This finding shows that the prepared NiWO₄ sample using sucrose solution evaporation has higher BET surface area compared to NiWO₄ synthesized by combustion method (< 11 m²g⁻¹) even though a spherical-like morphology was obtained in both cases [27]. Bi₂WO₆ synthesized by using co-precipitation method also resulted in similar spherical particles (after calcinations at 600, 700 and 800°C) as reported by Alfaro and de la Cruz [28], but
the size of particles were in microns; sizes (~1-2 μm) and BET values obtained were 0.3-1.5 m²g⁻¹, which was 10 times lower than the findings in this work shown in Table 2.

FESEM images can also allow the estimation of the average particle size distribution of samples by counting approximately 150 particles using an Image tool software. The particles are assumed spherical-like (Figure 2(a1- c1)). Figure 2(a1) shows the average particle size distribution (diameter) in the range from 0.80-0.94 μm for BaWO₄. The figure shows that 59% of the particles with a spherical-like morphology presented an average area of 0.84-0.88 μm. Figure 2(b1) shows the average particle area distribution of Bi₂WO₆ is 20-55 nm and that 62% of the particles presented an average area of 25-35 nm, smaller than BaWO₄ (in micron range). As for NiWO₄ (Figure 2c1) with the plate-like morphology the average particle area distribution is 30-90 nm, which is in close relationship with the above grain size (FESEM image). These results show that the sucrose-templated method is able to influence the growth process into nano-range for samples NiWO₄ and Bi₂WO₆ except for sample BaWO₄ which is in micron size. However, the particle size distribution of BaWO₄ synthesized using a sucrose-templated method shows smaller dimension (0.84-0.88 μm) compared to BaWO₄ synthesized by co-precipitation followed by domestic microwave-hydrothermal at 413 K for different times which resulted in a large self-assembled microcrystal of height (0.30–11.85 μm) and width (0.25–2.30 μm) [29].

### Raman spectra

The structural order at short-range for the three different phases of NiWO₄, BaWO₄ and Bi₂WO₆ nanoparticles was determined by Raman active phonon modes (Figure 4). Hardcastle et al. [30], using the di-atomic approximation method, concluded that for an ideal WO₄ unit, the shortest W-O bond should correspond to a Raman fingerprint located at 874 cm⁻¹ (vs (W=O)), with a standard deviation of approximately 55 cm⁻¹.

Considering the Raman active modes of scheelite-type AWO₄ compounds, there are two types of vibration modes, belonging to the internal and external vibrations. The first corresponds to the normal motion of atoms inside the [WO₄]²⁻ tetrahedrons, and the second involves the vibration WO₄ tetrahedrons against the divalent A atoms. Group theory calculation predicts 26 vibration modes for the tetragonal scheelite (BaWO₄) primitives’ cell at wavevector k=0, which can be represented in (1) [31]:

\[
\Gamma = 3A_g + 5A_u + 5B_g + 3B_u + 5E_g + 5E_u \quad (1)
\]

where all 13 vibrations A₉, B₉ and E₉ are Raman-active. As shown in Figure 4, the tetragonal BaWO₄ has two strong vibrations at 924 and 330 cm⁻¹ and four weak vibrations at 829, 797, 716 and 272 cm⁻¹. It is predicted to have less Raman vibrations when compared to monoclinic NiWO₄ because of the increased lattice symmetry. The two strong vibrations of 924 and 330 cm⁻¹ and weak mode at 797 cm⁻¹ can be assigned to the W-O stretching vibration of WO₄ tetrahedra. The medium mode at 272 cm⁻¹ is derived from symmetric stretching vibration of the BaO₆ octahedra. All these modes are characteristic of the tetragonal scheelite structure as reported previously [32-36]. However, in our samples, the vibrations were slightly shifted and some vibration modes were not detected. These observations can be attributed to some differences in their geometries, particle sizes and nature of the products.

Comparatively, Raman vibrations for monoclinic wolframite structure would be expected to give six internal stretching modes caused by each of the six W-O bonds in the WO₆ octahedrons and from group theoretical analysis of the monoclinic (NiWO₄) yields 36 lattice modes [15]:

\[
\Gamma = 8A_g + 10B_g + 8A_u + 8B_u \quad (2)
\]

Here, 18 even (g) vibrations are Raman-active modes. As for monoclinic NiWO₄, the corresponding spectrum in Figure 4 shows only three strong vibrations at 891,

### Table 2 Summary of metal tungstates specific surface area, pore volume and pore size distribution

| Sample   | S BET (m²g⁻¹) | Pore volume (cm³/g) | Pore size distribution (nm) |
|----------|---------------|---------------------|-----------------------------|
| Bi₂WO₆  | 3.58          | 0.62                | 1.54                        |
| NiWO₄   | 20.06         | 0.54                | 2.46                        |
| BaWO₄   | 2.30          | 0.05                | 1.92                        |
778 and 698 cm\(^{-1}\) and five weak vibrations at 328, 374, 552, 616 and 1036 cm\(^{-1}\) corresponding to the normal W-O vibration of the WO\(_6\) octahedra. Unlike the ideal WO\(_4\) structure (scheelite) where four normal vibrational modes of the tetrahedral structure are Raman active, WO\(_6\) structure has six normal modes of vibration of which only three are Raman active. The isolated WO\(_6\) wolframite structure found in the bulk crystalline NiWO\(_4\) has 891 cm\(^{-1}\) which is associated with the WO\(_6\) symmetric stretching vibration and this agrees well with the results reported by Ross-Medgaarden and Wachs [14].

The factor group analysis predicts that there should be 105 optical modes for P\(_\text{ca21}\) structure of Bi\(_2\)WO\(_6\) distributed among 26A\(_1\) + 27A\(_2\) + 26B\(_1\) + 26B\(_2\) irreducible representations. The A\(_2\), B\(_1\) and B\(_2\) modes are both Raman and IR active whereas the A\(_1\) modes are only Raman active. Bi\(_2\)WO\(_6\) shows two strong peaks at 797 and 295 cm\(^{-1}\) and weak peaks at 410 and 716 cm\(^{-1}\). The strongest peak at 797 cm\(^{-1}\) can be assigned to the symmetric and asymmetric stretching modes of the WO\(_6\) octahedra involved in the motions of the apical oxygen atoms perpendicular to the layer [30]. The weak Raman peak at 716 cm\(^{-1}\), is due to asymmetric stretching mode of the WO\(_6\) octahedra, involving mainly vibrations of the equatorial oxygen atoms within layers. The peak at 295 cm\(^{-1}\) region originates from the bending mode of the bismuth-oxygen polyhedra.

**Diffuse reflectance UV-visible spectroscopy**

Figure 5 shows the optical absorption spectra of BaWO\(_4\), NiWO\(_4\) and Bi\(_2\)WO\(_6\) nanoparticles with an absorption edge in 200–900 nm region. All samples have excellent optical transmission spectra as the maximum absorption edges appeared in the ultraviolet region: 223.0 nm for BaWO\(_4\), 320.6 nm for Bi\(_2\)WO\(_6\) and 299.0 nm for NiWO\(_4\). The excitation from O\(_2p\) to W\(_t2g\) in the (WO\(_4^2-\)) group absorbs ultraviolet irradiation in MWO\(_4\). In the excited state of the (WO\(_4^2-\)) groups, the hole (on the oxygen) and the electron (on the tungsten) remain together as an exciton because of their strong interactions. Further absorption peaks in the visible region are exhibited by NiWO\(_4\) which could be due to a charge transfer transition in which an oxygen 2\(p\) electron goes into one of the empty tungsten 5\(d\) orbital.

A unique feature of UV-vis for the isolated WO\(_4\) reference compounds is that they only possess a single ligand to metal charge transfer (LMCT) band in the general region of 218–274 nm, with many of the band maxima occurring at 220–250 nm. The exact location of this band maximum depends on the extent of distortion of the isolated WO\(_4\) structure [14]. Optical absorbances of samples BaWO\(_4\) and Bi\(_2\)WO\(_6\) show only one absorption band, while NiWO\(_4\) shows four absorption bands. Worth noting to report that the absorption peak of BaWO\(_4\) from this work was found close to what has been reported [19].

For the NiWO\(_4\) sample, 100 nm shift to a lower wavelength was observed as compared to the same material synthesized by the molten salt method [20]. Four bands observed from the NiWO\(_4\) sample at both UV and visible range (Figure 5(b)) are due to the oxidation state of the cations [37]. Cimino et al. [38] had reported that absorption bands at 1.21, 1.65–1.74, 2.00–2.11, 2.83–2.88 and 3.35 eV from Ni\(^{2+}\)O\(_6\) are due to the transition from \(^3\)A\(_{2g}\) to the excited states \(^3\)T\(_{2g}\), \(^1\)E\(_g\), \(^3\)T\(_{1g}\), \(^1\)T\(_{2g}\) and \(^3\)T\(_{1g}\), respectively. Similar data were also obtained by Lenglet et al. [39] who reported the same bands at about 1.08–1.13, 1.72–1.75, 1.77–1.95, 2.71–2.79 and 2.97–3.00 eV. In the present work, four absorbance bands at 299 nm
(2.97 eV), 453 nm (2.71 eV), 738 nm (1.68 eV) and 842 nm (1.47 eV) are observed; the first and second bands with high intensity are in the ultraviolet range while the third and forth with low intensity is in the blue range. The first band at 2.97 eV may be attributed to the charge transfer transition in the WO₆ matrix. Bands at 2.71 and 1.68 eV are assigned to the forbidden electronic transition from ³A₂g to ¹E₉ and ¹T₂g, respectively. The band at 1.47 eV can be assigned to the presence of Ni²⁺O₄ arising from Frenkel defects with dislocation of Ni²⁺ from the octahedral to tetrahedral sites. This result is in agreement with that of de Oliveira et al. [37].

Quantification of the band gap (E₉) was carried out for all three metal tungstate samples. The band gap transition is determined from the steep shape of the spectra and the equation αhv = A(hv − E₉)^m was employed where the absorption coefficient (α) is related to the incident photon energy (hv), A is constant, m is the index indicating the type of transition [38]. The nature of the electropositive ions (Ba²⁺, Ni²⁺ and Bi³⁺) seems to have small influence on the E₉ values. It is found that E₉ decreases according to the following sequence: BaWO₄ > Bi₂WO₆ > NiWO₄ (Table 3). The band gap of BaWO₄ (4.60 eV) agrees well with the values reported [39,40], while the value of the prepared NiWO₄ is significantly higher (3.05 eV) [41,42]. Ross-Medgaarden and Wachs [14] also reported the E₉ value of wolframite NiWO₄ as ~4.5 eV, which is higher than this finding with ligand-to-metal charge transfer (LCMT) band maximum between 247-252 and 342-344 nm, due to the distortion nature in isolated WO₆ units.

For Bi₂WO₆, the band gap value obtained (3.05 eV) is higher than that found by Fu et al. [43], as the E₉ value in d° perovskites was shown to depend upon the electro-
negativity of the transition metal ion, the connectivity of the polyhedral and the deviation from linearity of the M-O-M bonds. In addition, the forms of the solid samples often have strong effect on the optical properties of the material [22].

**PL spectra**

Figure 6 shows the PL spectra of BaWO₄, Bi₂WO₆ and NiWO₄ using the excited wavelength of 325 nm. Broad blue-green emission peaks centered at ~600 nm are observed. This profile of the emission band is typical of a multiphonon process, i.e., a system in which relaxation occurs by various paths, involving the participation of numerous states. The emission peaks are attributed to the recombination of electrons in the 1T₂ excited state and holes in the 1A₁ ground state, specified within the [WO₄]²⁻ excited complexes. The blue component is attributed to the regular lattice of which the emitting level comprises both metal cations (Ba, Ni and Bi) and tungstate contributions, while the green one originates from the defect centers associated with oxygen [44]. Meanwhile the broad peaks are due to the transition from the 3T₁ and 3T₂ excited states to the 1A₁ ground state [24].

It has been reported that metal tungstates exhibit blue luminescence spectra, which is based on the radiative transition within the tetrahedral (WO₄)²⁻ group [45]. From Table 4, BaWO₄ nanoparticles exhibit higher emission intensity than the other two samples (Bi₂WO₆ and NiWO₄). The PL intensity is controlled by the number of charged transfers and surface defects. Moreover, the emission peaks obviously shift to the region of long wavelength which may be due to the particle-forming effect and the increased size of nanoparticles [46,47].

For Bi₂WO₆, smaller grain size also contributes considerably to high PL intensity. Similar observations were also observed by Dong Young et al. who synthesized Bi₂WO₆ hydrothermally and obtained higher PL intensity with the smaller crystallite size of 23 nm as calculated from XRD [48]. These phenomenon closely agrees to that reported by Quintana-Melgoza et al. [25] in which the optical response of material is largely determined by its underlying electronic properties that are closely related to its chemical or ions, atomic arrangement and physical dimension for nanometer-sized materials. Low intensity of the PL curve has been shown to be due to the oxygen atoms playing the role of electron capturers, thereby depressing the recombination process. In addition, PL intensity also depends on whether the added tungsten metal acts as an electron capturer or not. The PL curve of NiWO₄ powder tends to shift slightly to a higher wavelength as compared to Bi₂WO₆ and BaWO₄. This blue shift is observed when the dimensions of nanocrystalline particles approach the

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**Table 3 Summary of metal tungstates wavelength and band gap energy**

| System     | Wavelength (nm) | Eg (eV) | Eg (eV) | Ionic radius of cation A (Å) |
|------------|-----------------|---------|---------|----------------------------|
| Bi₂WO₆     | 320.56          | 3.05    | 2.7     | 2.67 [43]                  |
| BaWO₄      | 223.03          | 4.60    | 4.8-5.58| 1.42 [39,40]               |
| NiWO₄      | 299.03          | 2.97    | 2.28-2.95| 0.69 [41,42] 4.5 [14]      |

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Figure 6 Photoluminescence spectra of BaWO₄, NiWO₄ and Bi₂WO₆ samples.
dependence of the PL intensity on smaller grain sizes is attributed to the quantum-size effect due to the wider band gap. Results also showed a great shift in PL spectra is due to the quantum size effect as a PL were detected at ~600 nm for all samples. The blue-exciton Bohr radius ($a_0$) due to the quantum-size effect of this free exciton should result in photon emission with energy equivalent to the band gap energy. Although there are different opinions explaining the origin of the emission bands and the nature of the optical transition, there is no clear answer for higher pore distribution and less particle area (20.06 m$^2$/g) contributed by NiWO$_4$ is believed to be responsible for the emission bands.

### Table 4 Summary of wavelength at maximum peak and peak intensity of BaWO$_4$, NiWO$_4$, and Bi$_2$WO$_6$ samples

| System    | Intensity (a.u.) | Wavelength (nm) |
|-----------|-----------------|-----------------|
| NiWO$_4$  | 921             | 615             |
| BaWO$_4$  | 2600            | 603             |
| Bi$_2$WO$_6$ | 1215           | 610             |

Conclusions

Three different phases of metal tungstates of BaWO$_4$ (scheelite), NiWO$_4$ ( wolframate) and Bi$_2$WO$_6$ (perovskite layer) were successfully prepared by the simple and economical sucrose-templated method. The highest surface area (20.06 m$^2$/g) contributed by NiWO$_4$ is believed to arise from higher pore distribution and less particle agglomeration due to the presence of sucrose. Raman spectra showed that the vibration modes of the products are in accordance with those of the tungstate compounds. Microstructure vibrations of three different phases of scheelite-type BaWO$_4$ were shown to have less Raman active modes when compared to wolframate NiWO$_4$, caused from the increased lattice symmetry while layered perovskite Bi$_2$WO$_6$ exhibited only four peaks involving oxygen motion, perpendicular and within the layer. Slight shifting of the detected vibration modes and that some vibration modes were not detected can be attributed to some differences in their geometries, particle sizes and nature of the products. The UV spectra revealed the highest band gap associated with BaWO$_4$ followed by Bi$_2$WO$_6$ and NiWO$_4$. Broad blue-green emission peaks in PL were detected at ~600 nm for all samples. The blue shift in PL spectra is due to the quantum size effect as a result of the wider band gap. Results also showed great dependence of the PL intensity on smaller grain sizes (~50-80 nm) with homogenous spherical particle morphology. The materials showed promising PL results for fluorescence lamp application.

Competing interests

The authors declare that they have no competing interests.

Authors' contribution

SMWZ carried out the experimental work, RY, AH, HNMEM and MND participating in the interpretation and discussion of the results. All authors read and approved the final manuscript.

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