Synthesis, Phase Transition, and Optical Studies of Ba$_{2-x}$Sr$_x$ZnWO$_6$ (x = 1.00, 1.25, 1.50, 1.75, 2.00) Tungsten Double Perovskite Oxides

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Abstract: Ba$_{2-x}$Sr$_x$ZnWO$_6$ double perovskite (DP) oxide compounds (x = 1, 1.25, 1.5, 1.75, 2) were successfully created by means of conventional solid-state techniques. The crystal structures of our series were studied using an X-ray diffractometer. The x = 1 compound has a cubic (Fm-3m) crystal structure, the 1 ≤ x ≤ 2 compounds have tetragonal (I4/m) symmetry, and the phase was transferred to monoclinic (P2$_1$/n) symmetry for the Sr$_2$ZnWO$_6$ (x = 2) compound. Scanning electron microscopy (SEM) was used to investigate the morphology of the series, showing that the samples had crystallized microstructures. Molecular bonds were investigated using Fourier transform infrared and Raman spectroscopies, which confirmed the double perovskite octahedral geometry for the samples in our series. Furthermore, the octahedral W–O$_6$ anti-symmetric stretching mode was found to occur. The optical properties of the Ba$_{2-x}$Sr$_x$ZnWO$_6$ series were studied using Ultraviolet–visible (UV–vis) diffuse reflectance and photoluminescence (PL) spectroscopies. The absorption edge of the samples appeared around the near-violet and visible spectra, between 336–360 nm. The band gap energy was investigated in two ways—using the absorption cutoff and Tauc plots—which increased from 3.52 to 3.7 eV with increasing substitution of Ba$^{2+}$ by Sr$^{2+}$. Furthermore, excitation and emission spectra were collected at room temperature. A broad band at 260–360 nm appeared in the PLE spectra for all samples, and the PL spectra of the samples had a band that spread from 320–450 nm.

Keywords: tungsten double perovskite; crystal structures; X-ray diffractometer; Raman spectroscopy; PLE spectra

1. Introduction

Double perovskite oxides are usually produced from alkaline metals at the A and A’ sites and transition metals at the B and B’ sites [1–3]. They exist in the solid state and dissolve in solutions such as Cs$_2$AgBiBr$_6$ [3], KLaMnWO$_6$, NaLaMnWO$_6$, NaNdMnWO$_6$, NaTbMnWO$_6$, NaNdCoWO$_6$, NaNdMgWO$_6$ [4], Sr$_2$Ca$_{1-x}$Eu$_x$Na$_2$MoO$_6$ [5], and Ba$_2$Zn$_{1-x}$Ni$_x$WO$_6$ (0 ≤ x ≤ 1) [6], in which, organic perovskites have organic roots as cations such as CH$_3$NH$_3$SnI$_3$ [7] and CH$_3$NH$_3$PbX$_3$ (X = Cl$^-$, Br$^-$, and I$^-$) [8].
In the crystal structure of an AA′BB′O₆ double perovskite oxide, the A and A′ cations reside in cubic octahedrons, and B and B′ are set at the center of an octahedron. They are mostly arranged in a rock salt cubic (Fm-3m) crystal structure, although they can change to another phase structure (depending on the ionic radii of the A and B cations) and adopt distorted orientations, such as the Dion–Jacobson structure or the Ruddlesden–Popper structure [9,10].

The stability and eventual distortion of the structure can be evaluated by using Goldschmidt’s tolerance factor, which is useful in evaluating the types of oxides in the perovskite. Theoretically, the tolerance factor can be used to estimate the type of crystal structure of the materials. In general, for single perovskites with the ABO₃ order, the tolerance factor (t) [3,11] can be written as

$$ t = \frac{(r_A + r_o)}{\sqrt{2}(r_B + r_o)}. \quad (1) $$

Furthermore, the tolerance factor can be calculated for an A₂₋ₓA′ₓBB′O₆ double perovskite series using the following equation [12]:

$$ t = \frac{1 - \left(\frac{x}{2}\right)r_A + \frac{x}{2}r_A + r_o}{\sqrt{2}\left(\frac{r_B}{2} + \frac{r_B}{2} + r_o\right)}. \quad (2) $$

where rₐ, rₐ', rₐ'', rₐ''', and rₐ'''' are the ionic radii of the A and B sites, and rₒ is the ionic radius of oxygen. Depending on the value of t, the crystal structure may be diverse: for t > 1.05, the structure is a hexagonal crystal; for 1.05 > t > 1.00, it is a cubic crystal with a space group (Fm-3m). For 1.00 > t > 0.97, it has a tetragonal (I4/m) structure; and for 0.97 > t, a monoclinic (P2₁/n) or orthorhombic structure is found [13,14].

The tungsten AA′BB′O₆ double perovskite oxide includes Ba, Sr, and Ca as cations in the A and A′ sites and tungsten with any transition elements as cations in the B and B′ sites. Some examples are Ba₂MgWO₆ and Ba₂ZnWO₆ [15], Ba₂Zn₁₋ₓNiₓWO₆ (0 ≤ x ≤ 1) [16], and Sr₂BWO₆ (B = Ni, Mg) [17].

The importance of double perovskite materials specially tungsten double perovskite oxide has been evidenced by the extent of their applications, such as in magnetic resonance (Sr₂FeWO₆) [17], as superconducting materials (Ba₂LaZrO₅.₅) [18] and photocatalytic materials (A₂ZnTiO₆; A = Pr, Gd) [19], in microwave communication (Ba₂Zn₁₋ₓCaxWO₆ (x = 0–0.4)) [20], in solar light-harvesting cells (La₂NiMnO₆) [21], and in photovoltaic applications (Ba₂Zn₁₋ₓNiₓWO₆; 0 ≤ x ≤ 1) [6].

The wide range of double perovskite oxide compounds is due to their multiplicity and ease of preparation. For example, solid-state reactions have been used as the preparation method for Sr₂CaWO₆, Sr₂MgWO₆ [22], and Ba₂MeWO₆ (Me = Mg, Ni, Zn) [23] compounds, while chemical co-precipitation routes have been used for La₂CoMnO₆ [24] and Sr₂Cd₁₋ₓCaₓWO₆ (0 ≤ x ≤ 1) [25] compounds.

In this study, due to the importance of double perovskite oxides in technological applications throughout diverse fields, in order to contribute to their characterization and properties, as well as to demonstrate the structural phase transition in these type of compounds, a conventional solid-state reaction was used to synthesize a Ba₂₋ₓSrₓZnWO₆ series (where x = 1.00, 1.25, 1.50, 1.75, 2.00). We then employed X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), UV-vis diffuse reflectance spectroscopy, and photoluminescence spectroscopy to characterize the structural and optical properties of the series.

2. Materials and Experimental

2.1. Preparation of Materials

A solid-state interaction route was used to synthesize Ba₂₋ₓSrₓZnWO₆ (x = 0, 0.25, 0.50, 0.75, 1). The series was created from BaCO₃, SrCO₃, WO₃, ZnO, and NiO, with high purity (99.99%) Alfa Aesar powders as raw in-house materials. The Ba₂₋ₓSrₓZnWO₆ (x = 0, 0.25, 0.50, 0.75, 1) samples were weighed in stoichiometric ratios, according to the following chemical equation:
\[(2 - x)\text{BaCO}_3 + x\text{SrCO}_3 + \text{ZnO} + \text{WO}_3 \rightarrow \text{Ba}_{2-x}\text{Sr}_x\text{ZnWO}_6 + 2\text{CO}_2 \uparrow, \quad (x = 0, 0.25, 0.50, 0.75, 1). \quad (3)\]

As the first step, the starting materials of the sample were intermixed and powdered in an Agate mortar and pestle with the addition of acetone for 2 h. Then, the samples were put in alumina crucibles and calcined in air using a high-temperature furnace (Eurotherm model 2416 temperature controller, Eurotherm, Worthing, UK) at 800 °C for 24 h. Thereafter, the samples were ground, formed into pellets of disk shape, and calcined in air at 1000 °C for 24 h. Finally, the mixture was ground and calcined at 1200 °C in air for 24 h at a rate of 10 °C per minute during the heating and cooling processes. All samples were ground for 2 h and acetone was added to increase the homogeneity in all previous steps.

2.2. Sample Characterization

XRD was used to investigate the purity and crystallinity of the samples after the heating steps [14]. A Bruker (AXS-D8) diffractometer (Karlsruhe, Germany) [26] was used to collect the data at room temperature using the settings 40 kV and 40 mA with Cu-Kα radiation (λ = 1.54 Å) in 2θ (20–80°) geometry at 0.02 steps per minute. The Fullprof program (Version 3.00, June-2015) was utilized as an analyzer program using the Rietveld refinement method to create the crystal structure parameters. Furthermore, the Debye–Scherrer equation [27] was used to find the particle size of the compounds, as follows:

\[ D(\text{crystalline size}) = \frac{0.94 \lambda}{\beta \cos \theta}, \quad (4) \]

where \( D \) is the particle size, \( \lambda \) is the wavelength (1.5405 Å), \( \beta \) is the full width at half maximum (FWHM), and \( \theta \) is the Bragg angle. In order to remove the contribution from instrumental broadening, the FWHM of the main peak of the sample in XRD traces of the sintered bulk sample was subtracted, as described by \( \beta = a^2 - b^2 \) (where \( a \) and \( b \) are the measured FWHM of equivalent diffraction lines in the sample, respectively).

The morphology and homogeneity of the \( \text{Ba}_{2-x}\text{Sr}_x\text{ZnWO}_6 \) \( x = 0, 0.25, 0.50, 0.75, 1 \) series were revealed using a JEOL JSM-6360 high-resolution Scanning Electron Microscope SEM (Stereo-scan LEO 440, Peabody, MA, USA), which included Energy Dispersive X-Ray Analysis (EDX).

A Satellite FTIR Mattson 5000 (wave number range: 400–4000 cm\(^{-1}\)) [28] was utilized to determine the transmittance mode of infrared spectra using samples collected during the KBr condensation process. The material to be analyzed was mixed with KBr at a ratio of 1:100 for FTIR investigation.

A Stellar Net-Inc High-Resolution Raman Spectrometer (Tampa, FL, USA, for 200–2200 cm\(^{-1}\) in 785 nm with 4 cm\(^{-1}\) resolution) was used to record the Raman spectra for the \( \text{Ba}_{2-x}\text{Sr}_x\text{ZnWO}_6 \) \( x = 0, 0.25, 0.50, 0.75, 1 \) series. A Raman Probe was attached to the FC/APC laser and SMA 905 spectrometer, and integrated Raman was used to collect the Raman filters and optics at a working distance from the sample of 4.5 mm, configured for a 785 nm laser.

The UV–vis diffuse reflectance spectra of the \( \text{Ba}_{2-x}\text{Sr}_x\text{ZnWO}_6 \) \( x = 0, 0.25, 0.50, 0.75, 1 \) series were compiled using a UV–vis spectrophotometer (Shimadzu, UV-2550, Kyoto, Japan), with BaSO\(_4\) as a reference, at room temperature. The UV–vis reflectance spectra were determined at the absorption edge and translated into absorbance using the Kubelka–Munk (KM) equation [29].

\[ F(R_{\infty}) = \frac{\alpha}{s} = \frac{(1 - R)^2}{2R}, \quad (5) \]

where \( F(R_{\infty}) \) is the KM function, \( \alpha \) is the absorption coefficient, \( s \) is the scattering coefficient, and \( R \) is the reflection coefficient.

The band gap of the \( \text{Ba}_{2-x}\text{Sr}_x\text{ZnWO}_6 \) \( x = 1.00, 1.25, 1.50, 1.75, 2.00 \) series was determined from the edge of the absorbance by means of the Tauc plot, with the help of the following equation:

\[ [F(R_{\infty})h\nu]^n = A(h\nu - E_g), \quad (6) \]
where $h\nu$ is the incident photon energy, $A$ is a proportional constant, $E_g$ is the band gap energy, and $n$ takes a value of 2 or 0.5 for direct or indirect transition, respectively.

The photoluminescence of the $\text{Ba}_{2-x}\text{Sr}_x\text{ZnWO}_6$ ($x = 1.00, 1.25, 1.50, 1.75, 2.00$) series was studied at room temperature using a PerkinElmer LS55 fluorescence spectrometer (Mundelein, IL, USA).

3. Results and Discussion

3.1. XRD

XRD studies are very important in determining a crystal’s structural parameters, such as the lattice crystal, atomic position, lattice parameters, and space group. Studies often refer to the significance of examining a material’s structure, as it governs the other properties of the material [30]. The XRD patterns of the $\text{Ba}_{2-x}\text{Sr}_x\text{ZnWO}_6$ ($x = 1.00, 1.25, 1.50, 1.75, 2.00$) series, which were created using conventional solid-state reactions, are demonstrated in Figure 1. The $\text{BaWO}_4$ and $\text{Ba}_2\text{WO}_5$ phases are found as minor peaks with weak intensities in the XRD pattern, which were ascribed to impurities in the $\text{Ba}_{2-x}\text{Sr}_x\text{ZnWO}_6$ structures around $26^\circ$ and $28^\circ$ [31] (indicated in Figure 1 by plus and star signs for $\text{BaWO}_4$ and $\text{Ba}_2\text{WO}_5$, respectively). The XRD result of each sample in the series was refined by the Rietveld method, which was applied in the Fullprof program. The Rietveld refinement of the series was observed to be a cubic (Fm-3m) structure for $\text{BaSrZnWO}_6$ ($x = 1$), which transformed into a tetragonal (I4/m) symmetry phase for $\text{Ba}_{0.75}\text{Sr}_{1.25}\text{ZnWO}_6$, $\text{Ba}_{0.50}\text{Sr}_{1.50}\text{ZnWO}_6$ (see Figure 2), and $\text{Ba}_{0.25}\text{Sr}_{1.75}\text{ZnWO}_6$ with compositions in the range of $1 < x < 2$. The structure was transformed into a new phase with monoclinic (P21/n) symmetry for $\text{Sr}_2\text{ZnWO}_6$ ($x = 2$).

![Figure 1. X-ray powder diffraction of the $\text{Ba}_{2-x}\text{Sr}_x\text{ZnWO}_6$ ($x = 1, 1.25, 1.50, 1.75, 2$) double perovskite series.](image-url)
The crystalline size was computed from the full width at half maximum (FWHM) at the highest peak of each sample in the series ($x = 1, 1.25, 1.50, 1.75, 2.00$) using the Scherer equation. The crystalline sizes varied between 57.56 and 84.59 nm for the double perovskite series. The tolerance factor was calculated using equation 2 with ionic radii taking the values 1.45 Å, 0.74 Å, 1.66 Å, 1.21 Å, and 0.74 Å for Sr$^{2+}$, Zn$^{2+}$, Ba$^{2+}$, O$^{2-}$, and W$^{6+}$, respectively. The tolerance factor was found to be 0.980 for the cubic crystalline sample when $x = 1$. In addition, the tolerance factor was found to be between 0.974 and 0.993 for the tetragonal crystalline samples when $1 \leq x \leq 2$. For the monoclinic sample, the tolerance factor was found to be 0.964 when $x = 2.00$, in agreement with the SPuDs software and Equation (2). The lattice parameters, tolerance factors, and crystalline sizes of the samples are presented in Table 1. The tolerance factor results were confirmed by the crystal structure determined by XRD refinement (see Figure 3). This indicates that the tolerance factor decreased as the substitution ratio increased, resulting in Ba$^{2+}$ having an ionic radius that is larger than the Sr$^{2+}$ ionic radii.

The phase transition for the series is found to occur from cubic to tetragonal and from tetragonal to monoclinic for $1 \leq x \leq 2$. Manoun et al. [31] found that the phase transition for their samples occurred in similar manner. The difference of our work in terms of preparation process and samples ratios is resulted in different lattice parameters and consequently different unit cell volumes. The unit cell volume is found to decrease gradually with increasing of Sr$^{2+}$ substituting which is consisted with the lower ionic radius of Sr$^{2+}$ (1.45 Å) compared to Ba$^{2+}$ (1.66 Å). In addition, the tetragonal distortion and monoclinic distortion when Ba$^{2+}$ is completely substituted with Sr$^{2+}$ is maybe due to the smaller size of Sr$^{2+}$.

![Figure 2. Rietveld refined XRD pattern of the Ba$_{0.75}$Sr$_{1.25}$ZnWO$_6$ sample.](image-url)
Table 1. Unit cell parameters, tolerance factors, and crystalline sizes of the Ba$_{2-x}$Sr$_x$ZnWO$_6$ ($x = 1, 1.25, 1.50, 1.75, 2.00$) double perovskite series.

| Composition          | BaSrZnWO$_6$ | Ba$_{0.75}$Sr$_{1.25}$ZnWO$_6$ | Ba$_{0.50}$Sr$_{1.50}$ZnWO$_6$ | Ba$_{0.25}$Sr$_{1.75}$ZnWO$_6$ | Sr$_2$ZnWO$_6$ |
|----------------------|--------------|-------------------------------|-------------------------------|-------------------------------|----------------|
| Program              | Fullprof     | Fullprof                      | Fullprof                      | Fullprof                      | Fullprof       |
| $\lambda_{K\alpha}$ (Å) | 1.5406 Å | 1.5406 Å                       | 1.5406 Å                      | 1.5406 Å                      | 1.5406 Å       |
| Atom number          | 6            | 6                             | 6                             | 6                             | 6              |
| 2$\theta$ Range (°)  | 20–80        | 20–80                         | 20–80                         | 20–80                         | 20–80          |
| Step scan            | 0.02         | 0.02                          | 0.02                          | 0.02                          | 0.02           |
| Zero point (° 2$\theta$) | 0.205620  | 0.196440                      | 0.181520                      | 0.198830                      | 0.296540       |
| Caglioti parameters  |              |                               |                               |                               |                |
| U                    | 0.016(9)     | 0.330(9)                      | 0.006(9)                      | 0.199(3)                      | 0.096(1)       |
| V                    | 0.005(7)     | -0.235(8)                    | 0.003(8)                      | -0.089(3)                     | -0.079(2)      |
| W                    | 0.010(1)     | 0.077(1)                     | 0.003(1)                      | 0.002(1)                      | 0.017(1)       |
| $\chi^2$             | 1.44         | 1.65                          | 1.45                          | 1.55                          | 1.61           |
| $R_\text{B}$          | 7.52027      | 8.44375                      | 5.08192                       | 7.62028                       | 8.54376        |
| $R_F$                | 9.40813      | 8.62935                      | 6.60579                       | 9.50814                       | 8.72936        |
| Crystal Structure     | Cubic        | Tetragonal                   | Tetragonal                   | Tetragonal                   | Monoclinic     |
| Space group          | Fm-3m        | 1 4/m                        | 1 4/m                        | 1 4/m                        | P2$_1$/n       |
| a (Å)                | 8.039(1)     | 5.642(2)                     | 5.667(1)                      | 5.610(1)                      | 5.639(1)       |
| b (Å)                | 8.039(1)     | 5.642(2)                     | 5.667(1)                      | 5.610(1)                      | 5.636(1)       |
| c (Å)                | 8.039(1)     | 8.011(3)                     | 8.020(2)                      | 7.951(1)                      | 7.944(1)       |
| $\alpha$ (Å)         | 90           | 90                           | 90                            | 90                            | 90             |
| $\beta$ (Å)         | 90           | 90                           | 90                            | 90                            | 90.315         |
| $\gamma$ (Å)        | 90           | 90                           | 90                            | 90                            | 90             |
| V (Å$^3$)            | 519.600(8)   | 255.077(8)                   | 257.580(7)                    | 250.262(6)                    | 252.557(4)     |
| Tolerance factor (T) | 1.002        | 0.993                        | 0.983                         | 0.974                         | 0.964          |
| Crystalline size (D) (nm$^3$) | 84.59     | 59.53                        | 61.64                         | 71.38                         | 57.56          |

The XRD pattern refinement of samples was carried out by using the cubic (Fm-3m) crystal, with the starting model taken from a previous study [15]. In this typical model, tungsten (W$^{6+}$), Zinc...
(Zn\(^{2+}\)), and Barium (Ba\(^{2+}\))/strontium (Sr\(^{2+}\)) are located in the 4a (0, 0, 0), 4b (1/2, 1/2, 1/2), and 8c (1/4, 1/4, 1/4) positions, respectively, whereas oxygen (O\(^{2-}\)) fills the (0, 0, z) positions. XRD pattern refinement was also carried out using a tetragonal (I4/m) structure, with the starting model taken from previous studies [31,32]. In this model, W\(^{6+}\), Zn\(^{2+}\), and Ba\(^{2+}\)/Sr\(^{2+}\) are located at the 2b (0, 0, 1/2), 2a (0, 0, 0), and 4d (0, 1/2, 1/4) positions, respectively. There were two crystallographically distinct oxygen atoms (O\(_1\)(x, y, 0) and O\(_2\)(0, 0, z)) in the unit cell. For all samples, the refinements of the occupancies of all the atoms revealed no substantial deviations from their stoichiometric standards. Noteworthy residuals of the refinements were acquired, as specified in Table 2.

Table 2. Atom coordinates of Ba\(_{2-x}\)Sr\(_x\)ZnWO\(_6\) double perovskite series (x = 1.25, 1.50, 1.75, 2) following Rietveld refinement of x-ray powder diffraction.

| Atom        | X      | Y      | Z      | B (Å\(^2\)) | Occ |
|-------------|--------|--------|--------|-------------|-----|
| Ba\(^{2+}\) | 0.250(3)| 0.250(3)| 0.250(6)| 0.691(2)    | 0.250|
| Sr\(^{2+}\) | 0.250(3)| 0.250(3)| 0.250(4)| 0.691(3)    | 0.250|
| Zn\(^{2+}\) | 0.500(8)| 0.500(4)| 0.500(3)| 1.055(4)    | 0.250|
| W\(^{6+}\)  | 0.000  | 0.000  | 0.000  | 0.365(3)    | 0.250|
| O\(_1\)\(^{2-}\)| 0.000  | 0.000  | 0.248(2)| 1.400(2)    | 1.000|
| O\(_2\)\(^{2-}\)| 0.000  | 0.000  | 0.248(9)| 0.600(6)    | 0.500|
| Ba\(_{0.75}\)Sr\(_{1.25}\)ZnWO\(_6\) |        |        |        |             |     |
| Ba\(^{2+}\) | 0.000  | 0.500(3)| 0.250(2)| 1.857(3)    | 0.188|
| Sr\(^{2+}\) | 0.000  | 0.500(4)| 0.250(3)| 1.857(5)    | 0.313|
| Zn\(^{2+}\) | 0.000  | 0.000  | 0.000  | 0.992(4)    | 0.250|
| W\(^{6+}\)  | 0.000  | 0.000  | 0.500(3)| 0.187(3)    | 0.250|
| O\(_1\)\(^{2-}\)| 0.319(4)| 0.227(3)| 0.000  | 1.770(4)    | 1.000|
| O\(_2\)\(^{2-}\)| 0.000  | 0.000  | 0.258(2)| 1.770(4)    | 0.500|
| Ba\(_{0.50}\)Sr\(_{1.50}\)ZnWO\(_6\) |        |        |        |             |     |
| Ba\(^{2+}\) | 0.000  | 0.500(2)| 0.250(3)| 0.600(4)    | 0.125|
| Sr\(^{2+}\) | 0.000  | 0.500(2)| 0.250(2)| 0.600(4)    | 0.375|
| Zn\(^{2+}\) | 0.000  | 0.000  | 0.000  | 1.900(4)    | 0.250|
| W\(^{6+}\)  | 0.000  | 0.000  | 0.500(3)| 0.941(3)    | 0.250|
| O\(_1\)\(^{2-}\)| 0.332(7)| 0.213(3)| 0.000  | 0.800(3)    | 1.000|
| O\(_2\)\(^{2-}\)| 0.000  | 0.000  | 0.251(5)| 0.800(7)    | 0.500|
| Ba\(_{0.25}\)Sr\(_{1.75}\)ZnWO\(_6\) |        |        |        |             |     |
| Ba\(^{2+}\) | 0.000  | 0.500(2)| 0.250(3)| 1.868(4)    | 0.063|
| Sr\(^{2+}\) | 0.000  | 0.500(5)| 0.250(4)| 1.868(7)    | 0.438|
| Zn\(^{2+}\) | 0.000  | 0.000  | 0.000  | 0.161(4)    | 0.250|
| W\(^{6+}\)  | 0.000  | 0.000  | 0.500(3)| 0.140(6)    | 0.250|
| O\(_1\)\(^{2-}\)| 0.330(2)| 0.202(2)| 0.000  | 1.666(3)    | 1.000|
| O\(_2\)\(^{2-}\)| 0.000  | 0.000  | 0.363(2)| 1.298(3)    | 0.500|
| Sr\(_2\)ZnWO\(_6\) |        |        |        |             |     |
| Sr\(^{2+}\) | 0.008(4)| 0.515(2)| 0.250(7)| 0.577(2)    | 0.500|
| Zn\(^{2+}\) | 0.000  | 0.000  | 0.000  | 0.402(3)    | 0.250|
| W\(^{6+}\)  | 0.500(1)| 0.500(4)| 0.000  | 0.402(3)    | 0.250|
| O\(_1\)\(^{2-}\)| 0.267(4)| 0.018(3)| 0.003(3)| 1.000(4)    | 0.500|
| O\(_2\)\(^{2-}\)| 0.250(4)| -0.006(3)| -0.009(4)| 1.000(4)    | 0.500|
| O\(_2\)\(^{2-}\)| -0.051(3)| 0.250(2)| 0.117(4)| 1.000(6)    | 0.500|

3.2. SEM and EDX

The SEM images of the samples in the series are shown in Figure 4a–e. All samples in the series had similar morphologies and were highly homogeneous with no impurities. Larger particle sizes and particles aggregates in assemblies were observed for all samples; this was caused by the higher
temperatures used in the preparation process. Lan et al. [21] showed an identical temperature effect in the morphology of \( \text{La}_2\text{NiMnO}_6 \) materials. Additionally, the materials in the SEM images were exposed to fine, small fragments that were created during the grinding process in the preparation step. All samples varied in grain size. The grain sizes for \( \text{Ba}_{2-x}\text{Sr}_x\text{ZnWO}_6 \), \( \text{Ba}_{0.75}\text{Sr}_{1.25}\text{ZnWO}_6 \), \( \text{Ba}_{0.5}\text{Sr}_{1.50}\text{ZnWO}_6 \), \( \text{Ba}_{0.25}\text{Sr}_{1.75}\text{ZnWO}_6 \), and \( \text{S}_{2}\text{ZnWO}_6 \) were 2–7 \( \mu \text{m} \), 2–6 \( \mu \text{m} \), 1.5–6 \( \mu \text{m} \), 1.5–5 \( \mu \text{m} \), and 2–6 \( \mu \text{m} \), respectively. Table 3 shows the EDX results, which were calculated with the help of the SEM data, which confirmed that the samples contained all elements of the raw material inputs. As an example, Figure 5 shows the EDX spectrum for the elements of the \( \text{Ba}_{0.75}\text{Sr}_{1.25}\text{ZnWO}_6 \) sample.

![SEM images](image-url)  

**Figure 4.** (a–e) SEM images of \( \text{Ba}_{2-x}\text{Sr}_x\text{ZnWO}_6 \) (\( x = 1, 1.25, 1.50, 1.75, 2 \)) double perovskite series samples.
Table 3. The EDX results for the Ba$_{2-x}$Sr$_x$ZnWO$_6$ ($x = 1, 1.25, 1.50, 1.75, 2.00$) double perovskite series samples.

| Elements | X = 1.00 |  | X = 1.25 |  | X = 1.50 |  | X = 1.75 |  | X = 2.00 |  |
|----------|----------|---|----------|---|----------|---|----------|---|----------|---|
|          | Weight%  | % | Atomic%  | % | Weight%  | % | Atomic%  | % | Weight%  | % | Atomic%  | % |
| C K      | 9.29     | 32.75 | 7.17     | 27.17 | 9.32     | 33.71 | 10.82    | 34.77 | 43.32    | 73.24 |
| O K      | 14.58    | 38.61 | 13.96    | 39.74 | 12.93    | 35.12 | 15.59    | 37.60 | 13.24    | 16.80 |
| Zn K     | 11.26    | 7.30  | 13.43    | 9.36  | 15.03    | 9.99  | 14.05    | 8.30  | 18.86    | 5.86  |
| Sr L     | 16.15    | 7.81  | 23.78    | 12.36 | 29.54    | 13.01 | 10.79    | 2.50  |          |      |
| Ba L     | 2.88     | 1.34  | 12.55    | 4.16  | 17.61    | 5.57  | 0.37     | 0.10  | 2.09     | 0.31  |
| W M      | 21.04    | 6.49  | 29.11    | 7.21  | 26.13    | 6.18  | 29.62    | 6.22  | 11.70    | 1.29  |
| Totals   | 100.0    | 100.00| 100.00   | 100.00| 100.00   | 100.00| 100.00   | 100.00| 100.00   | 100.00|

3.3. FTIR and RAMAN Spectroscopies

FTIR spectra of the perovskite structure have two distinctive absorption bands in the 850–400 cm$^{-1}$ area [33]. High-energy, strong, and anti-symmetric stretching of the W–O$_6$ octahedral bond was observed at 620 cm$^{-1}$; the reason for this is the higher charge of the W$^{6+}$ cations. Symmetric stretching vibration of the WO$_6$ octahedron appears as a high-intensity band around 825 cm$^{-1}$. As shown in Figure 6, which shows the transmittance of the series versus the wave number, all samples were confirmed to have molecular bands corresponding to the perovskite oxide form [34].

Raman spectra of the studied samples can be observed in Figure 7. The Raman mode of the Ba$_{2-x}$Sr$_x$ZnWO$_6$ samples are classified into two types of lattice vibrations: a bending vibration mode (W–O–W) in the 200–500 cm$^{-1}$ range and a stretching mode (W–O) in the middle of the 700–950 cm$^{-1}$ range [35,36].
Figure 6. FTIR transmittance spectra of the $\text{Ba}_{2-x}\text{Sr}_x\text{ZnWO}_6$ ($x = 1, 1.25, 1.50, 1.75, 2$) double perovskite series.

Figure 7. Raman shift spectra of the $\text{Ba}_{2-x}\text{Sr}_x\text{ZnWO}_6$ ($x = 1, 1.25, 1.50, 1.75, 2$) double perovskite series.
When decreasing Ba\(^{2+}\) from x = 1 to x = 0, the effect of increasing the Sr\(^{2+}\) cations was observed as an increase in both the bending and W–O stretching modes of the bonds. Furthermore, the Raman energy of the series experienced a blue shift, which may be due to Ba\(^{2+}\) having a larger ionic radius (149 Å) than Sr\(^{2+}\) (132 Å).

3.4. UV–Visible Diffuse Reflectance Spectroscopy

The UV-vis diffuse reflectance spectra in Figure 8 include all samples at room temperature and in the 200–800 nm region. A strong absorption band can be noted between 300 and 450 nm, resulting from the charge transfer transition (W\(^{6+}\) – O\(^{2-}\)) in the lattice, that is, from the highest occupied molecular orbital (2p) of oxygen (O\(^{2-}\)) to the lowest unfilled molecular orbital (5d) of tungsten (W\(^{6+}\)) [15,37,38]. The absorption band experienced a red shift with the increasing substitution of Barium (Ba\(^{2+}\)) with strontium (Sr\(^{2+}\)) cations.

![Figure 8](image)

**Figure 8.** Diffuse reflection spectra for the Ba\(_{2-x}\)Sr\(_x\)ZnWO\(_6\) (x = 1, 1.25, 1.50, 1.75, 2) double perovskite series.

The absorption coefficient was computed for the Ba\(_{2-x}\)Sr\(_x\)ZnWO\(_6\) series, from the UV–vis diffuse reflectance data, using the Kubelka–Munk (KM) function (see Equation (5)). The KM function (absorbance) is related to the wavelength, as shown in Figure 9. The absorbance was used to observe the absorption edge of the samples, which had values of 388, 345, 343, 337, and 326 nm for x = 1, 1.25, 1.50, 1.75, and 2, respectively. The band gap energy of the compounds was computed from the edge of absorption using the relationship \(E_g = \frac{1240}{\lambda}\), where \(\lambda\) is the wavelength of the absorption edge and \(E_g\) is the band gap energy [39]. Furthermore, the Tauc plot method was utilized to calculate the band gap energy for the compounds [21], as shown in Figure 10a, in accordance with Equation (5). The energy gap of the Ba\(_{2-x}\)Sr\(_x\)ZnWO\(_6\) series increased with increasing substitution of Sr\(^{2+}\) (see Figure 10b). The reason for this may be due to the ionic radii decreasing with the Ba\(^{2+}\)/Sr\(^{2+}\) ratio, which may have caused an increase of atomic divergence, sequentially leading to the energy band gap increment.
The band gap energies of all samples are given in Table 4. According to the optical energy gap of the compounds in the series, the materials can be classified as semiconductors [15,40].

Figure 9. Absorbance (KM function) as a function of wavelength for the Ba$_{2-x}$Sr$_x$ZnWO$_6$ ($x = 1, 1.25, 1.50, 1.75, 2$) double perovskite series.

Figure 10. (a) Tauc plot depicting the energy band gap in the Ba$_{2-x}$Sr$_x$ZnWO$_6$ ($x = 1, 1.25, 1.50, 1.75, 2$) double perovskite series; (b) The relationship between band gap energy and ratio of Sr$^{2+}$.

Figure 10. Cont.
Figure 10. (a) Tauc plot depicting the energy band gap in the Ba$_{2-x}$Sr$_x$ZnWO$_6$ (x = 1, 1.25, 1.50, 1.75, 2) double perovskite series; (b) The relationship between band gap energy and ratio of Sr$^{2+}$.

Table 4. Band gap energy (according to absorption edge and Tauc plot for direct transition) for the Ba$_{2-x}$Sr$_x$ZnWO$_6$ (x = 1, 1.25, 1.50, 1.75, 2.00) double perovskite series.

| X Ratio | X = 1 | X = 1.25 | X = 1.50 | X = 1.75 | X = 2 |
|---------|-------|-----------|-----------|-----------|-------|
| Cut-off wavelength (nm) | 388 | 345 | 343 | 337 | 326 |
| $E_g$ (eV) by cutoff wavelength | 3.44 | 3.59 | 3.61 | 3.67 | 3.8 |
| $E_g$ (eV) by Tauc plot | 3.50 | 3.58 | 3.60 | 3.69 | 3.7 |

3.5. Photoluminescence Spectroscopy

The luminescence values of the Ba$_{2-x}$Sr$_x$ZnWO$_6$ double perovskite series were investigated using a PerkinElmer LS55 Fluorescence spectrometer. Ethyl acetone was used as the solvent for powdered samples.

The excitation spectra of the Ba$_{2-x}$Sr$_x$ZnWO$_6$ (1.25 ≤ x < 2) series are shown in Figure 11, which were recorded with $\lambda_{em}$ = 342 nm for BaSrZnWO$_6$, $\lambda_{em}$ = 287 nm for Ba$_{0.75}$Sr$_{1.25}$ZnWO$_6$, $\lambda_{em}$ = 342 nm for Ba$_{0.50}$Sr$_{1.50}$ZnWO$_6$, $\lambda_{em}$ = 345 nm for Ba$_{0.25}$Sr$_{1.75}$ZnWO$_6$, and $\lambda_{em}$ = 344 nm for Sr$_2$ZnWO$_6$. A broad band was revealed between 260 and 320 nm, which is due to the electronic excitation of the O$^{2-}$ (2p) orbital to W$^{6+}$ (5d) orbital in octahedral WO$_6$ [36,37]. In addition, the excitation peaks of the DP samples increased with increasing substitution of Ba$^{2+}$ by Sr$^{2+}$ cations. Photoluminescence (PL) emission of the DP samples was investigated at $\lambda_{ex}$ = 286 nm for BaSrZnWO$_6$, $\lambda_{ex}$ = 287 nm for Ba$_{0.75}$Sr$_{1.25}$ZnWO$_6$, $\lambda_{ex}$ = 287 nm for Ba$_{0.50}$Sr$_{1.50}$ZnWO$_6$, $\lambda_{ex}$ = 288 nm for Ba$_{0.25}$Sr$_{1.75}$ZnWO$_6$, and $\lambda_{ex}$ = 285 nm for Sr$_2$ZnWO$_6$. The PL results show that spectral emission was spread between 320 and 450 nm (see Figure 12). Bugaris et al. [15] found a similar result for Ba$_2$ZnWO$_6$, whose emission peak reached its maximum at 539 nm when $\lambda_{ex}$ = 380 nm. The results here show decreasing intensities at the excitation peaks with an increase in substitution. The PL of BaSrZnWO$_6$ shows that its spectral
emission peak is 342 nm with an FWHM of 40 nm. Similarly, Ba$_{0.75}$Sr$_{1.25}$ZnWO$_6$, Ba$_{0.50}$Sr$_{1.50}$ZnWO$_6$, B0$_{1.25}$Sr$_{1.75}$ZnWO$_6$, and Sr$_2$ZnWO$_6$ have peaks at 342 nm, 342 nm, 345 nm, and 344 nm, with FWHMs of 45 nm, 40 nm, 40 nm, and 40 nm, respectively.

**Figure 11.** PLE of the Ba$_{2-x}$Sr$_x$ZnWO$_6$ (x = 1, 1.25, 1.50, 1.75, 2) double perovskite series.

**Figure 12.** PL of the Ba$_{2-x}$Sr$_x$ZnWO$_6$ (x = 1, 1.25, 1.50, 1.75, 2) double perovskite series.
4. Conclusions

\( \text{Ba}_{2-x}\text{Sr}_x\text{ZnWO}_6 \) \((x = 1, 1.25, 1.50, 1.75, 2)\) DP samples were prepared successfully by using conventional solid-state reactions. XRD data show that the sample with \( x = 1 \) was crystallized in a cubic (Fm-3m) structure, which transformed into a tetragonal (I4/m) phase for samples with \( 1 \leq x \leq 2 \) and into monoclinic \((P2_1/n)\) symmetry for samples with \( x = 2 \). This was confirmed by the tolerance factor, which was found to be 0.980 for the cubic sample, between 0.970 and 0.985 for the tetragonal \((1 \leq x \leq 2)\) samples, and 0.714 for the monoclinic \((x = 2)\) sample. The size of particle was observed to vary between 57.6 and 84.59 nm in the series. The SEM results revealed that the samples had crystallized microstructures with sizes ranging between 1.5 and 7.0 \( \mu \)m. The EDX results confirmed that there were no impurities and that the double perovskite samples contained the elements of the raw materials only. FTIR and Raman spectroscopy results revealed that the anti-symmetric stretching mode \((W-O)\) is octahedral around 620 cm\(^{-1}\) and the symmetric stretching vibration appears around 825 cm\(^{-1}\). UV–visible diffuse reflectance confirmed that all samples had a strong absorption band ranging between 300 and 450 nm, which may be due to the charge transfer transition from \( W^{6+} \) to \( O^{2-} \) in the lattice from the high orbital \((2p)\) of oxygen to the lowest unfilled orbital \((5d)\) of tungsten \((W^{6+})\). The band gap energy of the series was found to increase from 3.52 to 3.7 eV with an increase in substitution. The photoluminescence results were calculated at room temperature, while the excitation (PLE) spectra of the series were investigated for different \( \lambda_{cm} \). All samples were found to demonstrate a broad band in the range of 260–320 nm, which is a result of the electronic excitation of the \( O^{2-} \) \((2p)\) orbital to the \( W^{6+} \) \((5d)\) orbital in the \( \text{WO}_6 \) octahedron. The emission (PL) spectra were found to spread over a range of 320–450 nm for double perovskite samples at different \( \lambda_{ex} \).

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References

1. King, G.; Woodward, P. Cation ordering in perovskites. \textit{J. Mater. Chem.} \textbf{2010}, \textit{20}, 5785–5796. [CrossRef]
2. Knapp, M.C.; Woodward, P. A-site cation ordering in AA′BB′O\(_6\) perovskites. \textit{J. Solid State Chem.} \textbf{2006}, \textit{179}, 1076–1085. [CrossRef]
3. Zelewski, S.; Urban, J.M.; Surrente, A.; Maude, D.K.; Kuc, A.B.; Schade, L.; Johnson, R.D.; Dollmann, M.; Nayak, P.K.; Snaith, H.J.; et al. Revealing the nature of photoluminescence emission in the metal-halide double perovskite \( \text{Cs}_2\text{AgBiBr}_6 \). \textit{J. Mater. Chem. C} \textbf{2019}, \textit{7}, 8350–8356. [CrossRef]
4. King, G.; Thimmaiah, S.; Dwivedi, A.; Woodward, P. Synthesis and characterization of new AA′BWO\(_6\) perovskites exhibiting simultaneous ordering of A-Site and B-Site cations. \textit{Chem. Mater.} \textbf{2007}, \textit{19}, 6451–6458. [CrossRef]
5. Xia, Z.; Sun, J.; Du, H.; Chen, D.; Sun, J. Luminescence properties of double-perovskite Sr\(_2\)Ca\(_{1-x}\)Eu\(_x\)Na\(_2\)MoO\(_6\) red-emitting phosphors prepared by the citric acid-assisted sol–gel method. \textit{J. Mater. Sci.} \textbf{2010}, \textit{45}, 1553–1559. [CrossRef]
6. Alsabah, Y.A.; Alsalhi, M.S.; Elbadawi, A.A.; Mustafa, E.M. Influence of Zn\(^{2+}\) and Ni\(^{2+}\) cations on the structural and optical properties of \( \text{Ba}_2\text{Zn}_{1-x}\text{Ni}_x\text{WO}_6 \) \((0 \leq x \leq 1)\) tungsten double perovskites. \textit{J. Alloy. Compd.} \textbf{2017}, \textit{701}, 797–805. [CrossRef]
7. Hao, F.; Stoumpos, C.C.; Cao, D.H.; Chang, R.P.H.; Kanatzidis, M.G. Lead-free solid-state organic-inorganic halide perovskite solar cells. \textit{Nat. Photon.} \textbf{2014}, \textit{8}, 489–494. [CrossRef]
8. Qin, P.; Tanaka, S.; Ito, S.; Tetreault, N.; Manabe, K.; Nishino, H.; Nazeeruddin, M.K.; Grätzel, M. Inorganic hole conductor-based lead halide perovskite solar cells with 12.4% conversion efficiency. *Nat. Commun.* 2014, 5, 3834. [CrossRef]

9. Schaak, R.E.; Mallouk, T.E. Prying apart Ruddlesden–Popper phases: Exfoliation into sheets and nanotubes for assembly of perovskite thin films. *Chem. Mater.* 2000, 12, 3427–3434. [CrossRef]

10. Uma, S.; Raju, A.R.; Gopalakrishnan, J. Bridging the Ruddlesden–Popper and the Dion–Jacobson series of layered perovskites: Synthesis of layered oxides, A$_{2-x}$La$_2$Ti$_{3-x}$Nb$_x$O$_{10}$ (A = K, Rb), exhibiting ion exchange. *J. Mater. Chem.* 1993, 3, 709–713. [CrossRef]

11. Daniels, L.M. *Structures and Properties of Perovskites and Pyrochlores from Hydrothermal Synthesis*; University of Warwick: Coventry, UK, 2015.

12. Depianti, J.B.; Orlando, M.; Cavichini, A.; Corrêa, H.P.S.; Rodrigues, V.A.; Passamai, J.L.; O Piedade, E.L.; Belich, H.; Medeiros, E.F.; De Melo, F.C.L. Structural and magnetic investigation of Ca$_2$MnReO$_6$ doped with Ce. *Cerâmica* 2013, 59, 262–268. [CrossRef]

13. Serrate, D.; De Teresa, J.M.; Ibarra, M.R. Double perovskites with ferromagnetism above room temperature. *J. Phys. Condens. Matter* 2006, 19, 023201. [CrossRef]

14. Alsabah, Y.A.; Elbadawi, A.A.; Mustafa, E.M.; Siddig, M.A. The effect of replacement of Zn$^{2+}$ cation on the structural properties of Ba$_2$Zn$_{1-x}$Ni$_x$WO$_6$ double perovskite oxides (X = 0, 0.25, 0.50, 0.75, 1). *J. Mater. Sci. Chem. Eng.* 2016, 4, 61.

15. Bugaris, D.E.; Hodges, J.; Huq, A.; Løy, H.-C.Z. Crystal growth, structures, and optical properties of the cubic double perovskites Ba$_2$MgWO$_6$ and Ba$_2$ZnWO$_6$. *J. Solid State Chem.* 2011, 184, 2293–2298. [CrossRef]

16. Manoun, B.; Igartua, J.M.; Lazor, P. High temperature Raman spectroscopy studies of the phase transitions in Sr$_2$NiWO$_6$ and Sr$_2$MgWO$_6$ double perovskite oxides. *J. Mol. Struct.* 2010, 971, 18–22. [CrossRef]

17. Colis, S.; Pourroy, G.; Panissod, P.; Mény, C.; Dinia, A. Correlation between magnetic properties and nuclear magnetic resonance observations in Sr$_2$FeMoO$_6$ double perovskite. *J. Magn. Magn. Mater.* 2004, 272–276, 2018–2020. [CrossRef]

18. Jose, R.; John, A.M.; James, J.; Nair, K.; Kurian, K.; Koshy, J. Superconducting Bi(2223) films (TC(0) = 110 K) by dip-coating on Ba$_2$LaZrO$_{3.5}$: A newly developed perovskite ceramic substrate. *Mater. Lett.* 1999, 41, 112–116. [CrossRef]

19. Zhu, H.; Fang, M.; Huang, Z.; Min, X.; Chen, K.; Guan, M.; Tang, C.; Zhang, L.; Wang, M. Novel chromium doped perovskites A$_2$ZnTiO$_6$ (A = Pr, Gd): Synthesis, crystal structure and photocatalytic activity under simulated solar light irradiation. *Appl. Surf. Sci.* 2017, 393, 348–356. [CrossRef]

20. Gandhi, A.; Keshri, S. Microwave dielectric properties of double perovskite ceramics. *Ceram. Int.* 2015, 41, 3693–3700. [CrossRef]

21. Lan, C.; Zhao, S.; Xu, T.; Ma, J.; Hayase, S.; Ma, T. Investigation on structures, band gaps, and electronic structures of lead free La$_2$NiMnO$_6$ double perovskite materials for potential application of solar cell. *J. Alloy. Compd.* 2016, 655, 208–214. [CrossRef]

22. Gateshki, M.; Igartua, J.M. Crystal structures and phase transitions of the double-perovskite oxides Sr$_2$CaWO$_6$ and Sr$_2$MgWO$_6$. *J. Phys. Condens. Matter* 2004, 16, 6639. [CrossRef]

23. Khalyavin, D.D.; Han, J.; Senos, A.M.; Mantas, P.Q. Synthesis and dielectric properties of tungsten-based complex perovskites. *J. Mater. Res.* 2003, 18, 2600–2607. [CrossRef]

24. Reddy, M.P.; Zhou, X.; Jing, L.; Huang, Q. Microwave sintering, characterization and magnetic properties of double perovskite La$_2$CoMnO$_6$ nanoparticles. *Mater. Lett.* 2014, 132, 55–58. [CrossRef]

25. Faik, A.; Igartua, J.M.; Pizarro, J.L. Synthesis, structures and temperature-induced phase transitions of the Sr$_2$Cd$_{1-x}$Ca$_x$WO$_6$ (0 ≤ x ≤ 1) double perovskite tungsten oxides. *J. Mol. Struct.* 2009, 920, 196–201. [CrossRef]

26. Chen, C.; Zhang, H.; Zhang, X.X.; Wang, X.C. Antibacterial and absorbent acrylonitrile-vinylidene chloride copolymer fibres. *J. Text. Inst.* 2010, 101, 128–134. [CrossRef]

27. Grothe, H.; Tizek, H.; Waller, D.; Stokes, D.J. The crystallization kinetics and morphology of nitric acid trihydrate. *Phys. Chem. Chem. Phys.* 2006, 8, 2232–2239. [CrossRef]

28. Kavitha, V.T.; Jose, R.; Ramakrishna, S.; Wariar, P.R.S.; Koshy, J. Combustion synthesis and characterization of Ba$_2$NdSbO$_6$ nanocrystals. *Bull. Mater. Sci.* 2011, 34, 661–665. [CrossRef]

29. Wei, H.-J.; Xing, D.; Wu, G.-Y.; Jin, Y.; Gu, H.-M. Optical properties of human normal small intestine tissue determined by Kubelka-Munk method in vitro. *World J. Gastroenterol.* 2003, 9, 2068–2072. [CrossRef]
30. Elbadawi, A.A.; Yassin, O.; Siddig, M.A. Effect of the cation size disorder at the A-Site on the structural properties of SrAFeTiO$_6$ double perovskites (A = La, Pr or Nd). J. Mater. Sci. Chem. Eng. 2015, 3, 21–29.
31. Manoun, B.; Ezzahi, A.; Benmokhtar, S.; Ider, A.; Lazor, P.; Bih, L. X-ray diffraction and Raman spectroscopy studies of temperature and composition induced phase transitions in Ba$_{2-x}$Sr$_x$ZnWO$_6$ (0 ≤ x ≤ 2) double perovskite oxides. J. Alloy. Compd. 2012, 533, 43–52. [CrossRef]
32. Zhou, Q.; Kennedy, B.J.; Elcombe, M.M. Composition and temperature dependent phase transitions in Co–W double perovskites, a synchrotron X-ray and neutron powder diffraction study. J. Solid State Chem. 2007, 180, 541–548. [CrossRef]
33. Mostafa, M.; Ata-Allah, S.; Youssef, A.; Refai, H. Electric and AC magnetic investigation of the manganites La$_{0.7}$Ca$_{0.3}$Mn$_{0.96}$In$_{0.04x}$O$_3$; (0.0 ≤ x ≤ 1.0). J. Magn. Magn. Mater. 2008, 320, 344–353. [CrossRef]
34. Elbadawi, A.; Yassin, O.; Gismelseed, A.A. Effect of the internal pressure and the anti-site disorder on the structure and magnetic properties of ALaFeTiO$_6$ (A = Ca, Sr, Ba) double perovskite oxides. J. Magn. Magn. Mater. 2013, 326, 1–6. [CrossRef]
35. Rodrigues, J.; Bezerra, D.; Hernandes, A. Calculation of the optical phonons in ordered Ba$_2$MgWO$_6$ perovskite using short-range force field model. J. Raman Spectrosc. 2018, 49, 1822–1829. [CrossRef]
36. Diao, C.-L. First-principle calculation and assignment for vibrational spectra of Ba (Mg 1/2 W 1/2) O 3 microwave dielectric ceramic. J. Am. Ceram. Soc. 2013, 96, 2898–2905. [CrossRef]
37. Xiao, N.; Shen, J.; Xiao, T.; Wu, B.; Luo, X.; Li, L.; Wang, Z.; Zhou, X.-J. Sr$_2$CaW$_x$Mo$_{1-x}$O$_6$:Eu$^{3+}$, Li$^+$: An emission tunable phosphor through site symmetry and excitation wavelength. Mater. Res. Bull. 2015, 70, 684–690. [CrossRef]
38. Xu, D.; Yang, Z.; Sun, J.; Gao, X.; Du, J. Synthesis and luminescence properties of double-perovskite white emitting phosphor Ca$_3$WO$_6$:Dy$^{3+}$. J. Mater. Sci. Mater. Electron. 2016, 27, 8370–8377. [CrossRef]
39. Chen, F.; Zeng, G.; Yang, Q.; Li, X.; Zeng, G. Facile synthesis of visible-light-active BiOI modified Bi$_2$MoO$_6$ photocatalysts with highly enhanced photocatalytic activity. Ceram. Int. 2016, 42, 2515–2525. [CrossRef]
40. Kittel, C. Introduction to solid state physics. Am. J. Phys. 1967, 35, 547–548. [CrossRef]