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Chalcogenide perovskites $BaTi(OS)_3$ with band gap in the optimal Shockley-Queisser range

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ABSTRACT

In the constant search for more efficient and economical alternatives to renewable energy, perovskite-based solar cells have emerged as a promising technology in the field of solar energy. Among them, chalcogenide perovskites have gained considerable attention because of their unique properties and potential to overcome some of the limitations associated with traditional solar cell materials. In this study, a perovskite compound $BaTi(O_{1-x}S_x)_3$ was synthesized by sulfiding barium titanate ($BaTiO_3$) by heat treatment in a reactive atmosphere of CS_2 , using three different temperatures: 600, 700 and 800 °C. The structural, vibrational, and optical properties of the synthesized samples were determined as a function of the treatment temperature. Elemental analysis showed a sulfur content between 14.6 % and 20.2 %, depending on the treatment temperature. XRD showed a transition from tetragonal to hexagonal perovskite with increased sulfur concentration, recording interplanar distances of 4.069 Å, 3.366 Å and 2.453 Å in the planes (101), (110) and (201), with lattice parameters $a=6.73$ Å, $c=5.793$ Å and a crystallite size of 258.96 Å. IR spectroscopy identified predominant S-O bonds. The UV-Vis analysis indicated a reduction in the band gap from 1.53 eV to 1.47 eV as the temperature increased.

Introduction

The variety of materials for solar cells has been the subject of research for the last 50 years. This is because since 1980, scientists have been tasked with searching for alternative sources of energy generation that are environmentally friendly, avoiding the continued generation of energy by burning fossil fuels and thereby counteracting radical changes in the climate of the planet due to global warming [1-5]. Among the different photovoltaic technologies, perovskite solar cells have been the focus of attention because of their high efficiency, low manufacturing cost, and abundant elements on Earth. Interest in this technology has increased rapidly since 2009, when a PCE (Power Conversion Efficiency) of 3.8% was achieved. In 2016, the PCE had reached 22.1%, in 2019 it was 25%, and now it is 27%, according to the NREL efficiency record logs [6-11].

Perovskite cells have several advantages over traditional solar cells, such as silicon. First, the materials used in perovskite cells are less expensive and easier to produce than silicon [5,6,12-15]. These materials exhibit intrinsic properties including high absorption coefficient, tunable band gap, large carrier diffusion, ambipolar carrier transport capability, and high carrier mobility [8,16,17]. In addition, they show other notable characteristics such as dielectric, optical, ferroelectric, superconducting, piezoelectric, multiferroic, and photocatalytic properties [18-22]. As a result of all the positive aspects, perovskite solar cells could be reproduced on an industrial scale and become a real competitor to silicon cells [12-14,23]. Of the different groups of perovskites, those with the highest conversion efficiency records are organic-inorganic metal halide perovskites. However, they also have an intrinsic problem that limits their long-term functionality. This problem stems from the fact that hybrid lead halide perovskite (e.g. $CH_3NH_3PbI_3$) experiences chemical and structural instability because it is sensitive to humidity and temperature cycles, causing degradation, loss of efficiency, and in some cases structural changes over time. Another important problem is the known toxicity of lead (Pb), a heavy metal that can be harmful to human health and the environment [24-29]. One line of research to address this issue is the development of more stable perovskites that meet the requirements and properties for use in perovskite solar cells.

During the past five years, many reports have proposed an alternative family of perovskites, based on metal chalcogenides, which have the ideal characteristics to replace halide perovskites in photovoltaic applications [24,30-34]. Chalcogenide perovskites are ternary compounds that follow the chemical formula ABX_3 , where A and B are two cations and X is an anion [35]. For cation A, the proposed elements are Ba, Sr, or Ca, while for cation B, Ti, Zr, or Hf are proposed. Finally, X can be sulfur, selenium [36], combinations of these elements, or combinations with oxygen, so they actually represent an enormous

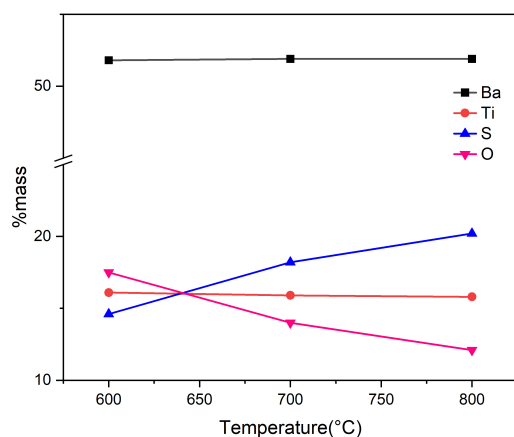


Figure 1. Mass percentage relationship of sulfur and oxygen with temperature

number of possible metal chalcogenide perovskites [19,37-41]. The vast majority of published reports are computational studies that predict optical, structural, and electronic characteristics that provide high thermodynamic and atmospheric stability. However, contrary to this large number of theoretical reports, experimental reports are still very limited, making experimental verification necessary [41-44].

Given this situation, experimental research is needed to determine the optimal properties of this compound and assess its possible applications. With this field of experimental research in full swing, this article presents a systematic study of the synthesis of chalcogenide perovskite $BaTi(O_{1-x}S_x)_3$. This compound was theoretically proposed in 2022[47] and experimentally demonstrated in 2023[18], revealing excellent optical and structural properties. However, the previous study only analyzed the effect of sulfidation time while maintaining a constant temperature. After this, there are no new experimental reports that expand knowledge about the properties and characteristics of this compound when other synthesis parameters, such as temperature, are varied, nor do they testing its potential as a sustainable next-generation photovoltaic absorber.

Results

Elemental composition and stoichiometry

The elemental composition was obtained by energy dispersive X-ray fluorescence spectroscopy (EDX-RF). The percentages of mass of the elements present in the $BaTi(O_{1-x}S_x)_3$ compounds at various temperatures ranged from 14.6 to 20.2% sulfur. The percentages measured for the perovskite treated at 600 °C were 14.6%, for the 700 °C it was 18.2% and for the 800 °C it was 20.2%. Obtaining the highest percentage of sulfur for the sample treated at the highest temperature. Considering that the ideal mass percentage of sulfur in $BaTiS_3$ perovskite is 34.18%, the measured mass percentages in the three samples were lower. These percentages allowed us to determine both the amount of oxygen remaining and the stoichiometries of the resulting compounds, which were $BaTi(O_{0.5}S_{0.5})_3$, $BaTi(O_{0.4}S_{0.6})_3$, $BaTi(O_{0.3}S_{0.7})_3$, respectively. The relationship between temperature and the percentages of mass of both oxygen and sulfur is shown in Figure 1. It is evident that as the treatment temperature increases, there is a noticeable increase in the mass percentage of sulfur, whereas the mass percentage of oxygen decreases. This trend highlights the dynamic interaction between temperature and elemental composition during the sulfide process. The increased sulfur content suggests a higher percentage of sulfur incorporation into the compound structure at elevated temperatures, possibly because of enhanced sulfur diffusion or more favorable reaction kinetics.

Crystalline structure

The crystal structure was determined using the results obtained from X-ray diffraction (XRD) characterization. Figure 2 shows the diffractograms of the samples $BaTi(O_{1-x}S_x)_3$ treated at 600, 700, and 800 °C, as well as the $BaTiO_3$ perovskite diffractogram, used as precursor material. All diffractograms were acquired under the same conditions, using a range of 20 to 50 degrees in 2θ . The diffractogram of commercial $BaTiO_3$ powder shows several diffraction peaks centered at 2θ equal to 22.20 °, 31.58 °, 38.94 °, and 44.89 °, which, according to Wahba et al. (2025) correspond respectively to the (100), (110), (111), and (002) planes of the tetragonal perovskite structure ($P4mm$)[45- 49]. In the diffractogram of the perovskite $BaTi(O_{0.5}S_{0.5})_3$ (600 °), diffraction peaks associated with two different crystal structures of the perovskite can be observed.

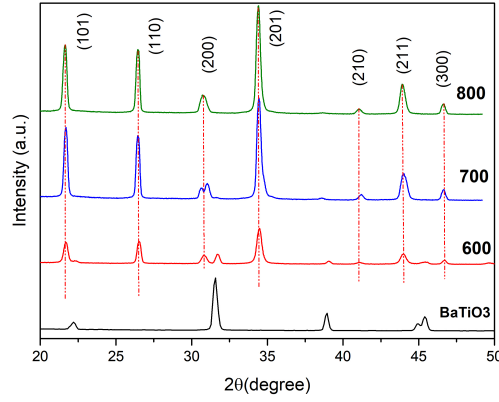


Figure 2. Diffractograms for the synthesized perovskites

Table 1. Interplanar distances, lattice constants and crystallite size

Temperature	Perovskite	$d_{(101)}$ (Å)	$d_{(110)}$ (Å)	$d_{(201)}$ (Å)	a (Å)	c (Å)	D (Å)
600	$BaTi(O_{0.5}S_{0.5})$	4.09	3.36	2.59	6.72	5.78	240.82
700	$BaTi(O_{0.4}S_{0.6})$	4.09	3.37	2.61	6.74	5.80	251.18
800	$BaTi(O_{0.3}S_{0.7})$	4.11	3.37	2.61	6.74	5.80	264.88
average value		4.096	3.366	2.453	6.733	5.793	258.96

On the one hand, the maximum centered at 2θ equal to 31.67° and 39.06° correspond respectively to the (110) and (111) planes of the tetragonal structure of $BaTiO_3$, while the peaks centered at 2θ equal to 21.69° , 26.52° , 30.79° , 34.48° , 43.99° and 46.73° are respectively associated with the (101), (110), (200), (201), (211) and (300), characteristic of the hexagonal structure ($P6_3/mmc$) of $BaTiS_3$ [40]. For the diffractogram of the sample $BaTi(O_{0.4}S_{0.6})_3$ (700°), the peaks are repeated at $2\theta = 21.69^\circ$, 26.42° , 30.67° , 31.02° , 34.41° , 41.09° , 43.90° , 46.66° associated with (101), (110), (200), (002), (201), (210), (211) and (300) of the hexagonal structure. Unlike in the previous case, the signal from the tetragonal perovskite structure is almost imperceptible, with only a tiny residual peak between $39\text{--}40^\circ$ attributable to it. Finally, for the diffractogram of the $BaTi(O_{0.3}S_{0.7})_3$ perovskite (synthesized at 800°), there are no longer any peaks associated with the planes of $BaTiO_3$, and the seven peaks centered at $2\theta = 21.65^\circ$, 26.44° , 30.71° , 34.41° , 41.09° belonging to the planes (101), (110), (200), (201), (210), (211), (300) are characteristic of the typical hexagonal structure of $BaTiS_3$ [50–52]. In the three diffractograms of the sulfide perovskite samples, the main peak is associated with the (201) direction of the hexagonal structure. We therefore see that the gradual replacement of oxygen by sulfur and the increase in sulfidation temperature induce a gradual transition from the tetragonal to the hexagonal structure as the synthesis temperature increases. Thus, the sample synthesized at a higher temperature only presents the hexagonal structure of the perovskite, without combined phases. An additional feature observed in the diffractograms is the difference in the overall intensity of the diffraction peaks, the lowest intensity being that synthesized at 600°C compared to those made at 700°C and 800°C . The low intensity in the perovskite synthesized at 600° indicates structural disorder or poor crystallization. In sulfur perovskites at 700° and 800° , the intensities are higher, indicating an improvement in structural order due to the increase in temperature, which favors the formation of more defined structures.

With these results, the crystallographic parameters of the samples were determined and are shown in the table 1. To determine the interplanar distances the Bragg's law $2d\sin\theta = n\lambda$, was used to subsequently obtain the lattice constants, and finally the Scherrer equation $\beta = \frac{K\lambda}{D\cos\theta}$, with Scherrer's counter $K = 0.9$ and the Cu length k_α is equal to $0.15406\text{ \AA}$ was used to determine the crystallite size. In Table 1, the calculated values for the crystallographic parameters of each of the synthesized samples are presented. In general, the interplanar distances remain constant with a mean value of $4.096\text{ \AA}$ for the in-plane interplanar distance (101), $3.366\text{ \AA}$ for the interplanar distance (110) and $2.453\text{ \AA}$ for the interplanar distance (201). Overall, the lattice counts are conserved with a mean value for $a = 6.733\text{ \AA}$ and for $c = 5.793\text{ \AA}$. The mean value of the crystallite size is $258.96\text{ \AA}$. In the literature it was discovered with the computational implementation of DFT (Liu et al. 2022) and experimental (Biglar et al. 2017) that the lattice counters are for $a = 6.84\text{ \AA}$ and for $c = 6.00\text{ \AA}$ for $BaTiS_3$, which compared to the calculated ones are considerably close, so our structure tends to hexagonal regardless of temperature.

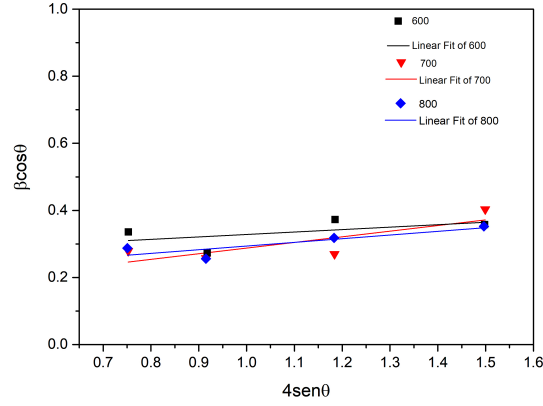


Figure 3. Lattice strain of $BaTi(O_{1-x}S_x)_3$ perovskite structures

Table 2. Lattice strain parameters in $BaTi(O_{1-x}S_x)_3$ perovskites

Temperature	Perovskite	ϵ
600	$BaTi(O_{0.5}S_{0.5})_3$	0.07293
700	$BaTi(O_{0.4}S_{0.6})_3$	0.16814
800	$BaTi(O_{0.3}S_{0.7})_3$	0.10953

Williamson-Hall analysis

To calculate the lattice strain parameter in the three samples obtained, we apply the Williamson-Hall analysis, taking the angles of the characteristic peak positions and the linewidth of the peaks and substituting them in equation $\beta = \frac{K\lambda}{D\cos\theta} + 4\epsilon\tan\theta$ gives the strain values. Figure 3 has a plot of the four main peaks of the three $BaTi(O_{1-x}S_x)_3$ perovskites, plotted $4\epsilon\sin\theta$ versus $\beta\cos\theta$ with their linear fit, which are the lines to the calculated data, which are the points 2.

In a structure with a certain interplanar distance d , undergoing treatment such as rapid cooling, heat treatment, plastic deformation, or thin film deposition can cause stresses in the structure, causing the interplanar distance to increase or decrease, giving a d' . This results in a difference between the original interplanar distance and the modified interplanar distance $\Delta d = d' - d$, so that when the stress parameter $\epsilon = 0$, then $\delta d = 0$, which means that the structure was not stressed; when $\epsilon > 0$, then $\delta d > 0$, which means that the network is stretched in the direction of d ; when $\epsilon < 0$, then $\delta d < 0$, therefore the network contracts in the direction of d . The resulting stress parameters in Table 2 tend to zero, from which it can be deduced that the structures of $BaTi(O_{1-x}S_x)_3$ have almost zero stress. These parameters were determined using the slope of the straight lines shown in Figure 3.

Molecular bond bands

The FTIR technique was used to obtain the molecular bond bands. Figure 4 shows the FTIR spectrum of the $BaTi(O_{1-x}S_x)_3$ perovskite samples at different treatment temperatures, where the intensity is normalized. Four main bands appear in all three samples. In the sample $BaTi(O_{0.5}S_{0.5})_3$, the molecular absorption bands are centered at the wavenumbers 998.94, 1065.96, 1105.97, 1132.01, and 1188.41 cm^{-1} , the molecular bands associated with the sample $BaTi(O_{0.4}S_{0.6})_3$ are located at 993.64, 1071.26, 1105.97, 1132.49 and 1185.52, and the bands related to the $BaTi(O_{0.3}S_{0.7})_3$ sample are centered at 993.24, 1071.26, 1105.49, 1132.01, and 1190.82 cm^{-1} . These five bands in each perovskite correspond to the molecular bonds $(S_2O_3)^{-2}$, $N - TiO_2$, $S - O$, and $(S_2O_4)^{-2}$, respectively. According to various authors such as Rubinson K.A et al. 2000 [53], the vibration of $(S_2O_3)^{-2}$ can appear in the range of 960-1000 cm^{-1} and 1040-1100 cm^{-1} , $N - TiO_2$ appears at approximately 1105 cm^{-1} , the $S - O$ appears in the range of 1083-1190 cm^{-1} , and the $(S_2O_4)^{-2}$ appears in the range of 1175-1195 cm^{-1} .

Vibrational Properties

Raman Vibrational Modes

Raman spectroscopy was used to determine the molecular vibration modes of $BaTi(O_{1-x}S_x)_3$ perovskites. The hexagonal crystal structure of $BaTiS_3$ belongs to the space group 186, denoted as P63mc [54,55]. The optical modes that can exist in this hexagonal structure are given by the equation $\Gamma_{opt} = A_1 + E_1 + 2E_2 + 2B_1$ where the modes A_1 and E_1 are polar modes, with

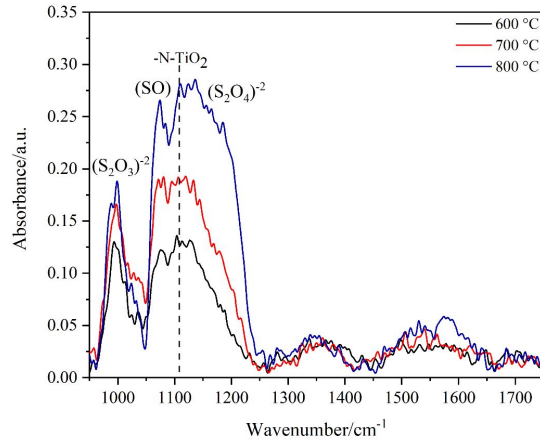


Figure 4. FTIR absorption spectrum

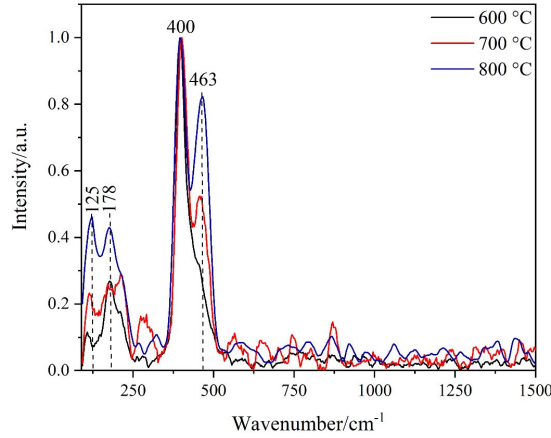


Figure 5. Raman shifts of $BaTi(O_{1-x}S_x)_3$ perovskites synthesized at 600, 700 and 800°C

transverse optical splitting (A_{1T} and E_{1T}) and longitudinal optical splitting (A_{1L} and E_{1L}), while the modes E_2 are non-polar modes and consist of two modes with low and high frequencies called E_2^{low} and E_2^{high} , respectively. All these modes are known as active modes. Finally, there are two modes B_1 that are silent. Figure 5 shows the Raman bands obtained for perovskites $BaTi(O_{1-x}S_x)_3$. For the three curves presented, four Raman modes are found at 125, 178, 400, and 463 cm^{-1} .

According to the literature reported to date, the band found at 125 cm^{-1} could be associated with the A_{1T} mode, the band at 178 cm^{-1} could correspond to the E_2 mode, while the band centered at 400 cm^{-1} could be identified as the A_{1L} mode. Until now, results are only available for $BaTiS_3$. To date, there are no theoretical or experimental results for the $BaTi(O_{1-x}S_x)_3$ system, so it can be said that this is the first time these bands have been assigned. Finally, the band observed at 463 cm^{-1} could correspond to E_2^{high} .

Optical properties

Absorption bands

To find the absorption bands of the perovskites $BaTi(O_{1-x}S_x)_3$, 1×10^{-3} grams of the perovskites were dissolved in ethyl alcohol. Figure 6 shows the absorption spectra obtained using UV-Vis spectroscopy. Several resulting bands stand out in these spectra because of their intensity, particularly those at wavelengths greater than 900 nm. However, these bands are due to the absorption of the ethyl alcohol used to disperse the perovskite. The bands associated with perovskite in this region are tested.

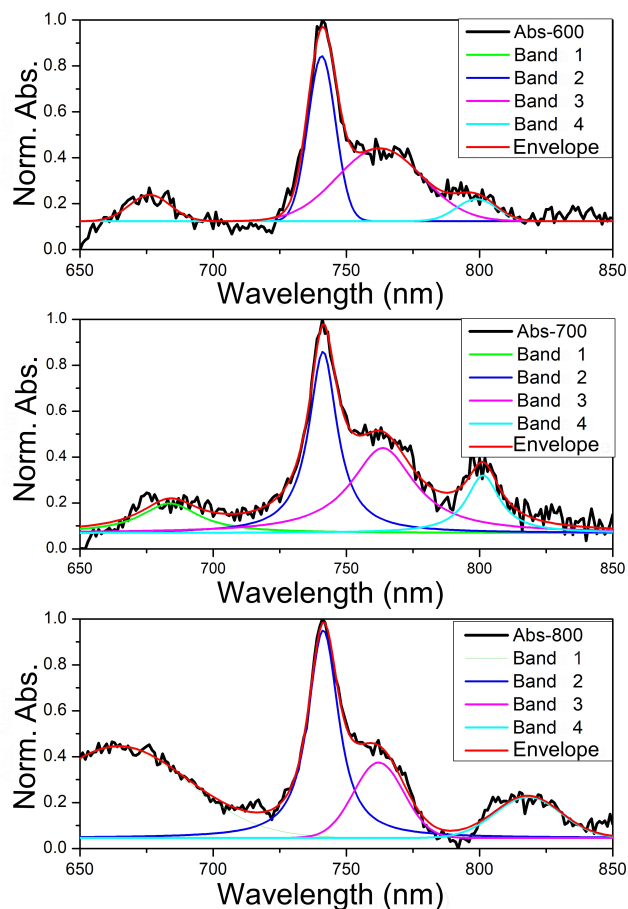


Figure 6. Absorption spectra of $BaTi(O_xS_{1-x})_3$ perovskites as a function of the normalized synthesis temperature

The study range will be limited to the region of the spectrum between 650 and 850 nm, where the band gap of this type of perovskite is expected to occur.

The three graphs shown in Figure 6 show four absorption bands whose centers are located at 675, 741, 763 and 793 nm for the spectrum of the perovskite synthesized at 600 °C. Similarly, the centers of the four absorption bands for the perovskite synthesized at 700 °C are located at 683, 741, 762 and 802 nm, respectively. Finally, for the perovskite prepared at 800 °C, the respective positions of the band centers are found at 670, 740, 763 and 818 nm. Both the band centered at 741 nm and the band at 763 nm (the most intense bands in the three spectra) are associated with the absorption of ethyl alcohol and will therefore not be considered in the rest of the analysis. As can be seen, the position of the fourth absorption band, which shifts to longer wavelengths as the temperature increases, is one of the bands that is undoubtedly associated with perovskite $BaTi(O_{1-x}S_x)_3$. According to the EDXRF results, the samples showed a higher percentage of sulfur as the synthesis temperature increased, so the shift observed in this band reflects a direct effect of the increase in the percentage of sulfur (decrease in the percentage of oxygen) in the stoichiometry of the samples.

Band Gap

To find the band gap energy of these samples, the Tauc method was applied, using the absorption spectra, and taking into account the Lambert-Beer equation, the absorption coefficient was obtained. For this calculation, it was assumed that the thickness of the analyte used to make the measurement is $l = 1$ cm, therefore $\alpha = 2.302 \text{ Acm}^{-1}$. To calculate the energy, equation $E = h\nu = \frac{hc}{\lambda}$ was used, substituting Planck's constant $h = 6.625 \times 10^{-34}$ Js, the speed of light $c = 2.998 \text{ m/s}$, and making the appropriate unit conversions, we obtain $E = \frac{1240}{\lambda} \text{ eV}$. For $\gamma = 2$ for the allowed transitions, the Tauc curves were determined for each of the synthesized perovskites, which are shown in Figure 7.

Extrapolating the straight line that fits the edge of the absorption band in the Tauc curves (Figure 7) shows that the band

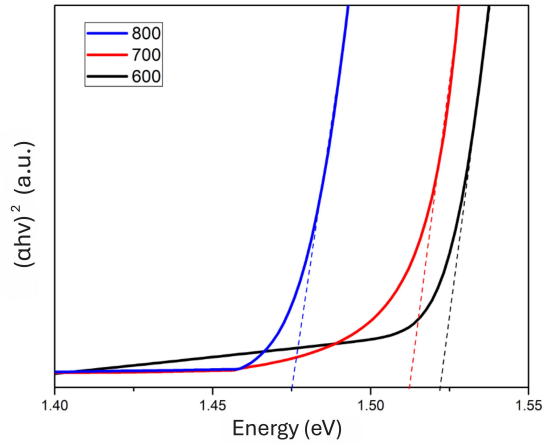


Figure 7. Tauc curves of $BaTi(O_xS_{1-x})_3$ perovskites with their respective band gap

gaps of the three synthesized perovskites are as follows: the perovskite $BaTi(O_{0.5}S_{0.5})_3$ synthesized at 600 °C has a band gap of 1.53 eV, the perovskite $BaTi(O_{0.4}S_{0.6})_3$ at 700 °C has a band gap of 1.51 eV, and the perovskite $BaTi(O_{0.3}S_{0.7})_3$ synthesized at 800 °C has a band gap of 1.47 eV. Compared to the band gap of $BaTiO_3$ (precursor material), which is 3.2 eV, it decreased by approximately 1.73 eV.

When plotting the forbidden band width as a function of temperature and as a function of sulfur percentage, as shown in Figure 8, it can be seen that there is a relation between temperature and the band gap, or between the percentage of sulfur and the band gap of perovskites $BaTi(O_{1-x}S_x)_3$. It can be observed that this relationship is very close to being linear. Therefore, to increase the range of analysis and given that the objective of this study is to determine the viability of using perovskite in photoelectric devices, a point was added based on the results of Gomez-Rosales et al. 2023, with the temperature and sulfur percentage values associated with an ideal band gap of 1.3 eV. To achieve maximum efficiency in solar cells. The band gap obtained in the samples synthesized at 700 and 800 °C is revealed to fit linearly with the predicted value for the perovskite $BaTi(O_{0.09}S_{0.91})_3$ theorized as ideal. The same relation is observed between the percentage of sulfur and the band gap (black line) in Figure 8. In both cases, it can be said that the forbidden bandwidth decreases with a higher sulfur concentration in perovskites $BaTi(O_{1-x}S_x)_3$, which is obtained as the synthesis temperature increases.

Discussion

The study of the stoichiometry of $BaTi(O_{1-x}S_x)_3$ perovskites in relation to temperature determined that there is an increase in sulfur ranging from 14.6% by mass to 20.2% by mass, yielding compounds with an anion formed of oxygen and sulfur, with different numbers of atoms, in the compound formed at 600 °C, there are 0.5 oxygen atoms and 0.5 sulfur atoms, while in the compound formed at 800 °C, there are 0.3 oxygen atoms and 0.7 sulfur atoms, thus demonstrating that at higher temperatures, there is more sulfur bonding in the compound and a lower percentage of oxygen. The analysis of the crystal structure of these perovskites, with respect to temperature, presented diffractograms that showed that as the temperature increased, their peaks became wider and more intense, so much so that in the region 30 to 32.5 °, an extra peak is no longer visible and tends to shift to the right, given that the structure of $BaTiO_3$ with which it started is lost, changing to the typical hexagonal structure of $BaTiS_3$. The impact of the increase in temperature on the lattice constants, interplanar distances, and grain size was also reflected. The average values of these crystalline parameters are $d_{101} = 4.096$ Å, $d_{110} = 3.366$ Å, $d_{201} = 2.453$ Å, $a = 6.733$ Å, $c = 5.793$ Å, and $D = 258.96$ Å, close to those of $BaTiS_3$. It was also found that the lattice of $BaTi(O_{1-x}S_x)_3$ perovskites is not stressed, as the stress parameters are too small and the stress can therefore be ignored. Therefore, it can be concluded that the increased treatment of $BaTi(O_{1-x}S_x)_3$ perovskites and their increased sulfur bonding improve their structure and properties. The study of the vibrational properties of the molecular bond bands of $BaTi(O_{1-x}S_x)_3$ perovskites shows molecular bands that correspond to the interaction of sulfur with oxygen, such as $(S_2O_3)^{-2}$, $S-O$, $(S_2O_4)^{-2}$. This study also indicates that there is a deformed hexagonal structure as a result of an increase in the size of the atoms with the replacement of oxygen by sulfur. Furthermore, it is consistent with what we see in the other two previous analyzes, namely that as the synthesis temperature increases, so does the percentage of sulfur in the perovskites, since in the spectra shown in Figure 4, the one with a temperature higher than 800 °C expands due to the increase in sulfur. Similarly, the molecular vibrational modes corresponding to the bands

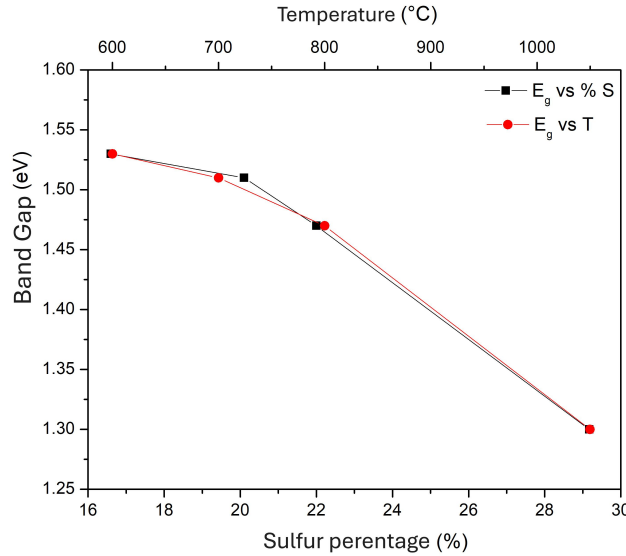


Figure 8. Linear relation between sulfur percentage, Band Gap and synthesis temperature

125, 178, 400, 463 cm^{-1} were obtained for the three perovskites $\text{BaTi}(\text{O}_{1-x}\text{S}_x)_3$, which correspond to the vibrational modes A_{1T} , E_2 , and A_{1L} , which are characteristic of BaTiS_3 . However, the 463 cm^{-1} band does not correspond to the vibrational system of BaTiS_3 or BaTiO_3 , but there are still no studies demonstrating the vibrational behavior of $\text{BaTi}(\text{O}_{1-x}\text{S}_x)_3$. This also confirms that, at high temperatures, higher sulfur concentrations in perovskites improve the vibrational properties. This is consistent with studies of stoichiometry and crystal structure. Tauc's analysis found that the band gap in the samples gradually decreased from 1.53 eV for the 600 °C sample to 1.51 eV for the 700 °C sample and finally to 1.47 eV, in accordance with the increase in the percentage of sulfur present in the samples. This reduction in the band gap has already been explained by several reports that focused on oxysulfide compounds. The valence band in pure oxides is dominated by the O 2p states, but due to the lower electronegativity of sulfur, in oxysulfide and sulfide compounds, it is narrowed by the S 3p states. Then, the band gap is reduced by the generation of a large number of states in the valence shell produced by the 3s and 3p orbitals of sulfur[56,57]. These results show that bandgap engineering is feasible for the $\text{BaTi}(\text{O}_{1-x}\text{S}_x)_3$ compound using the percentage of sulfur as a control. Currently, the narrowing of the band gap has only been experimentally achieved up to 1.47 eV; however, using the theoretical value of pure BaTiS_3 and the experimental values of the four synthesized $\text{BaTi}(\text{O}_{1-x}\text{S}_x)_3$ compounds, an almost linear dependence was found between the band gap and the amount of sulfur present in the $\text{BaTi}(\text{O}_{1-x}\text{S}_x)_3$ perovskite compound.

Conclusion

The stoichiometry of $\text{BaTi}(\text{O}_{1-x}\text{S}_x)_3$ is strongly affected by the synthesis temperature of the said perovskite, so that at higher temperatures a compound with a higher sulfur concentration was obtained. The relation between temperature and sulfur percentage has an approximate linear dependence, making it easily predictable by interpolation or extrapolation of the synthesis temperature required to achieve a given percentage. All synthesized perovskites have the typical hexagonal structure of BaTiS_3 , and the effect of the synthesis temperature is to improve the crystalline quality of the compound, thereby increasing the size of the crystallite, with a stress parameter that can be ignored, meaning that the structure is stress-free. As the synthesis temperature increases, there is an increase in the sulfur concentration in the perovskites and, associated with this, a gradual reduction in the band gap, decreasing from 3.2 to 1.47 eV, which places these perovskites within the ideal energy range for use in perovskite solar cells. Given the properties obtained in this work, it has been verified that the theoretically predicted properties of the chalcogenide perovskite $\text{BaTi}(\text{O}_{1-x}\text{S}_x)_3$ are suitable for proposing the use of these perovskites in applications of photoelectric devices, such as solar cells.

Methods

For the synthesis of $\text{BaTi}(\text{OS})_3$ perovskite, a high-temperature sulfuration process was performed. As precursor material, a Sigma-Aldrich brand BaTiO_3 powder with a particle size $< 3 \mu\text{m}$ and a purity of 99% was used. For the sulfur source, a

reactive atmosphere of argon and CS_2 vapor was utilized. The complete procedure is as follows: Ceramic crucibles containing powdered $BaTiO_3$ were placed in a Fotek MT-48 tubular furnace. As the initial temperature ramp, the furnace controller was set at a temperature of 600 °C. At the same time, a pure argon gas flux was opened at a flow rate of 3 liters per minute (LPM). Once the desired temperature was reached, the tube valve connected to the evaporator bottle that contained 125 ml of CS_2 , which was placed on an electric grill at 35 °C, was opened and held for 4 hours. During this process, the initial argon flow was used as the carrier gas. After this time, the CS_2 valve was closed while maintaining the argon flow; the oven was turned off and the argon flow was kept for two more hours. When the oven reached room temperature, the crucibles with the synthesized $BaTi(O_{1-x}S_x)$ perovskite powder were removed and placed in Petri containers for storage and subsequent characterization. This procedure was repeated for two other synthesis temperatures at 700 °C and 800 °C, respectively.

The elemental composition of the $BaTi(O_{1-x}S_x)$ perovskite powder was measured on the Rigaku EDX-RF equipment model NEX QC+ Quantez. The crystal structure of the synthesized powder was determined by XRD characterization using Bruker D8 ADVANCE ECO equipment, it was performed at room temperature, using Cu $K\alpha$ radiation, with a wavelength of 1.54056 Å. FTIR measurements were performed with a Thermo Scientific Nicolet model IS50 spectrometer to obtain the vibrational bonds present in the perovskite powder. The optical properties of the synthesized samples were determined by UV/Vis measurement with a PerkinElmer Lambda 35 UV/Vis spectrometer.

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Author contributions statement

F.L.G.G., A.I.N.O., and R.G.R. conceived and designed the experiments, performed the experiments, analyzed the results, contributed to the discussion and the drafting of the manuscript; E.O.C. performed the Raman spectroscopy measurements and contributed to data analysis; H.T.H. and J.J.O.S. provided the facilities and experimental equipment, in addition to contributing to the supervision of the work; additionally, J.J.O.S. participated in the conception and design of the experiments and contributed to the discussion, review, and editing of the manuscript; Á.G.D., A.A.O.H. and J.J.A.I. contribute to the discussion of the results and to the review of the final version of the manuscript. All authors read and approved the final version of the manuscript.

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