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Synthesis of $BaHfO_3$ through with reduction of KOH.

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***Abstract*—** In this work will be presented the results obtained in the synthesis and structural and morphological characterization of perovskite oxide Barium Hafnate ($BaHfO_3$) synthesized by the hydrothermal method assisted by microwave (MAH) with two concentrations of potassium hydroxide (KOH). One with concentration of 2.4M which will be called BHO24 and another one of 3.6 M which will be called BHO36, in order to reduce the difference between the amount of reagents (in this case barium chloride and hafnium chloride- $Bacl_2$ and $HfCl_4$) and the amount of mineralizing agent (in this case KOH) used in synthesis through the MAH. The objective of this study is to analyze the possibility of synthesizing a perovskite oxide by MAH with the minimum amount of KOH and to analyze if there is any change in the structure or morphology of the same. To analyze the structural change, the X- ray diffraction (XRD) and to analyze the morphological change was used the characterization technique of scanning electron microscopy (SEM).

Keywords — Concentrations KOH, MAH, Structural change and morphological change.

I. INTRODUCTION

The MAH is a synthesis method consisting of the interaction of electromagnetic radiation in the microwave range with matter [1], being the mechanisms of dipole rotation and ionic conduction responsible for the conversion of radiation energy to heat [2-5], its main advantages are time reduction, process steps and temperature, high purity and reduced operating costs [6-8]. Initially Komarneni [9] studied the effect of microwaves on the crystallization kinetics in hydrothermal synthesis of electronic ceramics and in 1992 they became the pioneers in obtaining perovskite by this method that they called HTMW [10], Rao and collaborators proved the feasibility of the method for several compounds [11].

The synthesis itself consists basically of three steps: dissolution, precipitation and dehydration. In the first step the amounts of the reagents are diluted in distilled and deionized water (dissolution). In the second step the results of the previous step are placed in the reaction cell (precipitation) and in the third one the cell is added to the microwave oven (dehydration). When analyzing works related to this synthesis method, it is verified that the concentration of the mineralizing agent (generally KOH) is much higher than the other reagents as described in the table 1.

Table.1: Reagent concentrations and concentration of mineralizing agent in published works [12-17].

Author	Reagent concentration	Concentration of the mineralizing agent
Moreira	$ZrOCl_2 8H_2O$ and $BaCl_2 2H_2O$ 0.01 M	KOH 6 M
Rafael	Matrix Ba and matrix Zr 0.01054 M	KOH 6M
Zhi Wang	$Bi(NO_3)_3 5H_2O$ and $Fe(NO_3)_3 9H_2O$ 1.2 M	KOH 12 M
Wagner	$CaCl_2 2H_2O$ and $ZrOCl_2 8H_2O$ 0.4 M	NaOH 6 M
Mazzo	$TiO(OH)_2$ and $CaCl_2 2H_2O$ 2 M	KOH 6M
Silva	$TiCl_4$ and $SrCl_2 2H_2O$ 0.2 M	KOH 6M

The insertion of a higher amount of KOH is related to the fact that for formation of the type oxide ABO_3 during a reaction in aqueous solution, a hydrolysis-condensation followed by nucleation-growth is required and a large amount of mineralizing agent is required when a non-

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alkaline precursor is used [18]. In addition, the OH^- groups act as catalysts of the reaction leading to high nucleation rates [19].

On the other [20] shows the synthesis of compound $BaTiO_3$ using TiO_2 and $Ba(OH)_2$ in the proportion of 1 per 1. It is observed that the KOH or NaOH used in MAH are responsible only by the formation of the hydroxides that occurs in the second phase (precipitation) not influencing the third stage (dehydration). Thus the proposal of this research is to verify if it really is necessary to use such a large amount of potassium hydroxide in the synthesis through the microwave radiation. Among the possible oxides that can be obtained, the $BaHfO_3$for study. Papers already published on the $BaHfO_3$demonstrate that it has a cubic structure, and its morphology is reported to be composed of spheres [21-25]. Some of the studied properties of this oxide are luminescence [36-38] and dielectric behavior [29]. In this work, however, only the structural and morphological characteristics will be analyzed.

II. MATERIALS AND METHODS

Compound BHO24 was prepared with 0.4M of $BaCl_2$, 0.4 M of $HfCl_4$ and 2.4 mol of KOH while compound BHO 36 was prepared with the same concentration of $Bacl_2$ and $HfCl_4$ and 3.6 mol KOH. Subsequently, were added to the oven microwave where they were kept for 20 minutes at a temperature of 140 °C with a nucleation rate of 10°C/min. After the synthesis, both were centrifuged at 3500 rpm (for ph reduction) and kept in the oven for 15 hours. With the obtained compound the X-ray diffraction technique was applied, the apparatus D8 ADVANCE BRUKER, with radiation (Cu) of wavelength $\lambda = 1,5418\ \AA$ and the scanning electron microscopy technique was used the microscope of the mark Jeol, model JSM-6610.

III. RESULTS AND DISCUSSION

Both in BHO24 and BHO synthesis36 a white powder was obtained, demonstrating that a large amount is not required to obtain the compound. The two presented diffraction peaks that can be indexed to the cubic phase of the $BaHfO_3$, Fig. 1, being consistent with the crystallographic sheet PDF 24 − 102, with network parameters a = b = c = 8.333 *Å*and space group (Pm-3m).

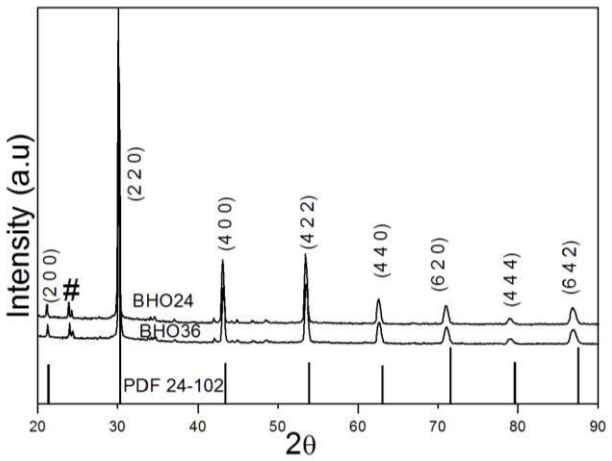

Fig. 1: X-ray diffraction of BHO24 and BHO36.

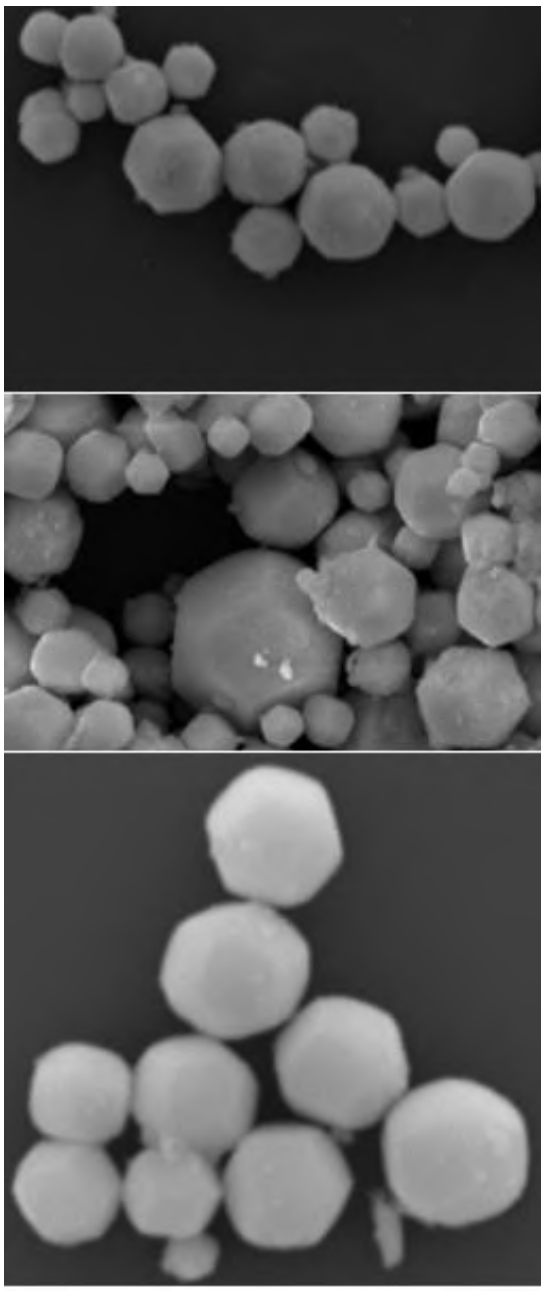

Fig. 2: SEM images of BHO24.

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It is also observed that both have peaks belonging to the secondary phase of barium carbonate ($BaCO_3$) identified by the JCPDS 05−0628 like Orthorhombic Witherite. The appearance of this phase is understandable since the $BaHfO_3$ moisture is susceptible and has already been found in other works [30, 27-28]. To analyze the morphological aspect, the characterization of scanning electron microscopy – SEM- Fig. 2 and Fig. 3.

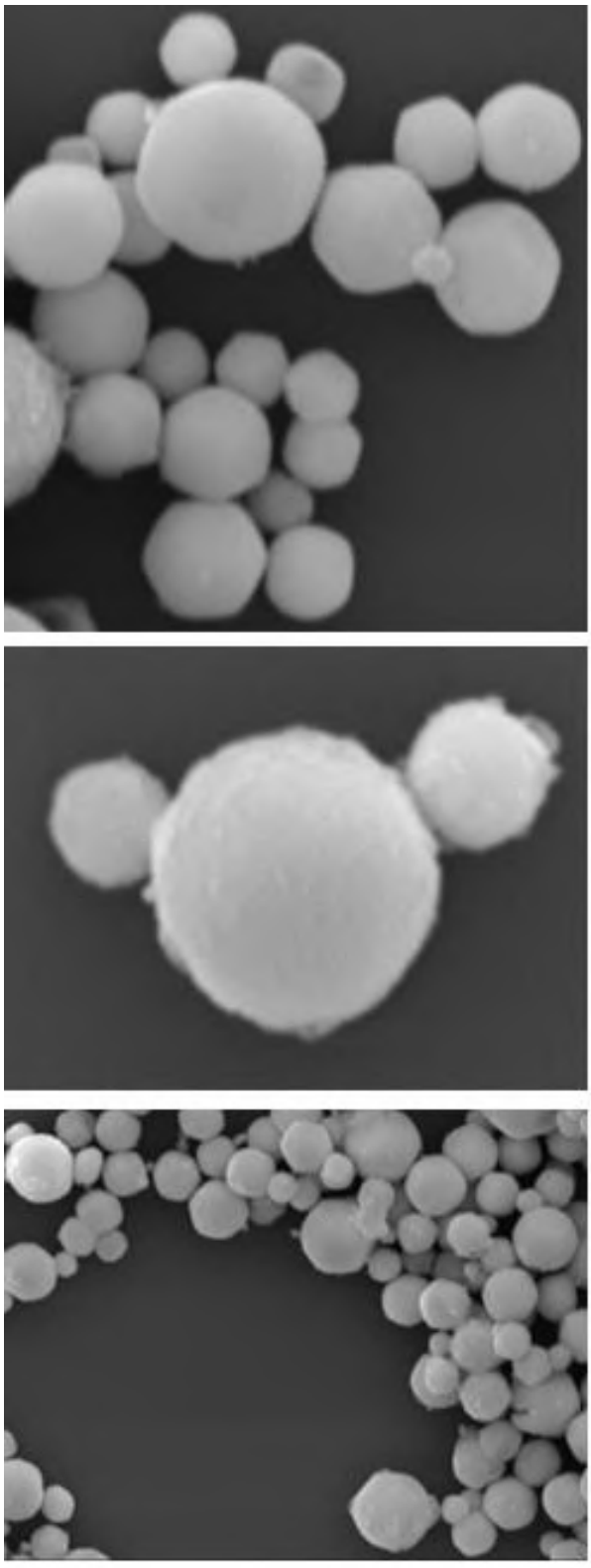

Fig. 3: SEM images of BHO36.

From SEM, observed that both BHO24 and BHO36 did not have completely rounded "spheres" such as $BaHfO_3$ was described in the literature, they have an almost hexagonal character and for HBO24 this behavior is more predominant. Another relevant detail is the non-homogeneity; we observe large and small spheres simultaneously.

IV. CONCLUSION

By means of synthesis and characterization results, it can be concluded that perovskite oxide can be obtained through MAH with reduction of KOH. With the reduction of KOH did not obtain any change in the structural character since both had the same diffraction peaks, but in the morphological character there was a small change. The sphereshad a "hexagonal" character being more present in the BHO24 and grew without uniformity.

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