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Synthesis, characterization and kinetic study of the $Sr_2FeMoO_{6-\delta}$ double perovskite: New findings on the calcination of one of its precursors

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HIGHLIGHTS

• Synthesis of Sr₂FeMoO₆ perovskite by solid state reaction.

• Morphological, Rietveld, and thermogravimetry analyses.

Study of perovskite kinetic parameters Sr₂FeMoO₆.

• Precursor calcination temperature.

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ABSTRACT

 $Sr_2FeMoO_{6-\delta}$ double perovskites are widely-recognized due to several important factors: high electronic conductivity and electrocatalytic activity, structural stability under reducing atmospheres, high transition temperature, enormous magnetoresistance, reasonable tolerance to carbon formation, and their desirable capacity to avoid sulfur poisoning. One of the methods most commonly-used to synthetize these perovskites is solid-state reaction. The precursor phases usually associated with this method are the oxides $SrMoO_4$ and $SrFeO_{3-\delta}$ when $Fe2O_3$, $SrCO_3$, and MoO_3 are the initial reagents used. Morphological, XRD (Rietveld), and thermogravimetry (calcination and reduction) analyses are steps or routes towards achieving the final result. While recent studies suggest that the temperature of calcination is always 900 °C and that reduction occurs at 1200 °C, they fail to explain why this occurs. This article demonstrates, according to the results of thermogravimetric analysis (TGA), that as calcination advances weight loss increases until a temperature of 850 °C is reached. In addition, it stresses the importance of the ball milling technique at ambient temperature to prevent sublimation of the MoO₃ compound at 700 °C in the later steps of synthesis, such as calcination and reduction. According to the kinetic

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study, the values of activation energy (Ea) and reaction order (n) were 130.47 kJ/mol and 1 respectively.

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Introduction

Currently, important research activities are underway to explore new materials that present conformations of the double perovskite type. The aim is to understand the source of their properties, improve them, and adapt laboratory methods for synthetizing these materials in order to scale them up to the level of technological production for various applications [1]. It is worth mentioning the good properties of the double perovskite group for hydrogen storage, for example in rechargeable batteries and dielectric properties [2,3]. According to current knowledge, the crystalline structures of perovskites are classified as ABO₃ (simple perovskite), A₂BB'O₆ (double perovskite, formed by B'O₆ and B"O₆ octahedrons), AA'B₂O₅ (layered perovskite), and A₂BO₄ (Ruddlesden-Poppertype perovskite).

Depending on their specific microstructure, electrical conductivity, the stability of the crystalline phase, and their electrochemical and catalytic capacity, each form provides distinct properties to the materials of the electrodes of a solid oxide fuel cell (SOFC) [4,5], but all these perovskites have shown both ionic and electronic conductivity, though to a greater or lesser degree. Respect to the four types mentioned above, the $A_2BB'O_6$ double perovskite (Fig. 1) has shown excellent properties as its desired ability to reduce sulfur poisoning, an ionic and electronic conductor in methane, hydrogen, argon-hydrogen, and air atmospheres at temperatures up to 800 °C [6–8]. Such characteristics of double perovskites are very important when considering SOFCs and hydrogen as fuel for clean and environmentally friendly electrical energy generation [9].

Table 1 lists some properties of the $A_2BB'O_6$ perovskites that are the object of this study [10-20]. It is important to



Fig. 1 – Structure of a double perovskite $Sr_2Fe_{1+x}Mo_{1-x}O_{6-\delta}$.

mention that this category of perovskites has also been a subject of study due to its great magnetoresistance, high Curie temperature and the multiferroic character of some compositions [21,22]; for example, huge magnetoresistance to low-field ambient temperature in 1998, where the double perovskite manganese-free, with a Curie temperature of 415 K, demonstrated intrinsic tunneling -type magnetoresistance at room temperature [23,24].

The Sr₂FeMoO₆ material is a specific case of a double perovskite that pertains to the general formula A₂BB'O₆, where A is an alkaline earth atom, such as Sr, Ba, La or Ca, and B, and the B' site corresponds to transitional metallic atoms, such as Y, Mn, Mo, Cr, Cu, Co, Ni, or Fe, among others [25,26]. The $Sr_2Fe_{1+x}Mo_{1-x}O_6$ perovskite, where $0 \le x \le (1/3)$, is one example of the A₂BB'O₆ category. The double perovskite (Sr₂-FeMoO₆), presents important thermal characteristics, for example, its thermal expansion coefficient (TEC) value is approximately $13.9 \times 10^{-6} \text{ K}^{-1}$, which is very close to one of the most used electrolytes with this type of material, in this case, the $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) compound that presents a TEC value of approximately $11.2 \times 10^{-6} \text{ K}^{-1}$ [27]. A very important aspect of the Sr₂FeMoO₆ double perovskite related to energy efficiency from the use of hydrogen as a fuel, is the possibility of using it as an anode and cathode in an SOFC due to its mixed ion-electronic character, electronic structure, high catalytic activity and especially the ability to generate high concentrations of oxygen vacancies due to weak Fe-O bonds, which allows to meet the necessary requirements of an SOFC as an electrical generator [28]. This is also due to the fact that double perovskite can process hydrogen with good structural stability, thermodynamics, as well as certain sulfur tolerance [29].

Synthetizing a one-phase Sr₂FeMoO₆ perovskite entails various difficulties. Some authors sustain that this double perovskite can be formed completely only in capsules of evacuated silica or in a highly-reducing atmosphere [30]. Achieving the constant formation of SrMoO₄, one of this type's precursors, is the principle challenge faced in synthetizing this compound. It is well known that; experimental conditions and fabrication processes have significant effects on the physical properties of double perovskites [31]. The mechanical ball milling method has been used by several researchers in materials science as they strive to obtain highly-active, dispersed particles of nanometric size, or close to the atomic level, through the collisions and friction that occur among the objects subjected to the ball milling process, the material being processed, and the walls of the recipient. This technique has been tested and is well-supported by various studies, in part because it has been applied in several fields of science [32-34].

The synthesis achieved through the solid-state reaction is an important feature of the present study, though other, more

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| Table 1 – Conductive capacity of some A ₂ BB'O ₆ perovskites in different atmospheres. | | | | | | |
|--------------------------------------------------------------------------------------------------------------|--------|-----------------------------------------------|------------|-----------|--|--|
| Perovskite | Т (°С) | Conductivity (S cm ⁻¹)/Atmosphere | | Reference | | |
| $Sr_2Mg_{1-x}Fe_xMoO_{6-\delta}$ (x = 0.5) | 800 | 28/(H ₂) | 10/air | [10] | | |
| $Sr_2Fe_{1.5-x}Ni_xMo_{0.5}O_{6-\delta}$ (x = 0.1) | 800 | 20.6/(H ₂) | _ | [11] | | |
| $Sr_2FeNb_{0.8}Mo_{0.2}O_6$ | 800 | 5.3/(5%H ₂) | 19.5/air | [12] | | |
| $Sr_2Fe_{1+x}Mo_{1-x}O_6$ (x = 1/3) | 800 | 16/(H ₂ 3%H2O) | _ | [13] | | |
| $Sr_2FeMoO_{6-\delta}$ | 800 | 186.9/(97%H ₂ -3%H ₂ O) | - | [14] | | |
| PrBaMn ₂ O ₅ | 800 | 8.16/(5%H ₂) | 91.5/air | [15] | | |
| $Sr_2MgMoO_{6-\delta}$ and $Sr_2MnMoO_{6-\delta}$ | 800 | 10/(H ₂ and CH ₄) | _ | [16] | | |
| (PrBa) _{0.95} (Fe _{0.9} Mo _{0.1}) ₂ O _{5+δ} | 800 | 59.2/(5%H ₂) | 217/air | [17] | | |
| $PrBaMn_{1.5}Fe_{0.5}O_{6+\delta}$ | 800 | 7.4/(5%H ₂ /Ar) | 112.5/air | [18] | | |
| $Sr_{2-x}MgMoO_{6-\delta}$ (x = 0.1) | 800 | 15.7/(H ₂) | - | [19] | | |
| $Sr_2FeMoO_{6-\delta}$ | 800 | 215.72/(dry H ₂) | 25/dry air | [20] | | |
| Own elaboration | | | | | | |

complex routes exist; for example, the sol-gel process [35]. High-energy mills are widely-utilized in ball milling processes not only for grinding, but also for cold-welding with the aim of producing alloys from the ground powder produced. Ball mills made of high-quality steel are potentially expensive but have the capacity to grind particles of mixtures up to 5 nm in size. This increases the surface and reaction velocities enormously.

For the mechanical grinding process, the steel ball and powder are placed in a vial that is agitated in complex, threedimensional cycles at a high frequency and a mean impact velocity of 4.2 m/s. Examples of the final product of this process, in relation to particle size, include catalyzers [36], new alloys, and ceramics, among others. In this sense, the procedure followed to produce a double perovskite is somewhat simpler compared to others. To give one example, the compacting and synthesis of the oxides to obtain a material consisting of one sole phase have been conducted using a solidstate reaction at 900 °C [13,37-41]. The duration of this process varies in different reports [19,37]. This temperature has been used to obtain identical results using a planetary mill [20]. It is surprising to find, however, that no publications have yet explained how these temperatures and time values were determined. High calcination and sintering temperatures often generate a thickening of the grains that negatively affects the electro-transport and magnetoresistance properties.

The importance of this method must be stressed in light of the characteristics and final analysis of the samples, especially in systems with a high degree of disorder, as in the case of studies of magnetic behavior [42]; for example, reversible magnetocaloric analyses of Sr₂FeMoO₆ double perovskites [43], and the compound $Sr_2FeNb_{0\cdot 2}Mo_{0\cdot 8}O_{6\cdot \delta}$ for stable anodic materials in redox environments [12]. Recent reports indicate that perovskites like $Sr_2Fe_{2-x}Mo_xO_{6-\delta}$ obtained by the solid-state reaction method have achieved high electrocatalytic activity as a product of the increase of Fe²⁺ ions and very low Gibbs free energy levels [44]. Another example is the Sr_{1.8}La_{0.2}FeMoO_{6-δ-} perovskite with added lanthanum since it has shown a higher yield (885 mW cm-2) than the Sr2FeMoO6 perovskite (740 mW cm⁻²) in hydrated hydrogen at a temperature of 800 °C [45]. Another perovskite that has been synthetized by the solidstate reaction method is $Sr_2FeMo_{0.65}Ni_{0.35}O_{6-\delta}$. In this case, the perovskite was utilized with Gd_{0.1}Ce_{0.9}O_{2-δ} material to achieve a reported increase in the power density of up to 550 mW cm^{-2} , which is greater than the 439 mW cm⁻² attained in the absence of the latter material [46].

The importance of this article is threefold: the simplicity of the synthesis process, lower obtaining temperatures, and mechanical alloying, as is sustained by various studies that have utilized the SrCO₃, MoO₃, and Fe_2O_3 reagents. There is a report, for example, on the calcination of this mixture of powders at 900 °C, followed by grinding, compacting and, finally, reduction in 5%H₂/Ar [24]. In other works, the powders are ground, compacted in pellets, calcined at 900 °C, ground again, and compacted at a pressure of 450 MPa. After that, they are reduced in an atmosphere of 6%H₂/N₂ at 1200 °C and, finally, ground in a high-energy mill in an argon atmosphere and compacted at the aforementioned pressure [38]. In another experiment, the precursors were mixed, ground, and heated at 900 °C for 10 h in an air atmosphere. They were then compacted in pellets for synthesis at 1280 °C in 5%H₂/Ar for 5 h at 5 °C/min. This was followed by grinding, compacting, and synthetization for 25 h [40]. While there are several similarities among these processes for fabricating double perovskites, two significant differences stand out: the application of mechanical alloying, and the synthesis conditions themselves.

In this work the double perovskite Sr_2FeMoO_6 has been synthesized through mechanical milling, using as initial reagents the oxides $SrCO_3$, MoO_3 , and Fe_2O_3 , with this process the sublimation of the compound MoO_3 is avoided. To achieve this perovskite, mechanical milling, calcination, reduction (H₂/Ar)) was carried out in a thermogravimetric analyzer, also the particle size was verified through SEM, as well as the presence of the intermediate and final phases through XRD. Additionally, to study the transformation kinetics of double perovskite, a kinetic study has been carried out from the data of the thermogravimetric analysis and the use of the Horowitz and Metzger method for the determination of the activation energy (*Ea*) and the order of reaction (*n*).

Experimental procedure

To obtain the Sr_2FeMoO_6 perovskite, stoichiometric quantities of dry powders of analytical grade were utilized. The first step used iron oxide Fe_2O_3 (>99.98%, Aldrich, U.S.), strontium carbonate $SrCO_3$ (>99.9% pure, Aldrich-Sigma, U.S.), and molybdenum oxide MoO_3 (>99.99% pure, Aldrich, U.S.). The weights of each reagent were considered according to the following:

 1.1535 ± 0.0001 g (SrCO₃), 0.3196 ± 0.0001 g (Fe₂O₃), and 0.5602 ± 0.0001 g (MoO₃), giving a total of 2.0333 g. These oxides were weighed on an analytical balance with a precision of 0.0001 g. To eliminate any free water that might have settled in the pores, fissures, or interstitial space of the surface of the powders due to adsorption, each reagent was dried separately in a drying oven for 6 h at 110 °C. Immediately afterwards, the powders are again weighed to obtain 1.1377 ± 0.0001 g SrCO₃, 0.3077 ± 0.0001 g Fe₂O₃, and 0.5546 ± 0.0001 g MoO₃, which finally form the stoichiometric quantities necessary to form the Sr₂FeMoO₆ perovskite. The next step involved mixing the powders in an agate mortar (hand mill) for 10 min, then grinding them in a high-energy mill (ball mill-Spex 8000 M) for 6 h at 1725 revolutions per minute to produce, among other substances (Eq. (2)), strontium molybdate (SrMoO₄), which is the first precursor phase of the double perovskite (Sr₂FeMoO₆) that is the object of this study. At this point, a mixture of 21.1 mg has been obtained.

The total of the previous mixture (21.1 mg), goes to a process of calcination in air at a temperature of 850 °C for a period of 2.22 h. It used a heating ramp of 15 °C per minute. At this stage and according to Eq. (3), the formation of the second precursor phase (SrFeO_{3- δ}) of the double perovskite is generated.

Finally, the powders obtained, which are mainly composed of the mixture of the two precursor phases $SrMoO_4$ and $SrFeO_{3-\delta}$ (Eq. (4)), were reduced in a hydrogen atmosphere (3% H₂) with argon (97%Ar) at a flow rate of 5 cm³/min. This reduction was performed at 1074 °C for 4 h at a heating velocity of 5 °C/min. Finally, a sample with an approximate weight of 12 mg is obtained (Sr_2FeMOO_6).

Both the calcination process and the reduction process are carried out in a thermogravimetric analyzer. To observe and record the weight loss of the sample due to the formation of carbon dioxide and water, we used a SETARAM Setsys Evolution 16/18 model thermogravimetric analyzer with a precision of 0.01 μ g. It is important to note that in each stage of the synthesis process a small amount of the sample was taken for analysis in an X-ray diffractometer (X D8 Advance Davinci X-ray diffraction system) to verify all the formation phases and the final perovskite produced. No impurities were found related to the steel balls used as reported by some researchers [47]. For the analyses of the microstructure and chemical composition, a scanning electron microscope (SEM) (SEM-Jeol-6400) with EDS-EDAx equipment was utilized.

Results and discussion

Formation reaction of the Sr₂FeMoO₆ perovskite

The general reaction of the Sr_2FeMoO_6 perovskite can be represented as:

$$Fe_2O_3 + SrCO_3 + MoO_3 + H_2 \rightarrow Sr_2FeMoO_6 + H_2O + CO_2$$
(1)

This transformation takes place in the absence of heat because the particle size —on the order of 100 nm— makes the reagents in the powder extremely reactive.

During the grinding process, the first precursor, $SrMoO_4$, appeared in accordance with the following reaction (see Fig. 9):

$$SrCO_3 + MoO_3 \rightarrow SrMoO_4 + CO_2$$
⁽²⁾

In the ensuing step (calcination), the second precursor, $SrFeO_{3-\delta}$, appeared in accordance with the reaction:

$$SrCO_3 + Fe_2O_3 \rightarrow CO_2 + SrFeO_{3-\delta}$$
 (3)

Finally, to obtain the double perovskite, the sample was subjected to a reducing process under a controlled atmosphere of H_2/Ar to H_2 (3%) at a temperature of 1074 °C for a period of 4 h in a thermogravimetric analyzer. The reaction in this stage is as follows:

$$SrFeO_{3-\delta} + SrMoO_4 + H_2 \rightarrow Sr_2FeMoO_6 + H_2O$$
 (4)

Microstructural and morphological analyses

As shown below, the material is milled in the high-energy mill, whose operating principle is shown in Fig. 2. Fig. 3, shows the form and size of the particles of the reagents after mixing in an agate mortar, but before grinding in the highenergy mil. A completely heterogeneous tendency in form and size around 1 μ m or less is visible. It is important to point out that the Fe₂O₃ and SrCO₃ powders are made up of particles of irregular shape that are smaller than those of MoO₃, which are laminar in shape. After grinding at 1725 rpm for 6 h, the particles became more homogeneous and finer, measuring approximately 100 nm, as shown in the micrographs in Fig. 3, obtained via SEM. Both the microstructure and porosity can be observed after the 3% reduction of H₂ at 1074 °C. Because the nanoparticles have a larger surface area than the larger particles, they are more reactive to some other molecules. According to the SEM images (Figs. 3 and 4), it is feasible to affirm that the mechanical alloying technique makes it possible to obtain a crystalline perovskite structure of sub-micrometric size with acceptable random distribution. Other authors have obtained similar results [48]. It is important to note that according to the SEM images (Fig. 4), micrometric and welldistributed particle size is observed. In this sense, the authors of this work could think that in future researches planned on this double perovskite and once the powders are converted into discs, we would have an interconnected porous morphology with a shape similar to a sponge. This is very important when considering the material of the electrodes (anode-cathode) of fuel cells (especially of the SOFC type), which require optimal distribution and pore size to ensure diffusion of the hydrogen (H₂) gas used as fuel for electric energy generation [49].

XRD and rietveld analyses

After the mechanical alloying process and drawing a sample for calcination in a thermogravimetric analyzer for 2.22 h at 850 °C, the SrMoO₄ phase appeared, formed from the MoO₃ oxide, as can be seen in the diffractogram in Fig. 5. This result



Fig. 2 – Operating principle of a ball mill. Powder particles are attracted by balls (left) within a vial (right).



Fig. 3 – Powders mixed of reagents in an agate mortar and pestle. Diversity in size and shape are noticeable.

contradicts findings published in other studies since, for example, it proves that the $SrMoO_4$ phase that formed before obtaining the Sr_2FeMoO_6 double perovskite could not be achieved by mechanical activation when using MoO_3 as the

starting material [30]. In fact, grinding by the mechanical alloying technique prevents the sublimation of MoO_3 oxide at 700 °C during calcination and reduction, thus promoting the formation of the desired phase, i.e., the SrMoO₄ phase, which was obtained in a 6-h grinding time.

The diffractogram in Fig. 5 clearly shows that the SrMoO₄ phase appeared in the greatest quantity, followed by the SrCO₃ phase, and then the Fe₂O₃ phase. Finally, the sample was subjected to a reduction process at 1200 °C for 4 h in the same thermogravimetric analyzer to form the double perovskite.

The Rietveld method is a powerful tool that makes it possible to obtain the structural parameters of diffraction patterns. Fig. 6 shows the complete formation of the double perovskite ($Sr_2FeMoO_{6-\delta}$) after the reduction process in an inert atmosphere, as well as a small amount of two secondary phases $SrMoO_4$ and Fe. The results of the Rietveld analysis are shown in Table 2. The I4/mmm spatial group ($Sr_2FeMoO_{6-\delta}$) has been utilized for Rietveld analysis because it presents a tetragonal structure through which the corresponding indexation has been carried out. Rietveld analyses have been



Fig. 4 – Powders milled in a high energy ball mill for 3 h and then reduced, show homogeneity in size and shape.

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Fig. 5 - Formation of first precursor phase SrMoO₄ during ball milling.

developed using MAUD software (Material Analysis Using Diffraction) to obtain values for two parameters of the crystalline network: 5.5866 Å (a = b), and 7.9107 Å for the parameter (c).

Fig. 6 also shows, in parentheses, the values of each reflection that corresponds to the $Sr_2FeMoO_{6-\delta}$ structure, from the reflection (200) at approximately 30° (20) to the one (332) at

almost 80° (20). These results have been achieved by other researchers [43,50].

The diffractogram indicates, in black, the profile that corresponds to the experimental approach, while the profile we calculated Is shown in red. The lower section of the diffractogram in Fig. 6 presents the difference calculated between these two profiles. Here, it is important to emphasize



Fig. 6 – Rietveld refinement of the $Sr_2FeMoO_{6-\delta}$ double perovskite diffraction pattern.

| Table 2 — Results Rietveld method as described in the text. | | | | | |
|-------------------------------------------------------------|--------|--------|--------|--|--|
| Chi square (Sig) | Rwp | Rexp | Rb | | |
| 1.3213 | 4.5864 | 3.4711 | 3.4234 | | |

the good fit between the observed vs. the calculated profile. This can be considered a plane behavior with respect to the differences between the two profiles; that is, between the experimental and calculated crystallographic reflections (hkl). One important aspect of Rietveld refinement involves the criteria of adjustment applied during the process since these indicate the progress of the procedure and aid in determining whether the model proposed is correct. For this purpose, the adjustment criterion called residue weight pattern has been calculated (Rwp, %). This index, which shows the progress of the refinement process, can be seen in the upper-right section of the graph in Fig. 6 and Table 2. In the present case, the Rwp (%) value obtained was \approx 4.5864, a relatively low figure that indicates: (i) an acceptable convergence in the minimization calculated, and (ii) that the model proposed is correct, as can be seen in the diffractogram in Fig. 6. The expected R factor (Rexp) is also presented in Table 2. Another important parameter is the "chi-square" parameter or "goodness of fit" (GoF), can be estimated from the comparison of the ratio between the parameters Rwp and Rexp. It is considered that the closer the chi-square value is to 1, better adjustment will be made; however, this is difficult to obtain due to the aberrations that can occur when performing X-ray diffraction [51]. In this investigation a value of 1.3213 has been obtained.

According to the MAUD software, 98.64% of the phase of the Sr_2FeMoO_{6-\delta} double perovskite was obtained, with respect

to the secondary phases, percentages were obtained of 1.31% and 0.05% for SrMoO₄ and Fe phases respectively. According to several researchers, this material has demonstrated high conductivity and electronic performance when using hydrogen as fuel in an SOFC [52]. With this 98.64% of the double perovskite (Sr₂FeMoO_{6- δ}) formed, it is possible to consider it in future tests of electrical conductivity as an electrode in SOFCs, as well as the use of hydrogen as fuel for the generation of electrical energy, which has been demonstrated in other investigations where the secondary phases (SrMoO₄ and Fe) have also been obtained in small percentages [53].

Thermogravimetric analysis

Thermogravimetric analysis is a high-precision technique used to observe the continuous change in the mass of a sample as a function of temperature or time in a controlled atmosphere. The loss of mass due to oxidation is the most common type observed in this analysis. The equipment utilized in our study included an oven, a microbalance, an autosampler, and a thermocoupler.

Fig. 7 shows the graph of the thermogravimetric and differential (DTG) processes of the Sr₂FeMoO_{6- δ} double perovskite. It was elaborated in a temperature range of 300–1350 K. As can be seen, it is divided into four zones (I-IV) according to the most important changes that occur as the temperature increases. What stands out in these four zones are two exothermic peaks (DTG) centered at an approximate temperature between 350 K (zone I) and 1000 K (zone III), respectively. The first peak (\approx 350 K) represents the loss of the humidity immersed in the material. The second (\approx 1000 K), located in zone 3, represents the most significant



Fig. 7 – Weight change during calcination. The greatest loss occurs in zone III and ends at 1123 K.

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Fig. 8 – Scheme showing the simplicity of the ball milling route in the synthesis. a) Milling at 1725 rpm and 6 h; b) Calcination and reduction at 850 °C (2.2 h) and 1200 °C (4 h) respectively.

loss during the process, which corresponds primarily to the thermal degradation of the compound MoO_{3} .

According to reaction (3), the formation of CO_2 gas causes the solid sample to lose weight. This loss is observed principally in zone III of the curve in Fig. 7, leading to the conclusion that the temperature of 1123 K marks the end of the calcination process; that is, when no further weight loss is produced. This temperature is lower than figures published in other studies, which generally report 1173 K [40]. Based on the reaction in Eq. (3) (Eq), it is possible to calculate the theoretical loss of CO_2 , considering the stoichiometric amounts of the reagents and products. This turned out to be 9.24%, well below the experimental value of 12.23% (Fig. 7). This means that the reaction contained other products that formed impurities -such as iron (Fe) or some derivative of Fe [54] - which increased the amount of loss. The second precursor phase in the process of forming the double perovskite emerges after calcination. This phase corresponds to the compound SrFeO₃₋ δ. In zone II of Fig. 7, reached at approximately 927 K (second peak begins), it is clear that the slope of the curve changes drastically. Before and after this point, various transformations are responsible for this change, including for example, the calcination reaction (Eq (3)) and the behavior of molybdenum oxide (MoO₃). This can explain why the experimental weight loss was greater than the theoretical loss. Here, it is important to note that the MoO₃ compound is highlyhygroscopic, so the elimination of water at a high temperature may contribute to this weight loss. There are reports that this decrease is produced very slowly below 723 K, but that in the range of 923–1073 K the transformation of MoO₃ increases



Fig. 9 – Activation energy (Ea) obtained through the Horowitz and Metzger method for $Sr_2FeMoO_{6-\delta}$ double perovskite.



Fig. 10 – Calculation of the maximum degree of advance (α) at the highest rate of degradation to calculate the double perovskite order of reaction (n) according to Horowitz-Metzger method.

(5)

markedly [55]. Above 1347 K, the weight of the sample remained constant, ending the reduction and producing the Sr_2FeMoO_6 double perovskite. Now that the TGA analysis has been performed and the double perovskite has been obtained at almost 100%, we will try to continue this research on the possibility of producing hydrogen at high temperatures as has been reported by other authors with other perovskites [56,57].

Finally, we would emphasize that the global process for synthetizing the double perovskite represented in Eq (1) and Fig. 8 manifests the simplicity of this approach. Indeed, it is by far the most conventional method of synthesis for preparing multiple-component ceramics compared to other, more complex methods, like the sol-gel approach [57,58]. In addition to the synthesis of materials, high-energy mechanical grinding provides a way to modify the conditions in which chemical reactions take place, whether by changing the reactivity of the ground solids to foster mechanical activation, by increasing the reaction velocities, by reducing the reaction temperature, or by inducing chemical reactions during grinding.

Kinetic analysis of the Sr₂FeMoO_{6-δ} perovskite

A kinetic study of the thermogravimetric process of the Sr₂FeMoO_{6-δ} double perovskite allows a better understanding of the origin of this oxide. In addition, the study of the kinetic parameters, such as activation energy (Ea) and reaction order (n), of the thermal transformation of the double perovskite, allows for better quality samples to be obtained [59], which can lead to better energy efficiency of hydrogen in SOFCs. This is particularly important in activation polarization sensitivity analysis [60]. To determine its kinetic parameters, we analyzed the TGA-DTG data in Fig. 9. It is well-known that the activation energy (Ea) and reaction order (n) are two of the most important kinetic parameters in thermoconversion processes. Horowitz and Metzger proposed a method for determining these two key parameters [61]. According to Fig. 9, Ea is obtained by calculating the slope that results from the graph of T-Ts (x-axis) vs. ln{ln $[1/(1-\alpha]]$ (y-axis).

Given that the correlation coefficient (R^2) presents a value of 0.9993, the Horowitz-Metzger method appears to be acceptable for predicting the *Ea* and reaction order (*n*). According to Fig. 9, a slope with a value of 0.01582 was obtained. Considering an approximate temperature value of 996 K at the point of maximum velocity of the DTG (Fig. 8), and the constant of ideal gases (R = 8.314 J K⁻¹ mol⁻¹), it is possible to calculate *Ea*, obtaining a result of approximately 130.47 kJ/mol. This value for *Ea* is similar to those reported in other publications [59]. The (low) magnitude of this value may be due to the relation that *Ea* maintains with ionic interdiffusion, which is also related to the distortion of the material [62].

Fig. 10 presents the graph of the degree of advance (α) vs. $d\alpha/dT$. According to Horowitz and Metzger's method, it is possible to calculate the reaction order (n) by placing the value of α_m at the point of maximum degradation velocity ($d\alpha/dT$). This generated a value of $\alpha_m \approx 0.3501$. Based on the approximation in Eq (5), we obtained a value for the reaction order of $n \approx 1$.

 $\alpha_m = n^{\frac{1}{1-n}}$

As can be seen, the Horowitz and Metzger method allows the kinetic parameters of activation energy (*Ea*) and reaction order (*n*) of the double perovskite to be determined simply and relatively quickly. In the use of this method highlights the excellent linear adjustment in virtually the entire process of thermal conversion, which is mainly due to the fact that this method allows working with ranges of degree of advance covering almost 100% of the reaction and not just the beginning of it, as in other kinetic methods, for example, the Friedman method [63].

Conclusion

The structural analysis carried out through the Rietveld method, allowed the quantification of the main phase, i.e., the double perovskite SrFeMoO₆ (98.64%), as well as the two secondary phases SrMoO₄ (1.31%) and Fe (0.05%). The "chi square" value in this analysis is 1.3213. Mechanical grinding promoted the reaction between the reagents SrCO₃ and MoO₃, which are involved in forming the first phase of the SrMoO₄ type. Parallel to this, the reagents SrCO₃ and Fe₂O₃ fostered the formation of the second phase, SrFeO $_{3-\delta}$, at 850 °C. This temperature was determined with the aid of thermogravimetric analysis. This same treatment could be evaluated to determine the reduction temperature when synthetizing this double perovskite based on the reagents Fe₂O₃, SrCO₃ and MoO₃. Finally, the reduction of the materials with H₂ allowed the complete formation of the Sr₂FeMoO₆ perovskite. We should note that the compound MoO₃ is sublimated at around 700 °C during the calcination stage. This represents an advantage due to the facility in obtaining the first precursor phase (SrMoO₄), compared to other methods of synthesis. In this approach, MoO₃ is maintained in the process of mechanical alloying and not sublimated until calcination. The morphology of the perovskite presents possibilities for applications as the anode or cathode in SOFC-type fuel cells due to the characteristics of its particles and its porosity as a function of its distribution and size. The kinetic analysis indicates an order of reaction of approximately 1 and the value of the energy activation (130.47 kJ/mol) is low, which is related to the interdiffusion of the ions involved in the ceramic. Finally, the authors want to mention that there will be a continuation of this research using the double perovskite of this work, with the aim of using hydrogen as fuel in a SOFC.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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