SOL-GEL SYNTHESIS OF THE DOUBLE PEROVSKITE SR2FEMOO6 ASSISTED BY MICROWAVE TECHNIQUE

J. Valdés[1*], A. Cuan[1], O. Navarro[2], R. Nava[1], B. Aguilar[2]

[1]Dirección de investigación y posgrado, Facultad de ingeniería,
Universidad Autónoma de Querétaro,
Cerro de las campanas S/N, Santiago de Querétaro, Querétaro, 76010, México.

[2]Unidad Morelia, Instituto de Investigaciones en Materiales,
Universidad Nacional Autónoma de México,
Antigua carretera a Pátzcuaro No. 8701, Col. Ex Hacienda de San José de la
Huerta, 58190, Morelia, Michoacán, México.

*Autor de correspondencia
jesvalher@hotmail.com

ABSTRACT

A sol-gel synthesis of the double perovskite Sr2FeMoO6 assisted by microwave technique was performed. A citric acid was used as chelating agent to modify the hydrolysis of the metal ions. The sol-gel synthesis was carried out in order to generate the precursor phases of the Sr_2FeMoO_6 system. Also, the conventional sol-gel synthesis was carried out for comparison purposes. The high pressures achieved with microwave heating generate phases with high crystallinity according to the X-ray pattern obtained. Besides, small rates of the metallic clusters of iron are present in the XRD pattern. Scanning electron microscope technique also was carried out for characterization of the precursor phases and the final system.

Keywords:
sol-gel synthesis; microwave heating; double perovskite; X-ray, SEM.

RESUMEN

El Sistema Sr_2FeMoO_6 fue sintetizado por la técnica de sol-gel asistido por microondas. Se utilizó ácido cítrico como agente quelante para modificar la hidrolisis de los iones metálicos. La síntesis por sol-gel fue realizada con el fin de generar las fases precursoras del sistema Sr_2FeMoO_6. Igualmente, para fines de comparación se sintetizó el sistema por el método de sol-gel y calentamiento tradicional. Las altas presiones logradas con el calentamiento por microondas generan fases con alta cristalinidad de acuerdo con los patrones de difracción de rayos X obtenidos. Pequeñas cantidades de Fe metálico se encuentran presentes en el patrón de rayos X. La morfología de las fases precursoras al igual que el compuesto final se analizó por la técnica de microscopía electrónica de barrido.

Palabras clave:
síntesis por sol-gel, calentamiento por microondas, doble perovskita, rayos X, SEM.

1. INTRODUCTION

An ideal double perovskite has the formula unit: A2B'B''O6, where A denotes an alkaline-earth or rare-earth ion, B' and B'' are transition-metal sites occupied alternately, there are oxygen bridges every B' and B'' atom pair give alternating B'O6 and B''O6 octahedral form (Kobayashi et al., 1998). The double perovskite Sr_2FeMoO_6, namely (SFMO), has a particular interest for its ferromagnetic and half-metallic behavior. The ordered lattice structure of SFMO consist of body centered cubic lattice with alternating FeO_6 and MoO_6 octahedral forms at the corners and the strontium atom in its center (Valenzuela et al., 2014). In particular, semi-metallic behavior has been investigated, in which only one-spin direction in the Fermi energy is present, due to its attractive properties for spintronics applications (Soto et al., 2014). Therefore, the SFMO is very attractive for applications in magnetic recording devices (Valenzuela et al., 2014) caused by the low field magnetoresistance of the grate in granular form (Cernea et al., 2013) and a relatively high Curie temperature (410-450K) (Kobayashi et al., 1998).

The synthesis of SFMO is traditionally prepared with the solid state method by mixing the SrMoO4 and SrFeO3-x precursors to form the double perovskite (Sr_2FeMoO_6) by calcination and reduction of them. This method requires a high temperature (1270°C) for the reduction and the grain size is in the micron scale, reducing its magnetoresistance (Zhai et al., 2012).

In the sol-gel citrate synthesis, the citric acid play the role as a chelating agent in order to modify the hydrolysis for the metal ions (Danks et al., 2016). This molecule with three carboxyl acid moieties is able to dissociate, and it is an effective chelating agent. The metal ions are attached in the OH of the carboxyl group liberating a H+ forming a metal citrate, the gelification process occurs with

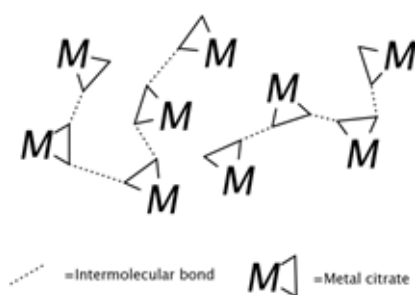the intermolecular bond of the metal citrates (Figure 1).

Figure 1. Schematic Gelification of the metallic citrates, there is a weakly interconnected network.

It has been reported that heating the porous of the gel at high temperatures causes densification (Hench and West, 1990). In addition, it is kwon that the microwave-assisted synthesis uses the property from some compounds, in a liquid or solid state, to transform electromagnetic energy into heat (Liu et al., 2007), the energy transfer is achieved from dielectric losses, which results in the dissipation of electromagnetic energy in heat (de la Hoz et al., 2005). In contrast with the conventional synthesis, heat transfer is slow and occurs from de surface to the bulk (generating a temperature gradient),while the microwave-assisted synthesis allows selective absorption of electromagnetic radiation, uniform heating and even promote reactions which would not occur in classical conditions (de la Hoz et al., 2005).In addition, heating a solution with microwaves in a closed container helps to develop a hydrothermal process(Komarneni et al. , 1992). The high pressure and temperature in the container modifies the behavior of the chemical species in the solution and stimulate the generation of new phases.

The intergrain magnetoresistance of polycrystalline Sr2FeMoO6 is known to depend on its grain size (Li et al., 2008) and the amount of insulating nonmagnetic SrMoO4 impurity formed during fabrication (Cernea et al., 2013). Also, the cationic disorder breaks down the half-metallic ferromagnetic behavior (Reyes et al., 2016). Therefore, the method and synthesis conditions must be chosen carefully, so new techniques of synthesis have to be developed to find a better crystalline phase of SFMO with a decrease of the cationic disorder. Based in this fact, the method of sol-gel microwave assisted synthesis is used in this work and it is compared with the traditional sol-gel method, where X-ray diffraction (XRD) and Scanning electron microscopy (SEM) techniques were applied for the characterization of the materials.

2. METHODOLOGY

The system Sr_2FeMoO_6 was synthetized by the sol-gel microwave assisted synthesis method from its precursor's phases, then a calcination of 900°C for 3 hours was performed, and finally a reduction in an atmosphere of Ar2%H was achieved to obtain the final system Sr_2FeMoO_6 .

Strontium nitrate Sr(NO3)2 (99.995%), iron (III) nitrate nonahydrate Fe(NO3)3-9H2O (99.95%), molybdenum (IV) oxide MoO3 (99.99%), citric acid Monohydrate (99%) and ammonium hydroxide solution (28.0-30.0%) to form Ammonium molibdate $(NH_4)_2 MoO_4$ are used to form the precursors agents. All reagents were provided by Sigma-Aldrich. The reagents were weighted according to their stoichiometric rate. Molar ratio citric acid: (2Sr+Fe+Mo) salts used were 4.3:1.

In a beaker of 200ml, 50ml deionized water were add and put into a magnetic steering at 80°C. 0.5ml of ammonium hydroxide solution and 144mg of molybdenum (IV) oxide were added in order to obtain ammonium molibdate, the solution were in stirring until transparency were reached, then 150ml of deionized water was added. 1g of citric acid, 423mg of Strontium nitrate and 404mg of iron (III) nitrate nonahydrate were added to the solution. The solution was maintained under steering at 80°C in order to evaporate

de water and to get a 50ml of the solution. The obtained sol was placed in a microwave "Synthos 3000" from Anton Paar (Figure 3). Two experiments were performed, the first (SGMW) with 15min to reach 170°C in the solution and 30min of reaction at this conditions the containers reach a stable pressure of 41bar, and the second (SG) without microwave heating. The precipitate of SGMW was dried out and then calcined in a muffle furnace Nobertherm. The sol of SG was dried out in a furnace at 90°C for 18H and then calcined in a muffle furnace Nobertherm. Soon after, the two experiments (SGMW and SG) were put into a muffle furnace at 900°C, were the average speed was about of 10°C/min and then they were maintained for 3 hours. The Sr_2FeMoO_6 system was reached in a reduction environment with a flow of Ar2%H at 1200°C for 3 hours.

The structure and microstructure of the precursors phases of SFMO powders and the SFMO final system were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The XRD patterns of SFMO and its precursor phases were recorded with a D8 ADVANCE diffractometer form Bruker-AXS. For the powder diffraction,

CuKα1 radiation (wavelength 1.5406 Å), LiF crystal monochromator and Bragg-Brentano diffraction geometry were used. The data were acquired at 25°C, with a step-scan interval of 0.020° and step time of 5s. The SEM was carried out using a JSM-IT300 operated at 10.0KeV.

3. RESULTS

3.1 X-ray diffraction analysis

Figure 2 shows the XRD Pattern of the samples SGMW and SG from the precursor phases of the double perovskite Sr_2FeMoO_6. It can be seen that both of the samples presents a phase of $SrMoO_4$ $SrMoO_4$ (PDF: 01-085-0586), but they differ in one compound $SrFe_{12}O_{19}$ (PDF:00-033-1340) for the SGMW sample and SrFe2O3 for the SG sample. The presence of $SrFe_{12}O_{19}$ in the SGMW sample can achieve metallic iron in the final step of the synthesis (as it can be seen in Figure 3). The intensity of the Bragg reflections in Figure 2 shows a better crystallinity for the SGMW sample compared with SG sample.

Figure 2. XRD Pattern of the SGMW and SG samples of the precursor phases (after the calcination process) of the double perovskite Sr_2FeMoO_6.
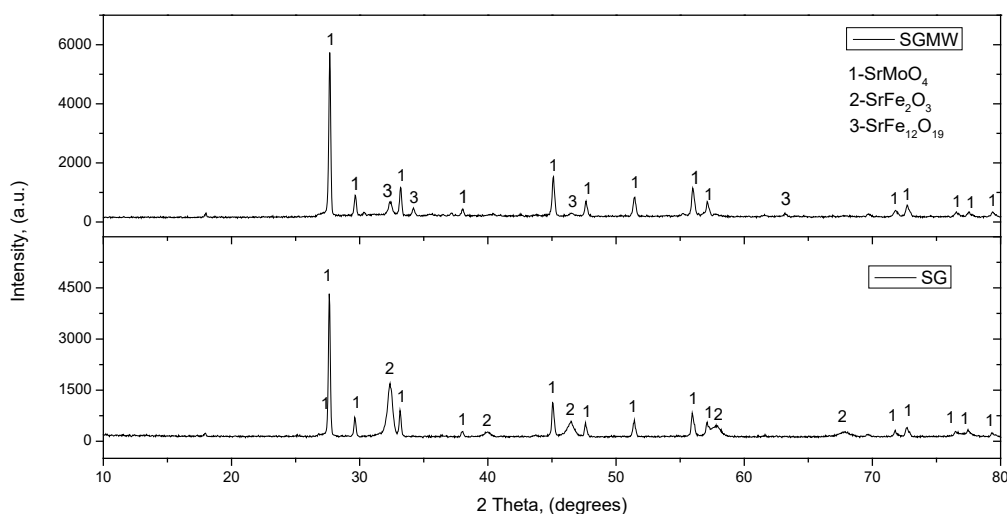
Figure 3 shows the XRD pattern of the SGMW and SG samples after the reduction process. In this final step the Sr_2FeMoO_6 (PDF: 01-072-6394) phase is formed. For the intensity in both samples, it can be seen that the SGMW sample shows a better crystallinity compared with the SG sample, the background in the SGMW XRD pattern changes between 25° and 45°, this change shows the presence of an amorphous phase.

Also the widths of the Bragg reflections in SGMW are bigger than those of SG, these phenomena talks about the crystallite size, where the crystallite size is smaller for the SFMO synthesized by microwaves than those obtained by the conventional Sol-gel technique, 24nm for SGMW and 415nm for SG sample (the crystallite size was obtained by Scherrer method).

Figure 3. XRD patterns of the SGMW and SG samples after the reduction process. In this final step the Sr_2FeMoO_6 phase is formed, the intensity of the Bragg reflections shows a better crystallinity for the SGMW sample.
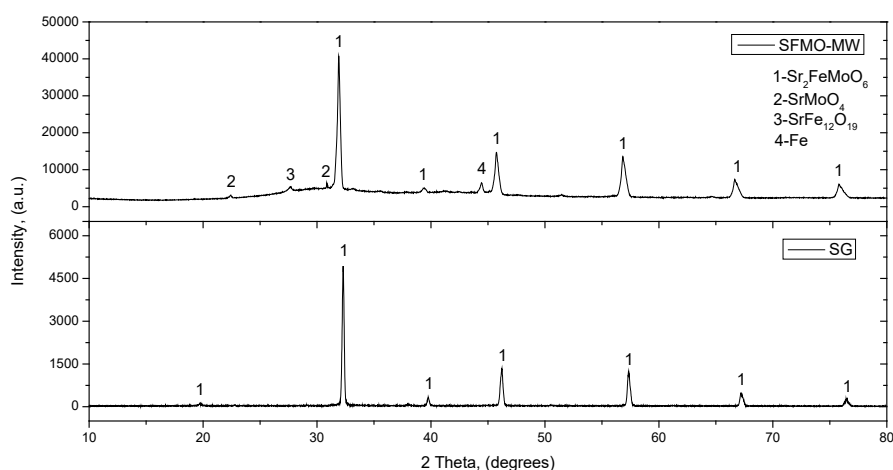
3.2 Scanning electron microscopy

The SEM was carried out using a JSM-IT300 operated at 10.0KeV. In order to see the morphology of the system a secondary electron image was carried out, a secondary electron (SE), Figure 4 illustrate the morphology of the SGMW sample and the SG sample after the calcination process. The notable difference in both samples is the spherical shape for the SGMW, this shape can be attributed for hydrothermal process involved in the microwave assisted synthesis. The SG sample shows a porous network of the precursor phases, this morphology is attributed to the drying process in the sol-gel process.

An energy dispersed X-ray (EDS) mapping analysis for chemical characterization was carried out, in the Figure 5 it is show the distri-

bution of the iron atom in the sample SGMW after the microwave assisted synthesis, it can be seen that there is iron all over the area except in the biggest spheres; Figure 6 shows the distribution of oxygen, strontium and molybdenum, a phase of oxide of strontium and molybdenum is in the biggest spheres. The spectrum of this analysis is shown in figure 7.

Figure 4. Secondary electrons image of the SGMW and SG samples; SGMW shows particles with an spherical shape; SG sample shows a complicated network of the precursor phases.
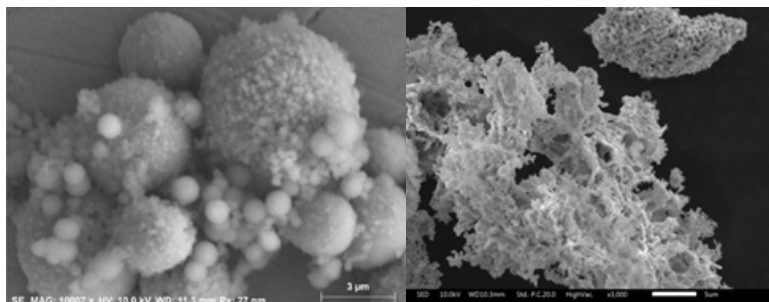

Figure 5. Image of the EDS analysis of the sample SGMW after the calcination process, the morphology of the sample is illustrated in the left side and the iron distribution in the same area is shown in the right side.
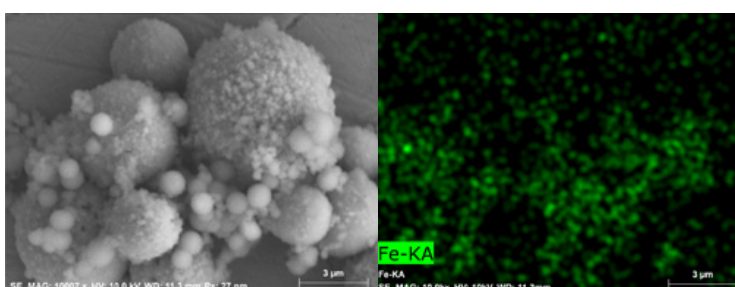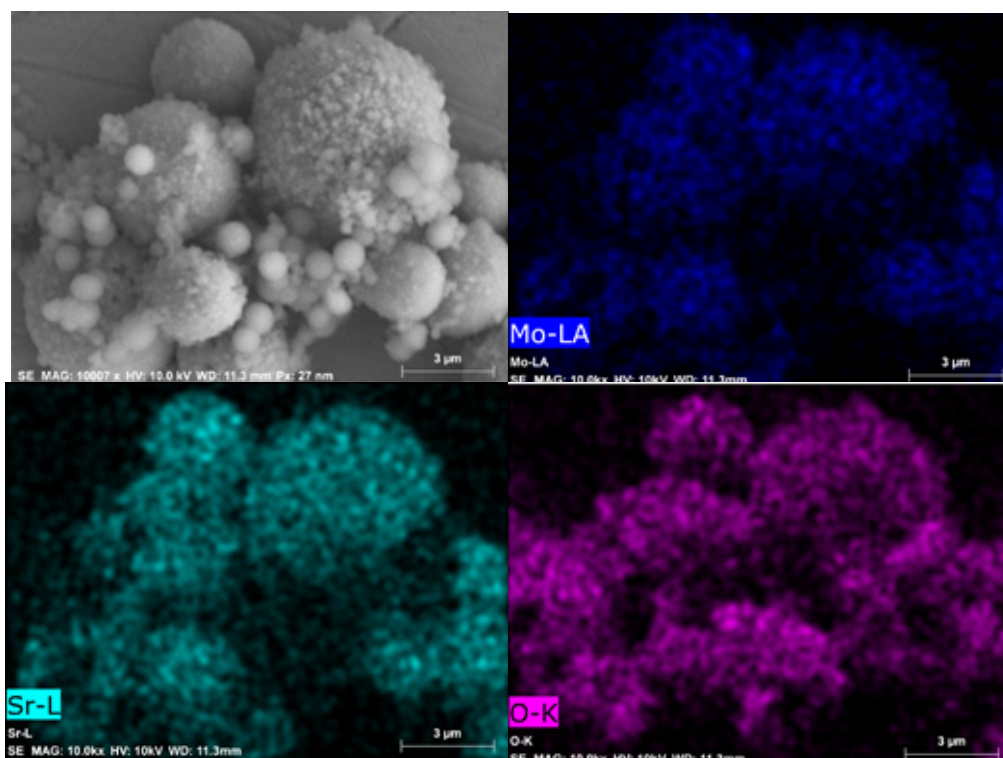

Figure 6. Image of the EDS analysis of the sample SMW1 after the calcination process, the morphology of the sample is illustrated in the upper right corner; the distribution of oxygen is in the upper left corner; the strontium distribution is shown at the bottom right corner; the molybdenum distribution is shown at the bottom left corner.
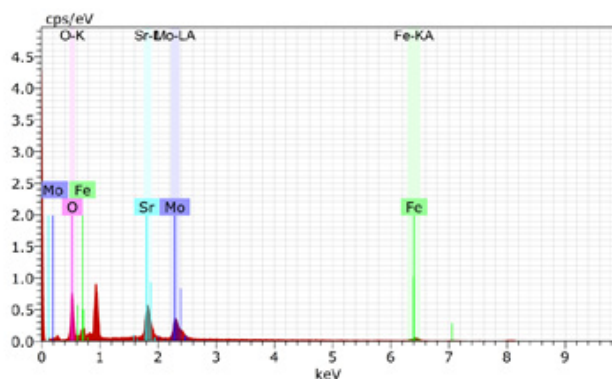
Figure 7. Spectrum of the EDS analysis for the sample SGMW after the calcination process.

4. DISCUSSION

The x-ray diffraction pattern for the SGMW sample (Figure 2) shows that the precursors $SrMoO_4$ and Fe_2O_3 were produced under the microwave synthesis condition, also the sample SGMW results in a better crystallinity that the sample SG, this can be seen for the intensity of the Bragg diffraction and its defined morphology, however, when the sample was calcined, the presence of $SrFe_{12}O_{19}$ was observed (Figure 2), instead of strontium and iron 1:1 compounds that were desirable, this change caused the creation of iron phases when the sample was reduced (figure 3). With regard to the morphology of the sample synthesized by microwaves (figure 4) we can see a change in the shape of the particles, changing to a spherical shape instead of disordered clusters shape and high porosity, this change of shape should be to the pressure reached inside the container when the sample was synthesized by microwave. Microwave assisted synthesis has given rise to new forms in the morphology of the system and future experiments will have to be done to get a sample of Sr_2FeMoO_6 without contaminating phases.

5. CONCLUSION

The sol gel process by metal citrates is a technique that depends on many factors such as the pH, the salts used, and the amount of water in the sol creation and also in the homogenous distribution of the metallic cations in the gel. Although the microwave-assisted synthesis process allows a uniform heating throughout the solution, increasing the pressure in the container can be a factor to generate the iron phase that are found together with the Sr_2FeMoO_6 final system, the XRD pattern of the synthesized samples with microwaves show an increase in the crystallinity of the system with respect to those synthesized in a conventional way. The morphology of the precursors formed by the microwave assisted synthesis is shown to be more uniform and in a defined way.

In order to find the ideal conditions in which the microwave-assisted synthesis improves the creation of the final system (Sr_2FeMoO_6) it is necessary to play with the conditions as the pH in the solution, the temperature and even change the type of acid that is used. The formation of the gel in the solution is of vital importance in a sol-gel process, improving the gelation process and homogeneity it can achieve much more promising results for the synthesis of these quaternary systems.

ACKNOWLEDGEMENTS

REFERENCES

Cernea, M., F. Vasiliu, C. Plapcianu, C. Bartha, I. Mercioniu, I. Pasuk, R. Lowndes, R. Trusca, G. V. Aldica, and L. Pintilie. 2013. Preparation by sol-gel

and solid state reaction methods and properties investigation of double perovskite Sr2FeMoO6. J. Eur. Ceram. Soc. 33:2483–2490.

Danks, A. E., S. R. Hall, and Z. Schnepp. 2016. The evolution of "sol–gel" chemistry as a technique for materials synthesis. Mater. Horizons 3:91–112.

Hench, L. L., and J. K. West. 1990. The sol-gel process. Chem. Rev. 90:33–72.

Kobayashi, K.-I., T. Kimura, H. Sawada, K. Terakura, and Y. Tokura. 1998. Room-temperature magnetoresistance in an oxide material with an ordered double-perovskite structure. Nature 395:677–680.

Komarneni, S., R. Roy, and Q. H. Li. 1992. Microwave-hydrothermal synthesis of ceramic powders. Mater. Res. Bull. 27:1393–1405.

de la Hoz, A., Á. Díaz-Ortiz, and A. Moreno. 2005. Microwaves in organic synthesis. Thermal and non-thermal microwave effects. Chem. Soc. Rev. 34:164–178.

Li, X. H., Y. P. Sun, W. J. Lu, R. Ang, S. B. Zhang, X. B. Zhu, W. H. Song, and J. M. Dai. 2008. Size dependence of electronic and magnetic properties of double- perovskite Sr2FeMoO6. 145:98–102.

Liu, S., Æ. X. Qian, and Æ. J. Xiao. 2007. Nanopowders by microwave assisted sol – gel route. :187–193.

Reyes, A. M., Y. Arredondo, O. Navarro. 2016. First principles study of the effects of disorder in the Sr2FeMoO6 perovskite. Rev. Mex. Física 62:160–163.

Soto, T. E., J. L. Valenzuela, R. Mondragón, R. Morales, J. Lemus-Ruíz, and O. Navarro. 2014. Synthesis of the off-stoichiometric oxide system Sr2Fe1+xMo1-xO6 with -1 <x <0.25. Phys. B Condens. Matter 455:6–9. Valenzuela, J. L., T. E. Soto, J. Lemus, O. Navarro, and R. Morales. 2014. Reaction kinetics of the double perovskite Sr2FeMoO6 by gas-solid reactions. Phys. B Condens. Matter 455:10–13.

Zhai, Y., J. Qiao, G. Huo, and S. Han. 2012. Synthesis, magnetic and electrical transport properties of magnetoresistance material Sr2FeMoO6 by microwave sintering. J. Magn. Magn. Mater. 324:2006–2010.