Synthesis and TDPAC Characterization of Multiferroics: The HoMnO$_3$ Case

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1. Introduction

This perovskite family structure presents a vast number of physical properties such as ferroelectricity, high-temperature superconductivity, and colossal magnetoresistance, which draw attention to the solid-state community. During the last two decades, the perovskite-like structures have been extensively studied thanks to their potential application in spintronic equipment and data storage and sensors [1]. Among these perovskite family the rare-earth manganites, the RMnO$_3$ (R=rare earth) compounds also point to applications in fundamental physics perspectives since spin-charge–orbital coupled systems in transition-metal oxides, i.e., a strong coupling between ferroelectricity and magnetism, offer a wide field of investigation [2]. Among techniques that characterize these structures, we emphasize, due to their local character on a subnanoscopic scale, the hyperfine interactions. It also has a great potential to produce valuable information about the interaction mechanisms in multiferroic oxides.

According to the literature, we observe that the Time-Differential $\gamma - \gamma$ Perturbed Angular Correlation (TDPAC) is the technique of hyperfine interactions with the greatest potential in the investigation of multiferroics [3]. It is a method of nuclear solid-state physics that investigates the magnetic and electric fields in crystal structures by a consecutive measurement of two gamma rays of a cascade decay of radioactive elements allocated to specific crystal lattices. Since it allows the measurement of dynamic interactions, which can be useful in the investigation of spin fluctuations and the movement of charge carriers.

According to the rare-earth ionic radius, we observe a different tendency of the structure formation and elements as Ho, Y, and Er, which form naturally hexagonal structures (space group P 63 c m) are on the verge of the orthorhombic (space group P b n m) sector [4]. In this scenario of investigation, synthesis and studies consequently present this phase competition. That is, the route of synthesis plays an important role in defining the proportion between compounds of stable hexagonal and a metastable orthorhombic at the resulting sample.

Since both phases of HoMnO$_3$ are available for studying the ferroelectricity-magnetism coupling, our first approach is to obtain routes that provide single-phase samples. In this sense, by an individual description of these phases, we can improve our analysis of the multiphase samples and isolate their properties. This procedure is fundamental to future works of more complex compounds, as HoMn$_2$O$_5$, for instance. In addition, we also left for further work the analysis of doped HoMnO$_3$ since it influences Gibbs free energy values and consequently in grain growth and can favor one specific phase next others [5].

The complete procedure of HoMnO$_3$ analysis is then composed by synthesis of hexagonal and orthorhombic phases, where the latter possess two routes according to literature, i.e., soft chem-

istry and high pressure [6]. After synthesizing, one has to dope samples with ^{111}In to insert probe nuclei into the Ho (or R) in the cell structure site for TDPAC analysis [7].

Recently, many techniques have been using on the perovskite-like synthesis, such as the solid-state method, citrate combustion, sol-gel, and Pechini method. In addition, we observe that $RMnO_3$ (R = Tb, Ho) investigation utilizing the TDPAC technique is no longer present in the literature. For this reason, we intend to create an entire procedure of synthesis and characterization of the $HoMnO_3$ compound by utilizing the sol-gel technique, since it is a simple-low-cost approach to sintering these compounds. Syntheses utilizing the sol-gel method are not frequent in literature, even though a few modified approaches take place. For this reason, a route for HoMnO3 employing sol-gel synthesis stands as a valuable investigation.

In this work, we investigate a synthesis route to obtain the hexagonal $HoMnO_3$ phase. Such an approach has been adapted from literature routes and according to our Lab structure limitations. We check the crystallographic structure of the sample by X-ray diffraction and then submit it to the ^{111}In doping process. Finally, TDPAC measurements are performed and ferroelectricity and magnetism are discussed. Perovskite synthesis routes and analysis are left for future works.

2.   Methodology

According to the literature, and since the hexagonal $HoMnO_3$ structure is stable, we observe multiple scenarios of this compound synthesis. It is given that high-temperature (more than $1000°C$) sintering enables the appearance of perovskite structures in the final sample amount [8].

On the other hand, the synthesis of orthorhombic metaphase $HoMnO_3$ require two possible routes, according to literature. They are utilizing low-temperature soft chemistry method or through a high-pressure treatment at $3.5GPa$ and $1020°C$ [8]. From this information, we intend to add an extra high-pressure treatment step to the previous hexagonal synthesis procedure to obtain orthorhombic structures. We prioritize the high-pressure technique since this route represents only an extra step to be added at the end of the hexagonal HoMnO3 synthesis.

The stoichiometric ratio of pure Mn and Ho have been dissolved in acid with stirring at room temperature. After dissolution, both liquids have been mixtured and raised to $80°C$. According to the sol-gel procedure, we have added ethylene glycol and citric acid to induce gelation. The resulting gel has been heated at $180°C$ while keeping the stirring until getting a dry black precipitate at the bottom of the becker. Remains have been grounded into fine black powders, and then it has been decomposed at $400°C$. The obtained powder has been ground and presintered in the oven in the atmosphere with a heating rate of $3°C/min$ for an initial temperature of 600 for $12h$ and then to $1000°C$ for $12h$ and with the same heating rate. We have performed the last sintering step by heating the resulting sample at $1100°C$ in pellet form for $12h$ [9].

We have used an agate mortar to ground the pellets into powder, which has been characterized by the RIGAKU SmartLab X-ray Diffractometer at room temperature. The structure refinements based on the XRD data have been performed with the GSAS software [10]. The equipment setup for this measurement has been adjusted for an angular speed of $2°/min$ with $0.05°$ step and angle scanning range between $10°$ and $80°$. In order to dope hexagonal $HoMnO_3$ and then apply the TDPAC technique, some drops of [111]$InCl_3$ have been deposited onto powder pellets. The ^{111}In thermal diffusion has been performed at a vacuum atmosphere in steps from 150 to $750°C$. Here, we have monitored the diffusion process by means of the TDPAC technique.

3. Results and Discussion

Results of refinement of Rietveld are displayed in Figure 1. From this analysis, we have been able to obtain a proper route of synthesis that provides about 90% of hexagonal $HoMnO_3$ against 10%. From this process, we intend to impose, in future analysis, a higher temperature and longer sintering time to obtain a quasi-pure final sample. However, through such proportion phases, we are already able to isolate the hexagonal ferroeletric-magnetic behavior.

The diffractogram and its correspondent refinement adjustments are present in Figure 1, where black crosses and the red curve stand for measurement data and calculated diffraction pattern, respectively. Additional information on the refinement data of both phases is summarized and presented in Table I.
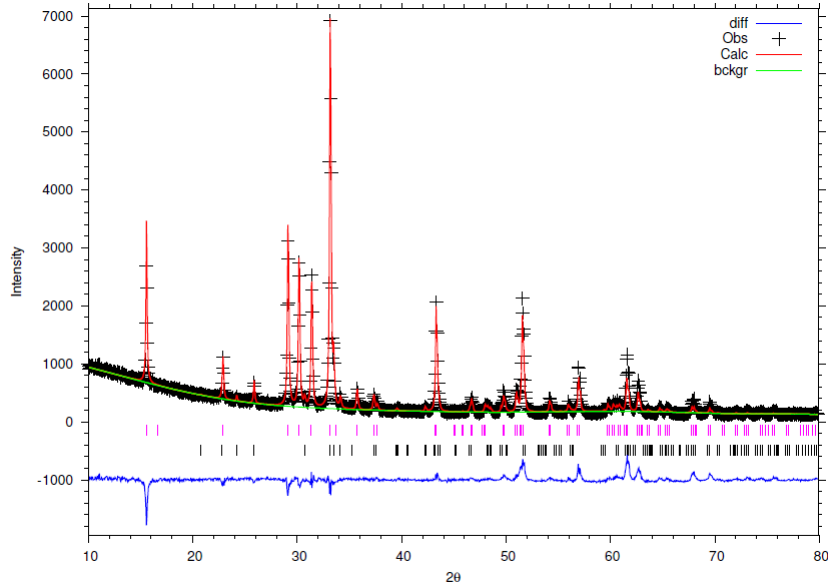

Figure 1: Room temperature X-ray powder diffraction patterns of $HoMnO_3$. The Rietveld refinement indicates a phase composition of 90% hexagonal and 10% of the orthorhombic compound, approximately. The green, red and blue curves stand for background, calculated curve, and the difference between calculation and measured data, respectively. Black crosses are diffractometer data values, and pink and black dashes indicate crystallographic peaks of hexagonal and orthorhombic phases, respectively.

Table I: Unit-Cell parameters, space group, and weight percentage for the refinements of HoMnO3 phases.

Phase	Space Group	Percentage	Cell Parameters						
			a(Å)	b(Å)	c(Å)	α	β	γ	Volume (Å^3)
Hexagonal	P 63 c m	90.05%	6.146	6.146	11.423	90.0	90.0	120.0	373.7
Orthorhombic	P b n m	9.95%	5.260	5.828	7.364	90.0	90.0	90.0	225.7

Initial PAC measurements have already been performed, and results are promising, but these outcomes are still premature, and further tests with $^{111}InCl_3$ diffusion and PAC monitoring remain necessary. Correspondent data are under preparation to fulfill this branch of hexagonal $HoMnO_3$ study and presentation in the INAC congress. From these results, we intend to expand this procedure of analysis for orthorhombic $HoMnO_3$ and also other $RMnO_3$-like systems. In this sense, TDPAC spectroscopy was applied to study the peculiarities and temperature evolution

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of local magnetic and electric structures and the centrosymmetric break of this compound.

4. Conclusions

Our preliminary conclusions indicate that the synthesis process of the hexagonal HoMnO$_3$ compound is successful, and just a few details have to be adjusted to decrease the orthorhombic phase in the final compound. According to the literature, we are led to believe that higher temperatures allow inhibiting the appearance of this metaphase.

Acknowledgments

References

[1] V. Hreb, I. Lutsyuk, V. Kochubei and L. Vasylechko, "New Mixed Manganites-chromites RMn1-xCrxO3 and Manganites-gallates RMn1-xGaxO3", *2020 IEEE 10th International Conference Nanomaterials: Applications & Properties (NAP)*, pp. 1-6 (2020)

[2] H.W. Brinks, H. Fjellvåg, A. Kjekshus, Synthesis of Metastable Perovskite-type YMnO3 and HoMnO3, *Journal of Solid State Chemistry*, vol. 129, pp. 334-340 (1997)

[3] G. N. Darriba, L. A. Errico, P. D. Eversheim, G. Fabricius, and M. Rentería, "First-principles and time-differential $\gamma - \gamma$ perturbed-angular-correlation spectroscopy study of structural and electronic properties of Ta-doped TiO2 semiconductor" *Phys. Rev. B*, vol. 79, pp. 115213 (2009)

[4] W. Prellier, M. P. Singh and P. Murugavel,"The single-phase multiferroic oxides: from bulk to thin film", *J. Phys.: Condens. Matter*, vol. 17, pp. 803 (2005)

[5] H. T. Wang, T. Zhou, B. Hong, Q. Tao and Z. A. Xu, "Magnetic Properties of Orthorhombic Perovskite Ho$_{1-x}$La$_x$MnO$_3$", *Chinese Phys. Lett.*, vol. 28, pp. 027501 (2011)

[6] K. Uusi-Esko, J. Malm, N. Imamura, H. Yamauchi, M. Karppinen, "Characterization of RMnO3 (R=Sc, Y, Dy-Lu): High-pressure synthesized metastable perovskites and their hexagonal precursor phases", *Materials Chemistry and Physics*, vol. 112, pp. 1029-1034 (2008)

[7] E. L. Muñoz, M. E. Mercurio, M. R. Cordeiro, L. F.D. Pereira, A. W. Carbonari, M. Rentería, "Dynamic hyperfine interactions in 111In(111Cd)-doped ZnO semiconductor: PAC results supported by ab initio calculations", *Physica B: Condensed Matter*, vol. 407, pp. 3121-3124 (2012)

[8] B. Lorenz, Y. Q. Wang, Y. Y. Sun, and C. W. Chu, "Large magnetodielectric effects in orthorhombic HoMnO3 and YMnO3", *Phys. Rev. B*, vol. 70, pp. 212412 (2004)

[9] A. Tozri, E. Dhahri, "High-temperature dielectric behavior of hexagonal HoMnO3", *Journal of Physics and Chemistry of Solids*, vol. 152, (2021)

[10] B. H. Toby, "EXPGUI, a graphical user interface for GSAS", *J. Appl. Cryst.*, vol. 34, pp. 210-213 (2001)