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# Structural and magnetic evaluation of the $CaTi_{1-x}M_xO_3$ (M = Dy, Ho, Gd) (x = 0.5) System

# Evaluación estructural y magnética del sistema $CaTi_{1-x}M_xO_3$ (M = Dy, Ho, Gd) (x = 0,5)

# Avaliação estrutural e magnetica do sistema $CaTi_{1-x}M_xO_3$ (M = Dy, Ho, Gd) (x = 0,5)

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## Abstract
In this work we studies and evaluates the structural and magnetic properties of $CaTi_{1-x}M_xO_3$ system where M = Dy, Ho, and Gd, using a substitution level of x = 0.5, in order to improve the magnetic response of synthesized materials by the solid state reaction method. For each system stoichiometric quantities of $TiO_2$, $Ho_2O_3$, $Dy_2O_3$, $Gd_2O_3$ and $CaCO_3$ precursors were used, which were treated at 973,15 K for 2 hours and grounded to ensure the homogeneity of compositions. The structural characterization was initiated by a modelling process provided by the SPuDS software, which allowed to evaluate the critical tolerance values of the structures under temperature conditions. The X-ray diffraction analysis and Rietveld refinement using the GSAS and EXPGUI software, revealed that all samples exhibit an orthorhombic configuration with spatial group *Pnma* (62). The magnetic characterization evaluates the magnetic behavior of the systems according to the magnetization curves as a function of temperature and the hysteresis curves as a function of the external field that is applied to each of the proposed systems, resulting in a paramagnetic behavior. These results demonstrate that it is necessary to complement this information to provide more effective tools in the synthesis of these materials, when determining the effect of the mass transport properties, that could affect the distribution of cation B and thus to clarify the optimal structure (with possible vacancies Of oxygen), which would lead to the formation of complex extended defects in the solids.

***Keywords:*** *paramagnetic, perovskite, rietveld refinement, solid state reaction.*

## Resumen
En este trabajo estudian y evalúan las propiedades estructurales y magnéticas del sistema $CaTi_{1-x}M_xO_3$ donde M = Dy, Ho y Gd, utilizando un nivel de sustitución de x = 0,5, con el fin de mejorar la respuesta magnética de los materiales sintetizados por el método de reacción en estado sólido. Para cada sistema se utilizaron cantidades estequiométricas de $TiO_2$, $Ho_2O_3$, $Dy_2O_3$, $Gd_2O_3$ y $CaCO_3$, las cuales se trataron a 973.15 K durante 2 horas, para asegurar la homogeneidad de las composiciones. La caracterización estructural se inició mediante un proceso de modelado proporcionado por el *software* SPuDS, que permitió evaluar los valores críticos de tolerancia de las estructuras bajo condiciones de temperatura. El análisis de difracción de rayos X y refinamiento de Rietveld utilizando el *software* GSAS y EXPGUI reveló que todas las muestras exhiben una configuración ortorrómbica con grupo espacial *Pnma (62).* La caracterización magnética evalúa el comportamiento magnético de los sistemas de acuerdo con las curvas de magnetización, en función de la temperatura y en función del campo magnético externo que

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se aplica a cada uno de los sistemas propuestos. De esto resulta un comportamiento paramagnético. Estos resultados demuestran que es necesario complementar esta información, para proporcionar herramientas más efectivas en la síntesis de estos materiales, al determinar el efecto de las propiedades de transporte masivo, que podrían afectar la distribución del catión B y así aclarar la estructura óptima (con posibles vacantes de oxígeno), lo que conduciría a la formación de complejos defectos extendidos en los sólidos.

***Palabras clave:*** *paramagnético, perovskita, reacción de estado sólido, refinamiento rietveld.*

**Resumo**

O trabalho atual estuda e avalia as propriedades estruturais e magnéticas do sistema $CaTi_{1-x}M_xO_3$ onde M = Dy, Ho e Gd, usando um nível de substituição de x = 0,5, para melhorar a resposta magnética dos materiais sintetizados por o método de reação no estado sólido. Para cada sistema foram utilizadas quantidades estequiométricas de $TiO_2$, $Ho_2O_3$, $Dy_2O_3$, $Gd_2O_3$ e $CaCO_3$, que foram tratadas a 973,15 K por 2 horas para assegurar a homogeneidade das composições. A caracterização estrutural foi iniciada através de um processo de modelagem fornecido pelo software SPuDS, que permitiu avaliar os valores críticos de tolerância das estruturas sob condições de temperatura. A análise de difração e refinamento de raios-X de Rietveld usando o software GSAS e EXPGUI revelou que todas as amostras exibem uma configuração ortorrôbica com um grupo espacial *Pnma (62).* A caracterização magnética avalia o comportamento magnético dos sistemas de acordo com as curvas de magnetização em função da temperatura e como função do campo magnético externo que é aplicado a cada um dos sistemas propostos, resultando em um comportamento paramagnético. Estes resultados mostram que é necessário complementar esta informação para fornecer ferramentas mais eficazes na síntese desses materiais, ao determinar o efeito das propriedades de transporte em massa, o que pode afetar a distribuição do catião B e, assim, esclarecer a estrutura ideal (com possíveis vagas de oxigênio), o que levaria à formação de defeitos complexos prolongados em sólidos.

***Palavras chave:*** *paramagnético, perovskita, reação de estado sólido, refinamento rietveld.*

## Introduction

The $CaTiO_3$ is a perovskite with a basic cubic structure present in a wide variety of materials, where A is an element of the representative metal group (IIA) and B is a transition metal (IVB) [1]. The properties of this system are governed by the elements A and B, which could be modified by means the synthesis methods through of substitution, doping or modification. Special attention deserves the substitutions made with elements of the rare earth series, achieving promising physicochemical properties due to the chemical stability related with these atoms, creating a series of distortions in the lattice which are reflected in the magnetic properties and electronic conduction levels [2]. On the other hand, although the solid state reaction method has been adequate to obtain this type of systems, starting from corresponding high purity oxides with excellent results at compositional and structural level, some drawbacks are important due to impurity generated by the low kinetic reaction related with the solid state at high temperatures [3]. For this reason, with the aim of reduce these adverse effects, some authors evaluate the possibility of increase the magnetic response of these oxides by means the incorporation of Dy, Ho, and Gd which make these systems were effective in various technological applications, such as magnetic and optoelectronic devices, described and proposed in literature [4]. Although the incorporation of rare earth in systems derived from $CaTi_{1-x}M_xO_3$ system, represent a great interest in several nanotechnology areas for the manufacture of advanced equipment and opto-electronic materials in the automotive and biomedical industry, is clear that the electronic configuration $4f^n$ of these atoms, is the main responsible of spin-electron interactions in an electric field, this phenomenon can be controlled by modifications of the cations of $CaTiO_3$, which is widely described in the literature, generating new developments in materials science [1,5]. This work focuses on the synthesis, structural and magnetic characterization of the $CaTi_{1-x}M_xO_3$ system, where M = Dy. Ho, Gd with a degree of substitution of x = 0.5 by the solid-state reaction method, with the purpose of evaluate the effect of ionic radii on the stability and properties of the structure.

## Methodology

The synthesis of the $CaTi_{0.5}M_{0.5}O_3$ (M = Dy, Ho, Gd) perovskite, starting from corresponding metal oxides of CaO, $TiO_2$, $Dy_2O_3$, $Ho_2O_3$ and $Gd_2O_3$ 99.9 % all from Sigma-Aldrich. In all cases, the solids were grounded in an agate mortar for 4 hours, to promote a high degree of homogenization. The solids were identified as follows: $CaTi_{0.5}Dy_{0.5}O_3$ (CTDO), $CaTi_{0.5}Ho_{0.5}O_3$ (CTHO) and $CaTi_{0.5}Gd_{0.5}O_3$ (CTGO), which were pressed in a pellet form using hydrostatic press operated at 2.0 MPa. The pellets were treated at 1273.15 K for 24 hours and sintering at 1423.15 K for 24 hours respectively in air atmosphere. The structural parameters were evaluated by X-ray diffraction in a PANalytical X'Pert diffractometer with Cu Kα radiation (λ = $1.54x10^{-10}$ m), between 20° to 90°. The analysis of the diffraction patterns were done through the Rietveld routine using the GSAS software. The magnetization measurements based on the applied magnetic field and temperature were carried out on a Versalab vibrating sample magnetometer (VSM), with temperatures between 50 K and 300 K and magnetic fields between -30 kOe and 30 kOe.

## Results and discussion

From the X-ray diffraction analysis shown in Figure 1, is clear that the $CaTi_{0.5}M_{0.5}O_3$ system (M = Dy, Ho, Gd) is present in an orthorhombic structure with a spatial group *Pbnm (62)* which constitutes the main crystalline phase. The average grain size domains indicate values around $3.5x10^{-8}$ $-3.7x10^{-8}$ m for the obtained materials, which were calculated using the Debye-Scherrer equation from the highest diffraction signals [6].

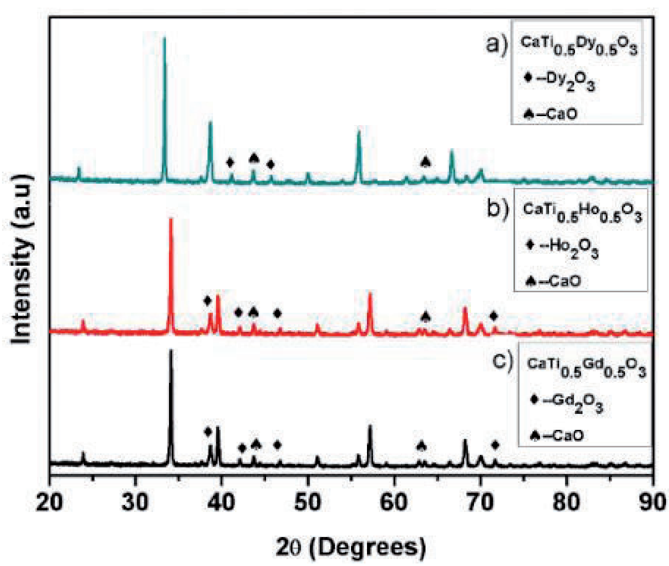


**Figure 1.** X-ray diffraction patterns for a. CTDO, b. CTHO and c. CTGO systems.

The analysis of the lattice parameters and crystalline phases based on the Rietveld refinement method shown in figure 2, show that the modification of $CaTiO_3$ with Dy, Ho and Gd was effective and the presence of secondary phases is insignificant [7,8]. Two impurities were identified in each system, corresponding with rare earth oxides, which are identified with the (♦) and (♠) symbols for the CaO and $RE_2O_3$ respectively. In the case of CTDO system the solid shown an *I a-3 (206)* spatial group while in the CTHO and CTGO systems was clear a classification according with *Fm-3m (225)* spatial group respectively. These structures were indexed from corresponding crystallographic data and summarized in the Tables 1-3.

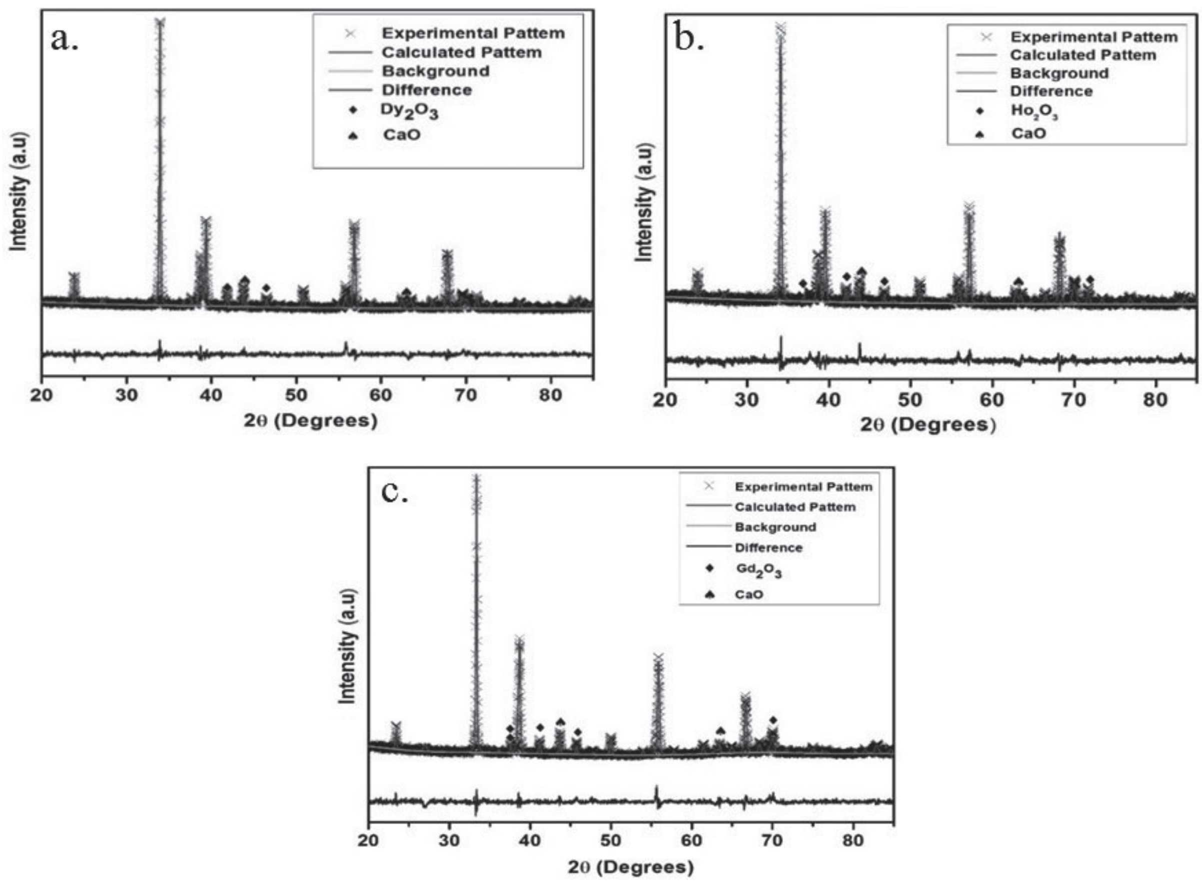


**Figure 2.** Rietveld refinement for the **a.** CTDO, **b.** CTHO and **c.** CTGO systems.

**Table 1.** Lattice parameters and crystalline phase data derived from Rietveld refinement method for the CTDO system.

| **Lattice Parameters** | | | |
|---|---|---|---|
| **System:** | **$CaTi_{0.5}Dy_{0.5}O_3$** | **$Dy_2O_3$** | **CaO** |
| a(Å) | 5.3954 (0.0004) | 10.6530 (0.0001) | 4.8107 (0.0001) |
| b(Å) | 5.4225 (0.0005) | 10.6530 (0.0001) | 4.8107 (0.0001) |
| c(Å) | 7.6245 (0.0009) | 10.6530 (0.0001) | 4.8107 (0.0001) |
| Cell volume (Å$^3$) | 223.0710 (0.0420) | 1208.9970 (0.0340) | 111.3390 (0.0140) |
| $\chi^2$ = 1.04 | **$R^2$ =** 6.45 | **Rwp (%) =** 9.36 | **Rp (%) =** 7.08 |
| **Angles:** α=β=γ=90° | | **Space Group:** *Pbnm* (62) | |

| **Atomic Positions** | | | | |
|---|---|---|---|---|
| **Atoms** | **X** | **Y** | **z** | **OCC** |
| Ca | 0.0061 | 0.5354 | 0.2500 | 1.0 |
| Ti | 0.0000 | 0.0000 | 0.0000 | 0.5 |
| Dy | 0.0000 | 0.0000 | 0.0000 | 0.5 |
| O | 0.9642 | 0.9754 | 0.2500 | 1.0 |
| O | 0.0026 | 0.5109 | 0.0924 | 1.0 |

**Table 2.** Lattice parameters and crystalline phase data derived from Rietveld refinement method for the CHDO system.

| Lattice Parameters | | | | |
|---|---|---|---|---|
| **System:** | **$CaTi_{0.5}Ho_{0.5}O_3$** | **$Ho_2O_3$** | **CaO** | |
| a(Å) | 5.3816 (0.0004) | 10.5832 (0.0001) | 4.8081 (0.0008) | |
| c(Å) | 5.4319 (0.0008) | 10.5832 (0.0001) | 4.8081 (0.0008) | |
| c(Å) | 7.6632 (0.0010) | 10.5832 (0.0001) | 4.8081 (0.0008) | |
| Cell Volume ($Å^3$) | 224.019 (0.0480) | 1185.373 (0.0420) | 111.156 (0.0580) | |
| **$\chi^2$ =** 1.12 | **$R^2$ =** 13.45 | **Rwp (%) =** 10.12 | **Rp (%) =** 7.79 | |
| **Angles**: α=β=γ=90° | | **Space Group:** *Pbnm* (62) | | |
| **Atomic Positions** | | | | |
| **Atoms** | **X** | **y** | **z** | **OCC** |
| Ca | 0.4964 | 0.0038 | 0.2500 | 1.0 |
| Ti | 0.0000 | 0.0000 | 0.0000 | 0.5 |
| Ho | 0.0000 | 0.0000 | 0.0000 | 0.5 |
| O | 0.6600 | 0.1862 | 0.2500 | 1.0 |
| O | 0.1477 | 0.3328 | 0.1730 | 1.0 |

**Table 3.** Lattice parameters and crystalline phase data derived from Rietveld refinement method for the CGDO system.

| Lattice Parameters | | | | |
|---|---|---|---|---|
| **System:** | **$CaT_{0.5}Gd_{0.5}O_3$** | **$Gd_2O_3$** | **CaO** | |
| a(Å) | 5.4101 (0.0004) | 10.7873 (0.0001) | 4.8117 (0.0001) | |
| c(Å) | 5.4423 (0.0011) | 10.7873 (0.0001) | 4.8117 (0.0001) | |
| c(Å) | 7.6333 (0.0021) | 10.7873 (0.0001) | 4.8117 (0.0001) | |
| Cell Volume ($Å^3$) | 224.756 (0.0800) | 1255.288 (0.0410) | 111.407 (0.0110) | |
| $\chi^2$ = 1.16 | **$R^2$ =** 11.89 | **Rwp (%) =** 11.01 | **Rp (%) =** 8.31 | |
| **Angles:** α=β=γ=90° | | **Space Group:** *Pbnm* (62) | | |
| **Atomic Positions** | | | | |
| **Atoms** | **X** | **y** | **z** | **OCC** |
| Ca | 0.4939 | 0.0354 | 0.2500 | 1.0 |
| Ti | 0.0000 | 0.0000 | 0.0000 | 0.5 |
| Gd | 0.0000 | 0.0000 | 0.0000 | 0.5 |
| O | 0.5719 | 0.4838 | 0.2500 | 1.0 |
| O | 0.2104 | 0.2891 | 0.0372 | 1.0 |

The magnetic characterization as a function of the temperature for all samples, suggest that the different modifications exhibit a paramagnetic behavior (M vs T), due to the presence of unpaired electrons in the $4f^n$ orbital in Dy, Ho and Gd cations, whose electrons suffer an orientation process along magnetic field direction (a) (figures 3-5).Through the hysteresis curve (M vs H), this paramagnetic behavior is corroborated by a linear trend in figure (b).

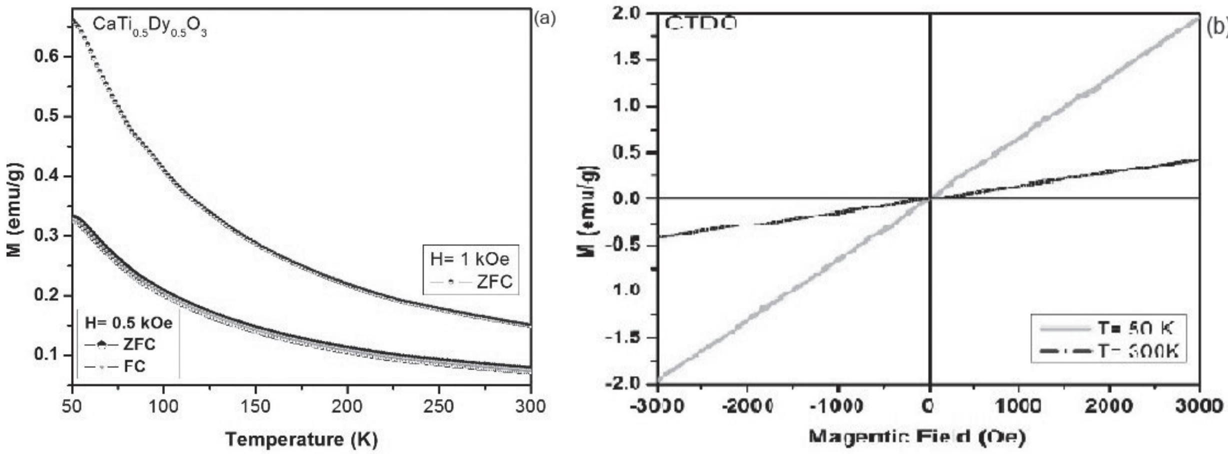


**Figure 3. a.** ZFC-FC magnetization curves at 1 kOe and 0.5 kOe for the $CaTi_{0.5}Dy_{0.5}O_3$ sample. **b.** M-H curves of CTDO system at 50 K and 300K.

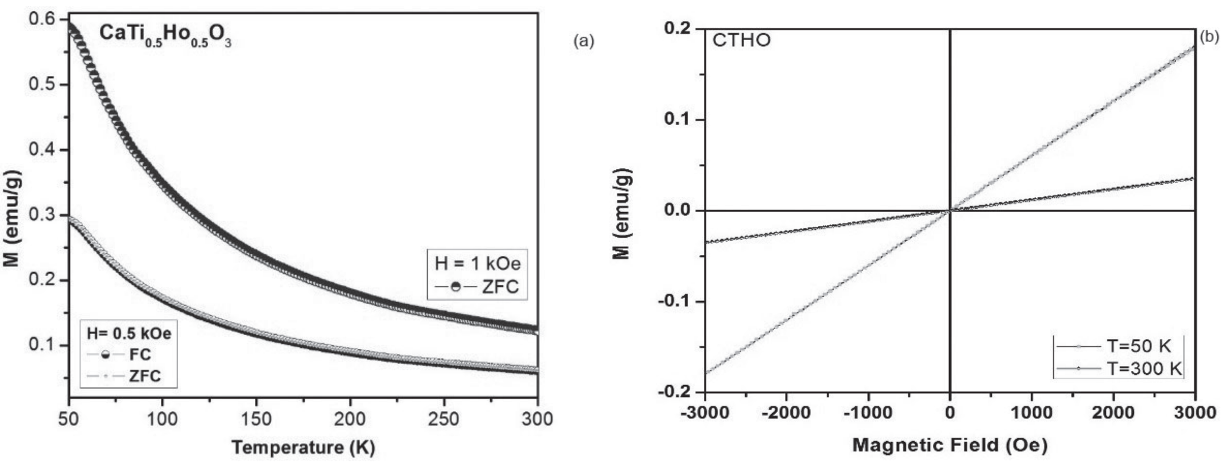


**Figure 4. a.** ZFC-FC magnetization curves at 1 kOe and 0.5 kOe for the $CaTi_{0.5}Ho_{0.5}O_3$ sample. **b.** M-H curves of CTHO system at 50 K and 300K.

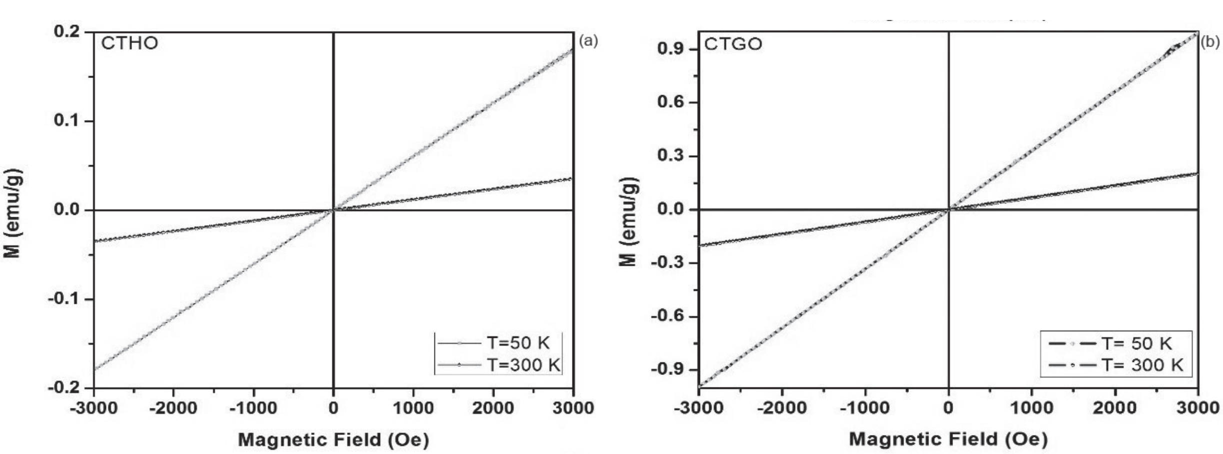


**Figure 5. a**. Magnetization vs temperature (ZFC-FC) at 1 kOe and 0.5 kOe for the $CaTi_{0.5}Gd_{0.5}O_3$ sample. **b.** M-H curves of CTGO system at 50 K and 300K.

Such results, corroborate a cationic distortion of $Ti^{3+}$ and $RE^{3+}$ cations, mainly provoked for the electronic interaction given by the metal occupation, due to the doping level (x = 0.5) used, which induces the modification of the structure and its magnetic character by modification bond distances between cations which results in the appearance of defects or dislocations and oxygen vacancies, when rare earths replace site $Ti^{3+}$, forming octahedral coordination [2,9,10,11].

In systems developed from manganites such as $CaMnO_3$, modified with Mo, this behavior can be observed in the form of paramagnetic-antiferromagnetic transition in substitutions of x = 0.1 at temperatures around 150K. [12]. Similarly, it is produced by modifying rare earth systems, such as the cerium oxide system modified with Praseodymium $Ce_{0.6}Pr_{0.4}O_2$, whose paramagnetic behavior increases as the temperature is reduced T ≤ 150K [13]. The above results are attributed to the sintering temperature of 1423,15K which gives it some degree of distribution to the material in terms of its structural and magnetic characteristics, which is evidenced in Mn-doped $CaTiO_3$ systems, which at a temperature of 1473,15K Has an antiferromagnetic behavior [5].

## Conclusions

The incorporation of rare earths in the $CaTi_{0.5}M_{0.5}O_3$ (M = Dy, Ho, Gd) system, synthesized by the standard solid state method, gives the material an orthorhombic crystal structure with a space group *Pbnm (62)* and Paramagnetic character given by the measurements of magnetization as a function of temperature and applied magnetic field, due to the ionic radius of the rare earth, observed in a range of 0.97 (Å) to 1.02 (Å) of these elements, which interact from such way with the titanium, giving rise to vacancies of oxygen that allow the distortion of the structural parameters; Heat treatment in this range of materials in terms of their structural and magnetic properties is also an influential factor given by order and ionic interaction at the electronic level.

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