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Exploration of the Structural, Electronic and Magnetic Properties of the New Perovskite Semiconductor Material $CaCo_{0.5}Zr_{0.5}O_3$

C. E. Deluque Toro[1], A. V. Gil Rebaza[2,3], J. Roa Rojas[4]

[1] Grupo de Nuevos Materiales, Facultad de Ingeniería, Universidad del Magdalena, Santa Marta, Colombia.
[2] Departamento de Física, Facultad de Ciencias Exactas (UNLP), Instituto de Física La Plata – IFLP, CONICET-CCT La Plata, La Plata, Argentina
[3] Grupo de Estudio de Materiales y Dispositivos Electrónicos (GEMyDE), Universidad Nacional de La Plata, Argentina
[4] Grupo de Física de Nuevos Materiales, Departamento de Física, Universidad Nacional de Colombia, Bogotá DC, Colombia

ABSTRACT

The study delves into the structural, electronic, and magnetic characteristics of the newly discovered perovskite semiconductor, $CaCo_{0.5}Zr_{0.5}O_3$. The material was synthesized using the standard solid-state reaction method, and its crystal structure was analyzed via Rietveld refinement of the X-ray diffraction pattern, revealing an orthorhombic structure within the Pcmn space group. To obtain a comprehensive understanding of its properties, morphological and compositional analyses were conducted using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). These analyses confirmed an average grain size of 1.19 ± 0.02 μm and underscored the material's minimal impurity content as per the EDX results. Thorough exploration of the electronic and magnetic properties was carried out through Ab-initio calculations. The Density of States (DOS) and band structure analyses provided critical insights: the material displays characteristics of a ferromagnetic semiconductor, featuring an average gap of 0.89 eV and a net magnetic moment of 2.0 μB. This in-depth analysis illuminates the distinct properties of $CaCo_{0.5}Zr_{0.5}O_3$, laying a foundational understanding for its potential applications in semiconductor technology.

INTRODUCTION

The physical properties of perovskite-type materials are intricately influenced by deviations from their idealized structures. Numerous investigations have been conducted on perovskite-type materials incorporating Calcium as the "A" cation and employing either Cobalt or Zirconium as the "B" cation. These studies have systematically addressed the subject matter from both theoretical and experimental standpoints [8-11]. In the present inquiry, a confluence of theoretical and experimental methodologies is applied to the emergent material $CaCo_{0.5}Zr_{0.5}O_3$. Within this compound, cobalt and zirconium atoms equitably share the position of the B cation within the ABX_3 perovskite-like structure, thereby instigating distortions in the octahedral sites. This unique configuration engenders distinct electronic and magnetic properties attributed to varying electronic orderings. Initially, an analysis of potential cell variants was undertaken to discern the most energetically stable positions for Co and Zr atoms. Calculations encompassed Non-magnetic (NM), Antiferromagnetic (AFM), and Ferromagnetic (FM) configurations. Notably, the ferromagnetic (FM) configuration demonstrated superior stability, as corroborated by subsequent electronic density and band structure calculations specific to this configuration.

EXPERIMENTAL METHOD

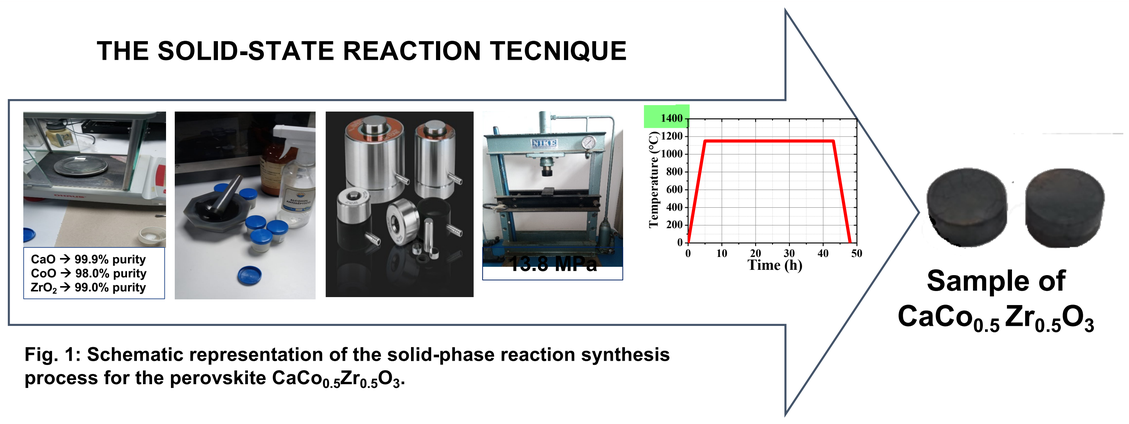
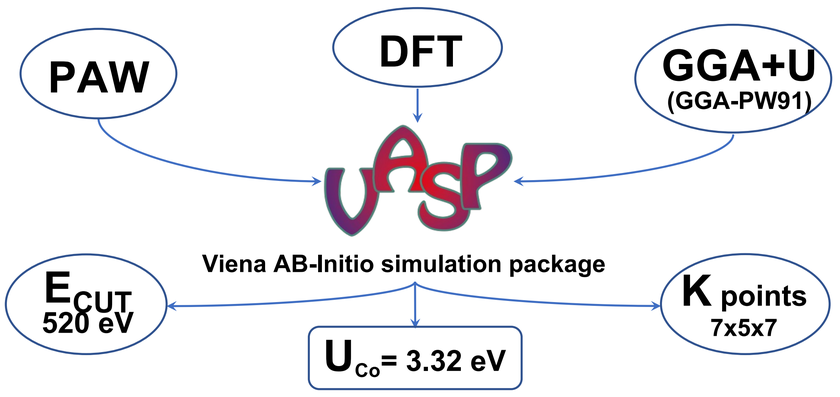


Fig. 1: Schematic representation of the solid-phase reaction synthesis process for the perovskite $CaCo_{0.5}Zr_{0.5}O_3$.

THEORETICAL CALCULATIONS



RESULTS AND DISCUSSION EXPERIMENTAL

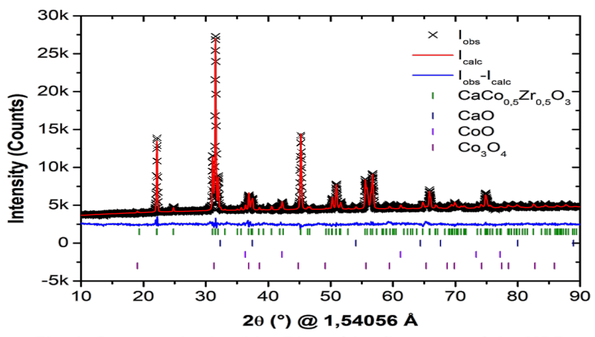


Fig. 2: Pattern obtained by Rietveld refinement of the XRD of perovskite $CaCo_{0.5}Zr_{0.5}O3$.

$CaCo_{0.5}Zr_{0.5}O_3$ –pbmn space group Latice Parameter a=5,59029Å b=8,00913Å c= 5,74830Å

Atom	Wyckoff postion	x	y	z	Uiso	Goodness of fit
Ca+2	4c	0,01023	0,25000	0,04024	0,03513	RWP =2,11%
Co+2	4b	0,00000	0,00000	0,50000	0,00154	Rw =2,08%
Zr+4	4b	0,00000	0,00000	0,50000	0,00154	R(F2)=7,33%
O-2(1)	4c	0,60578	0,25000	-0,02175	0,02175	X2=2,05
O-2(2)	8d	0,29550	0,05225	0,28951	0,02175	

Table1. Crystal structure parameters of the $CaCo_{0.5}Zr_{0.5}O_3$ material at room temperature, obtained by Rietveld refinement.

- Refinement of the X-ray diffraction pattern shows $CaCo_{0.5}Zr_{0.5}O_3$ as the majority phase with 96%.
- The material crystallizes in an orthorhombic structure with a Pcmn space group.

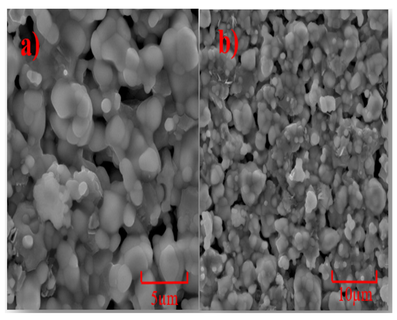


Fig. 3: SEM micrographs of the $CaCo_{0.5}Zr_{0.5}O_3$ composite surface amplified at 10kx (a) and 5kx (b).

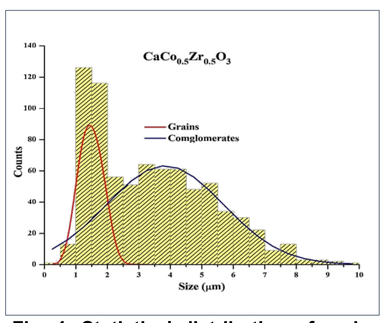


Fig. 4: Statistical distribution of grain size and clustering of the $CaCo_{0.5}Zr_{0.5}O_3$ material samples.

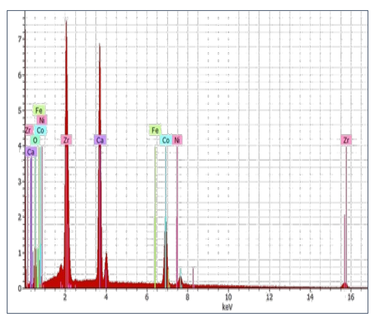


Fig.5: EDS compositional spectrum obtained from perovskite $CaCo_{0.5}Zr_{0.5}O_3$.

- SEM images reveal granular behavior and the formation of conglomerates.
- No cationic impurities are detected in the material.

DISCUSSION AND THEORETICAL RESULTS

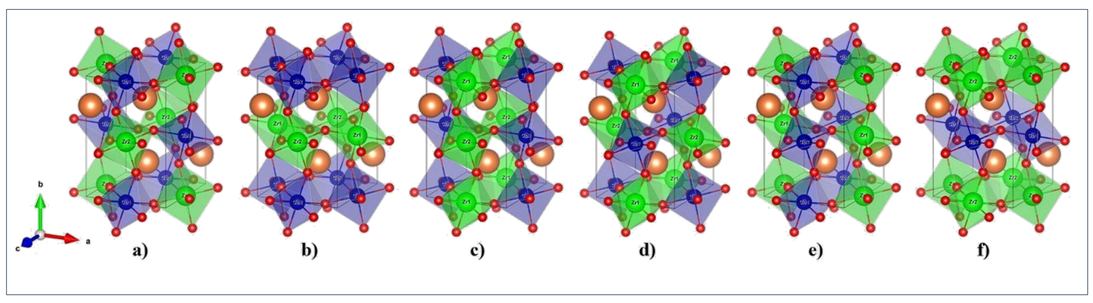


Fig. 7: Possible cell variants of the material CaCo0.5Zr0.5O3, according to the positions that the Co and Zr atoms can occupy.

- The positions obtained from the refinement allowed energy minimization studies to be carried out and determined that the structure shown in (d) is the most stable.

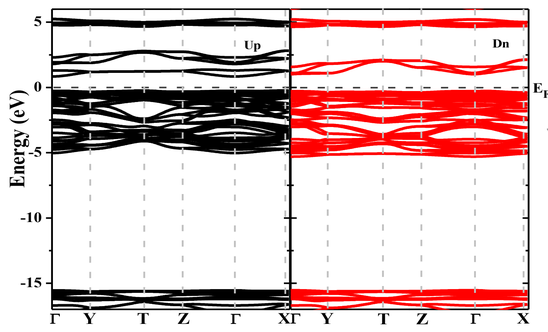


Fig.8: Band structure of the $CaCo_{0.5}Zr_{0.5}O_3$ compound.

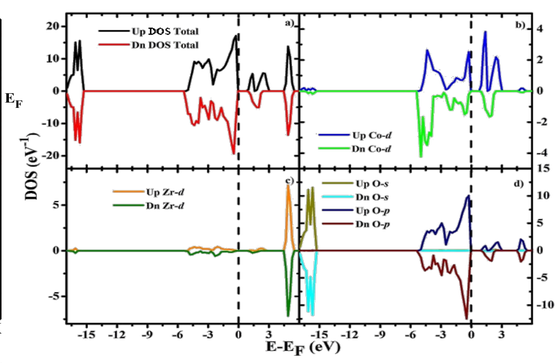


Fig.9: Density of total electronic states of the compound $CaCo_{0.5}Zr_{0.5}O_3$ (a) and partial contributions of Co (b), Zr (c) and O (d).

- The band structure and DOS show the semiconductor character with average gap of 0.89 eV, with majority contributions from the 2p-O and 3d-Co orbitals.

CONCLUSION

The SEM images reveal granular associations with irregular distribution and shape, while the poorly defined grain boundary indicates a process of diffusion and grain growth. The presence of some degree of porosity and minimal impurity content is also observed, aligning with the findings of the EDX study. Additionally, the analysis of the density of states (DOS) and the band structure indicates that the material exhibits behavior characteristic of a ferromagnetic semiconductor, featuring a net magnetic moment of 2.0 μB and an average gap of 0.89 eV. This behavior is primarily attributed to the predominant contributions of the 2p-O orbitals in the valence band and their hybridization with the 3d-Co orbitals.

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