

Desenvolvimento de módulo de Análise de Dados para identificação de situações de fraude e corrupção em processos de contratação pública

Francisco Valente Pereira

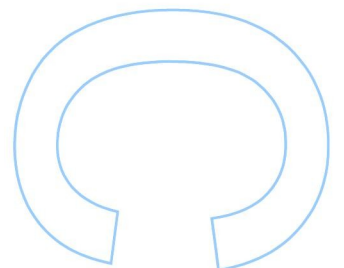
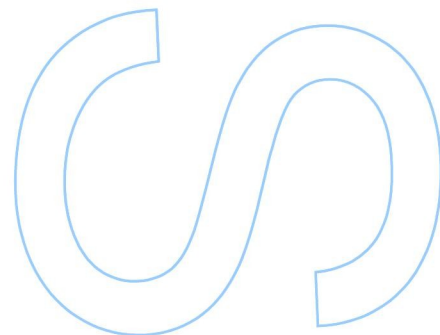
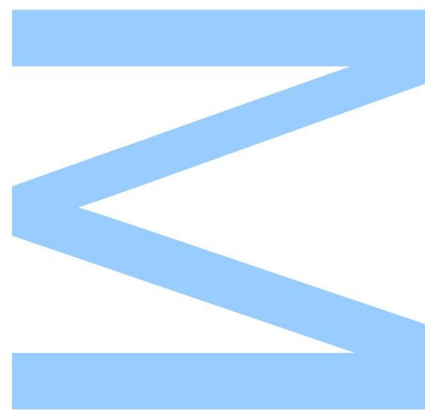
Master's in Computational Statistics and Data Analysis
Department of Mathematics
Faculty of Sciences of the University of Porto
2024

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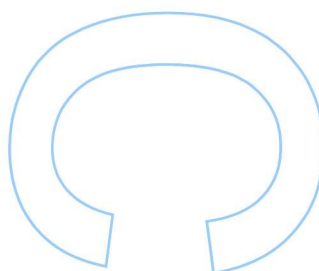
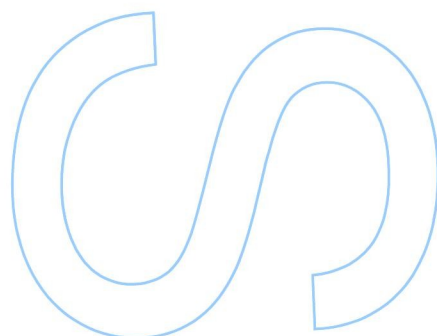
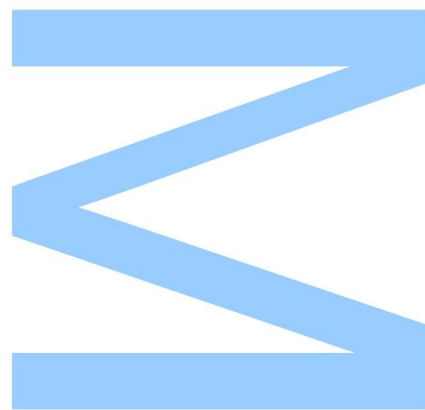




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O Presidente do Júri,

Porto, / /



Francisco Valente Pereira

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pública**



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Acknowledgements

Resumo

Abstract

Motivation

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List of Abbreviations

AFM Antiferromagnetic	FWHM Full Width at Half Maximum	PAC Perturbed Angular Correlation
CERN European Organization for Nuclear Research	GGA Generalized Gradient Approximation	PAW Projected Augmented Wave
C_nMO CaO(CaMnO ₃) _n	GIPAW Gauge Including Projected Augmented Wave	PBE Perdew Burke Ernzerhof (functional)
CMO Ca ₃ Mn ₂ O ₇	HFI Hyperfine Interaction	PDOS Projected Density of States
C_nMTO CaO(CaMn _{1-y} Ti _y O ₃) _n (y = 1/8)	HIF Hybrid Improper Ferroelectric	PP Pseudo Potential
CMTO Ca ₃ Mn _{1.75} Ti _{0.25} O ₇	IFIMUP Instituto de Física dos Materiais da Universidade do Porto	QTAIM Quantum Theory of Atoms in Molecules
CTO Ca ₃ Ti ₂ O ₇	ISOLDE On-line Isotope Mass Separator	RP Ruddseden-Popper (perovskite)
DFT Density Functional Theory	KS Kohn-Sham	RT Room Temperature
DJ Dion-Jacobson (perovskite)	LDA Local-Density Approximation	SCF Self Consistent Field (calculation)
DOS Density of States	LPV Layered Perovskite	SOPT Second Order Phase Transition
DSC Differential Scanning Calorimetry	MHF Magnetic Hyperfine Field	TDPAC Time Differential PAC
EFG Electric Field Gradient	NMR Nuclear Magnetic Resonance	USPP Ultra Soft PP
FCUP Faculdade Ciências da Universidade do Porto	NMR Nuclear Magnetic Resonance	WFM Weak Ferromagnetism
FLAPW Full-Potential Linearized-Augmented Plane-Wave	NTE Negative Thermal Expansion	XC Exchange Correlation
FM Ferromagnetic	OOD Oxygen Octahedra Distortions	XRD X-ray Diffraction
FOPT First Order Phase Transition	OOR Oxygen Octahedra Rotations	XRPD X-ray Powder Diffraction
FRAMs Ferroelectric Random-Access Memories	OOT Oxygen Octahedra Tilts	

CHAPTER 1

Introduction

1.1 Intership

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1.1.1 Something else

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CHAPTER 2

Conclusions and Future Work

2.1 Conclusions

In this work, we synthesized $\text{Ca}_3\text{Mn}_{2-x}\text{Ti}_x\text{O}_7$ $n = 2$ Ruddlesden-Popper samples with various compositions ($x = 0.1, 0.25, 0.3$) via a common solid-state reaction method and studied its structural phase transitions and properties through different methods: X-Ray Powder Diffraction (XRPD), Raman Spectroscopy, Perturbed Angular Correlation (PAC), and Density Functional Theory (DFT) simulations, with special focus on the $x = 0.25$ (C_2MTO) system.

After the last annealing of the synthesis process, Rietveld refinements on the XRPD data were performed to check the purity of the formed $n = 2$ phases. We observed an approximate 12% presence of $\text{Ca}_2\text{Mn}_{0.875}\text{Ti}_{0.125}\text{O}_4$ ($n = 1$ C_1MTO) in C_2MTO , however with a - and b -lattice parameters considerably lower (by $\approx 0.6\text{\AA}$) of what can be found in the literature for the undoped Ca_2MnO_4 system.

Raman and PAC spectroscopies, respectively in the 93 – 653K and 74 – 1224K temperature ranges, revealed a first order structural phase transition from what appears to be a the ferroelectric $A2_1am$ (s.g. 36) phase to an intermediate and paraelectric $Acaa$ (s.g. 68) symmetry within a 300 – 550K temperature range, where both structural phases coexist. Thus, when comparing CMTO to the undoped $\text{Ca}_3\text{Mn}_2\text{O}_7$ (C_2MO), we report an increase in the percentage of the ferroelectric phase at room temperature by introducing the $x = 0.25$ Ti^{4+} doping. However, our results point to the possibility of the ground state not corresponding to the $A2_1am$ symmetry, but to one with inequivalent A-sites at the rock-salt of the RP system. PAC spectroscopy also revealed a second order structural phase transition from the intermediate orthorhombic $Acaa$ (s.g. 68) to the tetragonal $I4/mmm$ (s.g. 139) at 1150K.

We came across an unexpected result at temperatures below 300K, where we clearly detected the probing of a second local environment, albeit without a clear physical origin. Interestingly, PAC measurements did not found evidence of the C_1MTO phase observed from XRPD refinements, and we believe this suggests that the $A2_1am$ space group might not correspond to the ground state symmetry for every composition of $\text{Ca}_3\text{Mn}_{2-x}\text{Ti}_x\text{O}_7$ mixed B-site systems. Phonon calculations on these doped systems in the $A2_1am$ symmetry could reveal if there are any lattice

instabilities, shedding a light on whether the $A2_1am$ still corresponds to the ground state when Ti is added.

The C_2MO system was studied with DFT in its ground state $A2_1am$ symmetry. We determined a Hubbard- U correction by first principles ($U = 6$ eV) to properly describe the Mn- $3d$ states, and then performed a series of structural and electronic properties calculations with our *ab-initio* value and with $U = 0$ and $U = 3.9$ eV, a value commonly found in the literature. We determined the cell parameters and bulk moduli for the mentioned U values as well as multiple electronic properties, such as the projected density-of-states (PDOS), Bader charges, and the Electric Field Gradient at multiple sites. When we manage to define and adjust the most adequate parameters to compute the EFGs for this system, we intend to probe the Ti^{4+} doped $Ca_3Mn_{2-x}Ti_xO_7$ structures, and analyse how the EFGs vary as a function of doping concentration.

2.2 Future Work

In the future, we intend to deepen the discussion at several stages of this system's characterization. Regarding the observation of a C_1MTO phase impurity in XRPD experiments, and the underestimated lattice parameters, we intend to pursue a new refinement considering also the intermediate *Acaa* phase. To complement this measurements, XAS and XPS spectroscopies would help us to confirm the oxidation states of Mn and Ti in the sample, to account for some deviations in the XRPD patterns. Additionally, neutron diffraction would confirm the structural and magnetic structural properties of these samples.

More complex Raman Spectroscopy setups could be pursued to study the evolution of the softer modes that drive the $A2_1am - Acaa$ structural phase transition, and DFT calculations could assign the peak positions for each mode in the doped C_2MTO structure.

The interpretation PAC results below 300K is still open to discussion, and we'll be pursuing other methods to clarify them. Doped CMTO DFT calculations of the EFG parameters is a work in progress and the study of other doped systems is also scheduled, to later compare with undoped systems. In fact, $n = 1$ $Ca_2(Mn,Ti)O_4$ RP compounds have already been measured by PAC and will be analysed in the future. Future phonon calculations on these B-site mixed systems may become a key point in understanding these systems.

APPENDIX A

Add appendices.

