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Motivation

The doping with other elements than the native cationic metal can enhance certain properties of oxides and turn them better materials for specific applications or make them suitable for new ones .

The role of the dopant and its influence in the host oxide is desirable to be understood so that a general model of the connection between dopant–oxide pairing and the functional performance must be developed.

Lack of quantitative experimental data on the local neighbourhood of the dopant, which can give information about the local structure and the electronic structure in this region, has prevented the formulation of a general theoretical description of the doping phenomenon in oxides.

The nature of the dopant (e.g. its valence) plays an important role in the electronic structure and presence of defects (e.g. oxygen vacancy) in its neighborhood, which may affect the properties of the oxide.

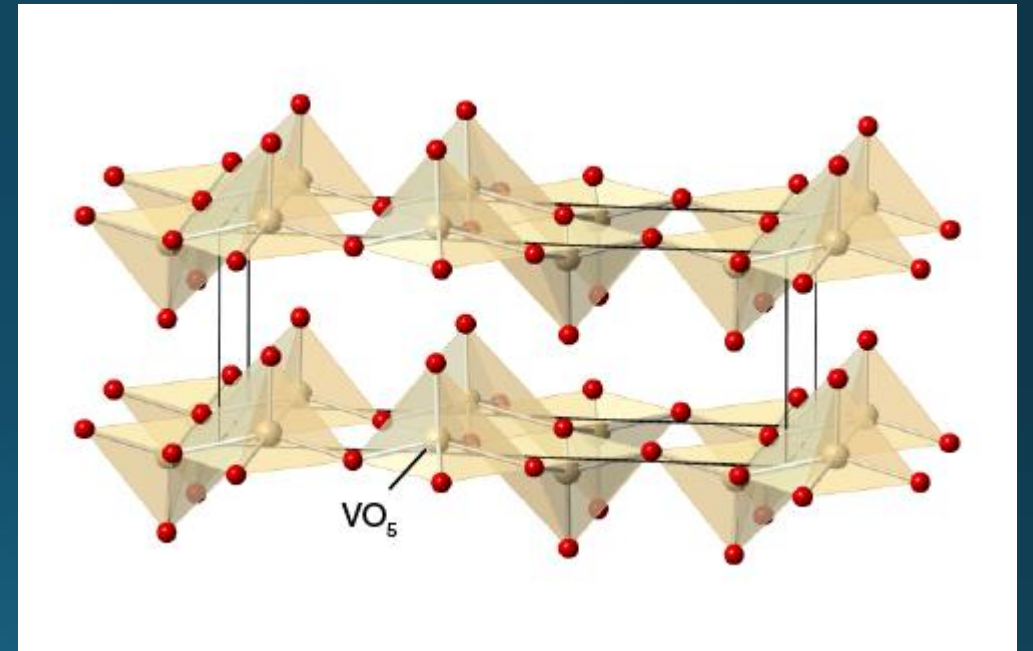
Oxides to be investigated

Vanadium oxides: V_2O_5 , VO_2 , V_2O_3 and VO exhibits four common oxidation states +5, +4, +3, and +2, respectively.

V_2O_5 crystallizes in an orthorhombic structure with layers of VO_5 square pyramids sharing edges and corners. These layers are weakly bond along the c-axis and the space between them permits the accommodation of guest ions.

This property along with the reversibility of valences of vanadium cations, high abundance, and theoretical high capacity makes this material an attractive candidate for the intercalation of Li-ions producing the Lithium ion batteries (LIB)

Nanostructured vanadium oxides have been widely explored to enhance the electrochemical kinetics for V_2O_5 electrodes in LIB.



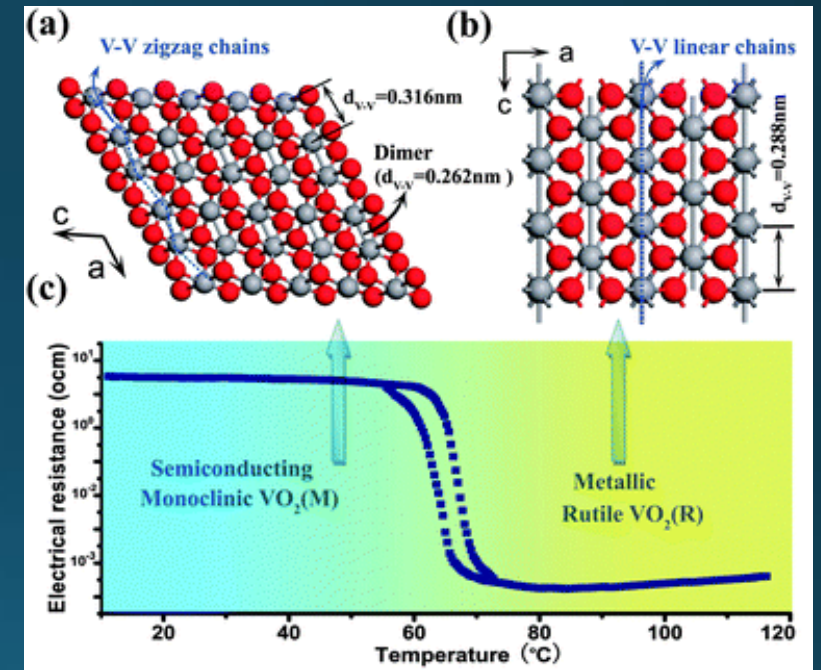
Oxides to be investigated

Vanadium oxides: V_2O_5 , VO_2 , V_2O_3 and VO exhibits four common oxidation states +5, +4, +3, and +2.

VO_2 undergoes a sharp metal-to-insulator transition (MIT) at 341 K (68 °C) along with a structural phase transition from monoclinic to the rutile structure.

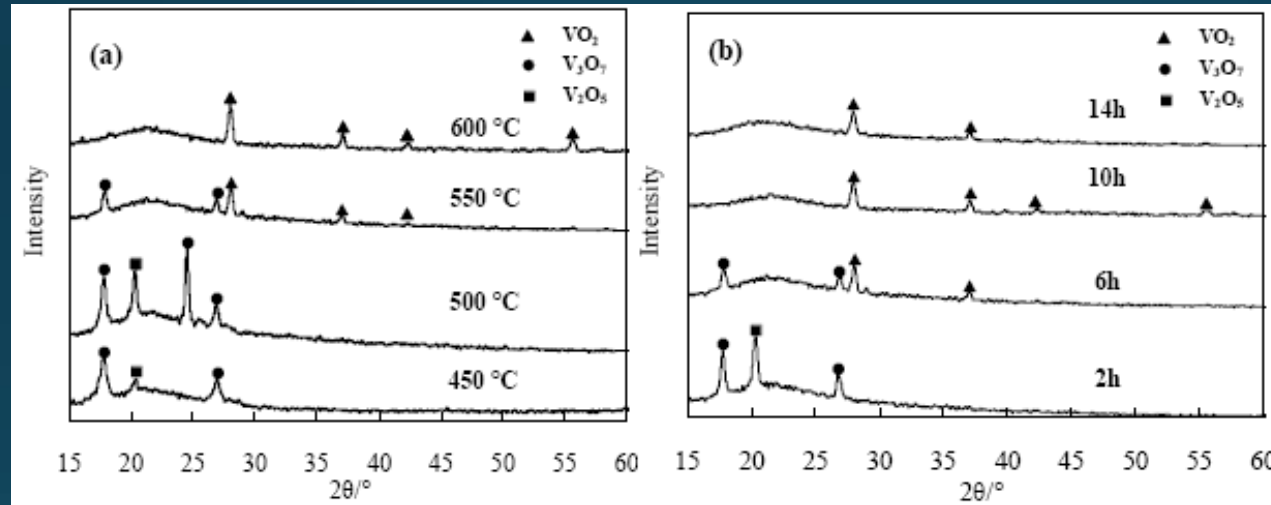
The origin of the unexpected insulating phase is not a consensus yet.

Doping can change the transition temperature (W-doped VO_2 : transition at 288 K).



Oxides to be investigated

Vanadium oxides: V_2O_5 , VO_2 , V_2O_3 and VO exhibits four common oxidation states +5, +4, +3, and +2.



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Interestingly V_2O_5 can be transformed in VO_2 by annealing at around 600 °C, causing a change in the Vanadium valence (+5 to +4)

Methodology and Justification

Samples of vanadium oxides will be prepared at the hyperfine interactions laboratory in IPEN, São Paulo.

Sol-gel method will be used to prepare bulk samples as well as it is ideal to produce thin film samples deposited on substrates by **spin-coating** technique.

This method allows a total control of doping, for instance the thickness.



Nanoparticles of vanadium oxides will be prepared by **thermal decomposition**, which produce small and monodisperse particles.



All samples will be characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and Rutherford backscattering (RBS). Extended x-ray absorption fine structure (EXAFS) spectroscopy and X-ray absorption near edge structure (XANES) will be carried out for thin film samples in the synchrotron accelerator in Campinas, SP, Brazil.

Methodology and Justification

Oxide samples will be doped with different probe ions having different valences to investigate the local effect of doping on the charge density, oxygen vacancy occurrence, and electronic structure by measuring the **electric field gradient tensor**.

PAC measurements will be carried out at different temperatures to follow the behaviour of the observed parameters as well as dynamic process particularly measured by ϵ^- -PAC.

$$V_{zz} \text{ and } \eta = \frac{V_{xx} - V_{yy}}{V_{zz}}$$

Cd ion (from $^{111}\text{In} \rightarrow ^{111}\text{Cd}$ or $^{111\text{m}}\text{Cd} \rightarrow ^{111}\text{Cd}$) has valence +2

$^{111}\text{In} \rightarrow ^{111}\text{Cd}$: possible after effects (fast electronic re-arrangement)
 $^{111\text{m}}\text{Cd} \rightarrow ^{111}\text{Cd}$: no after effects.

In ion ($^{117}\text{Cd} \rightarrow ^{117}\text{In}$) has valence +3,

Complementary measurements of $^{111}\text{In}/\text{Cd}$ since in both cases incorporation is done on one element and the measurement of the other

Sn ion ($^{119\text{m}}\text{Sn} \rightarrow ^{119}\text{Sn}$) has valence +4

ϵ^- -PAC measurements: possible dynamic process

Ta ion ($^{181}\text{Hf} \rightarrow ^{181}\text{Ta}$) has valence +5

$^{181}\text{Hf} \rightarrow ^{181}\text{Ta}$ probe nuclei will be produced at the nuclear reactor of IPEN, São Paulo, implanted elsewhere and exported to ISOLDE/CERN for measurements "offline" or during the Long Shutdown.

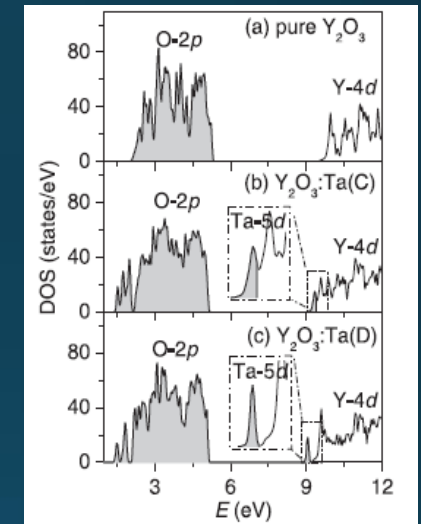
Methodology and Justification

First-principles calculations, using full-potential augmented plane waves plus local orbital method (FP-APW+lo) based on the DFT will be performed (by WIEN2k code) in order to simulate the doping in the host oxides to interpret mainly the experimental hyperfine interactions results.

Confronting experimental determination with theoretical predictions of the EFG using all-electron *ab initio* electronic structure calculations can provide information such as structural deformations, localization and charge state of defect centers and impurities, character of impurity levels

Since the substitutional dopant impurity has a nominal different character (donor or acceptor) depending on its valence, the different charge states of the impurity can be simulated by removing or adding electrons

For thin films, two *ab initio* methods with different basis set (FP-APW+lo method and a linear combination of numerical localized atomic-orbitals basis set, implemented in WIEN2k and SIESTA packages, respectively) will be used



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Earlier findings

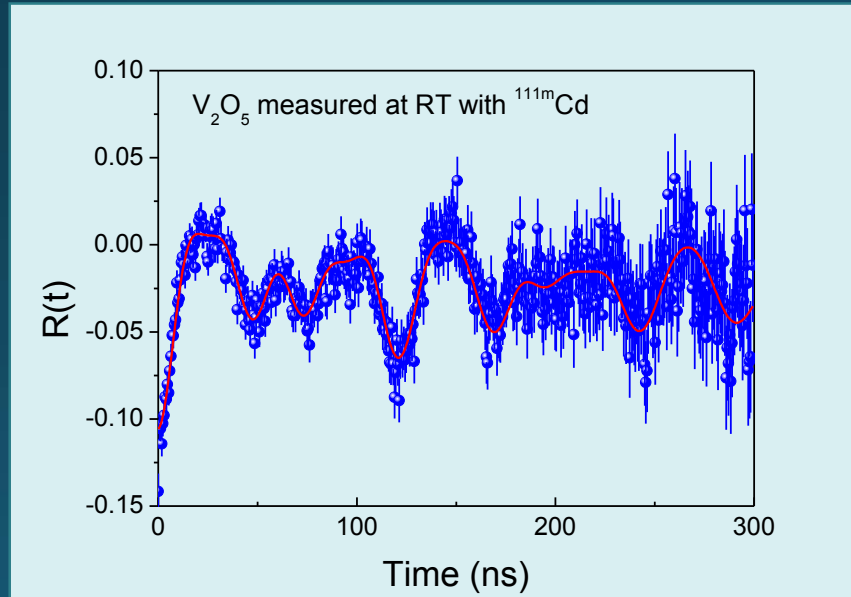
Hyperfine Interactions **80** (1993) 965-970



V_2O_5	Vacuum at 870 K (60 min)		Air at 870 K (30 min)		
ν_Q (MHz)	88.1(3)	221(2)	91.4(6)	224(3)	265
η	0.62	≈ 0	0.61	≈ 0	≈ 0

VO_2 : $\nu_{Q1} = 42.9(7)$ MHz with $\eta_1 = 0.38(4)$ at RT and $\nu_{Q2} = 89.2(2)$ MHz with $\eta_2 = 0.20(2)$ at 420 K

First result at ISOLDE



V_2O_5	Sol-gel	
ν_Q (MHz)	85.7(1)	77(2)
η	0.58(1)	≈ 0

Objectives and expected results

Investigation (through hyperfine interactions) of the doping mechanism in V_2O_5 and VO_2 oxides using perturbed angular correlation spectroscopy (γ -PAC and ϵ^- -PAC) as well as first-principles calculations based on density functional theory (DFT), by tracking the local modification produced by dopants (probe nuclei: ^{111}Cd , ^{117}In , ^{119}Sn) implanted into samples.

As ISOLDE offers a variety of radioactive nuclei, we will choose as dopants ions with different valences than that of the native cations and investigate the influence of the excess or lack of electrons.

Since hyperfine interactions have the short range of the atomic distances, we will investigate **the neighborhood** of the dopants (which are the probe atoms) and the local effect of the doping.

Samples of the oxides with higher concentration of dopants (2-5%) are intended to be investigated too.

Our goal in the present project is to contribute for a description of the doping effects at an atomic level.

In parallel, intrinsic properties of the host oxides, such as crystal phase transition, dynamic phenomena, will also be investigated.

IMPORTANT

It is important to emphasize that the results of this proposal can either contribute to the formulation of a general theory about the doping mechanism in semiconductor oxides as well as produce new materials for technological applications.

The proposal will strengthen the collaboration between synergetic institutes

The proposal will benefit students, particularly brazilian students, which will have the oportunity to come to ISOLDE for the experiments.

The proposal will facilitate the association of Brazil to ISOLDE.

TAC meeting: RILIS for Sn: narrow band operation required for isomeric selection? Yes, because we need as much as ^{119m}Sn as possible. Would require additional setting up time. OK, as long as we have enough implantation time