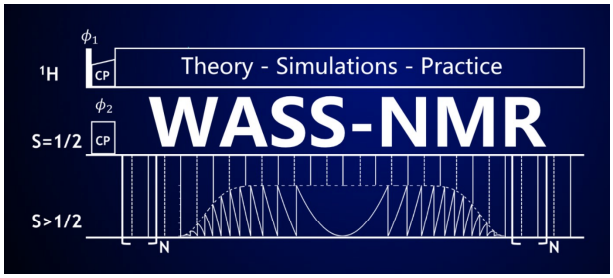

Book of Abstracts

Workshop on Advanced Solid State NMR (WASS-NMR)

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Local: São Carlos, SP, Brasil

Comitê Organizador:
Prof. Marcos de Oliveira Junior (IFSC-USP)
Prof. Thiago Branquinho de Queiroz (CCNH-UFABC)
Prof. Hellmut Eckert (IFSC-USP)
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Uso de ecos dipolares em crioporosimetria por RMN e aplicações na determinação de nanoporos em materiais.*

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As últimas três décadas testemunharam grande desenvolvimento de técnicas de ressonância magnética nuclear no domínio do tempo (RMN-DT) para a caracterização de meios porosos, baseadas em diferentes princípios físicos e capazes de estimar dimensões de poros desde a escala nanométrica até centenas de micrômetros. Enquanto poros com dimensões na faixa de centenas de nm a dezenas de μm são passíveis de caracterização por várias técnicas de RMN-DT baseadas em relaxometria e difusão molecular, poros com dimensões de dezenas a centenas de nm podem ser caracterizados utilizando as chamadas técnicas de crioporosimetria. De modo geral, a crioporosimetria explora variações nas temperaturas de fusão de fluidos confinados em espaços nanométricos, as quais podem ser caraterizadas de modo bastante eficiente por diferentes técnicas de RMN-DT. A caracterização de materiais nanoporosos encontra aplicações em várias áreas como, por exemplo, caracterização de estrutura porosa de polímeros sintéticos e biopolímeros, de biomassas naturais, ou de solos de diversas origens. Este projeto de mestrado envolve a implantação, teste e caracterização da metodologia convencional de crioporometria por RMN usando técnicas de ecos de spins isolados (usualmente referidos como ecos de Hahn), assim como a avaliação do uso de técnicas baseadas em ecos dipolares, as quais tem se mostrado bastante eficientes para sondar processos dinâmicos. Além disso, pretende-se empregar as metodologias para caracterizar estruturas de nanoporos em diversos materiais, o que inclui biopolímeros porosos, biomassas naturais e solos de diferentes origens.

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Green urethanesil host based on castor oil doped with Eu^{3+} complex for sustainable luminescent solar concentrator application[†]

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Hilights

Hybrid material based on Castor Oil and 3-(triethoxysilyl)propyl isocyanate. Incorporation of $[Eu(tta)_3(H_2O)_2]$ complex. Cylindrical luminescent solar concentrator for PV energy production enhancement.

Abstract

It is consensus that the tremendous growing in global energy consumption since the beginning of the twentieth century, mainly coming from fossil sources, has led to the recent climate changes. Under this scenery, there is no doubt that the energy of the future is going to be based on natural and renewable sources. Over the last years, much attention has been dedicated to obtaining new materials to be used in photovoltaic (PV) energy production. Several strategies have been adopted in order to improve the PV energy conversion. Notwithstanding, some challenges concerning PV need to be overcome, mainly related to the efficiency of the process. In this sense, luminescent solar concentrators (LSCs) has been successfully used during the last decades for such purpose. Efficient UV absorption, efficient emission quantum yield, photostability, and sustainability are characteristics extremely import concerning LSCs. In the present study we present and discuss outstanding results concerning a sustainable organic-inorganic hybrid (OIH) material based on Castor oil (CO) and containing a Eu^{3+} complex, namely SiCO-$[Eu(tta)_3]$. Such material was obtained by using the sol-gel process, following the casting method. The results have shown that the SiCO-[Eu(tta)3] material presents satisfactory thermal stability, broad transparency window (90% of transmittance in the visible and infrared) and efficient UV-to-visible conversion. Furthermore, the photoluminescence results have revealed an expressive increase in the emission quantum efficiency when the $[Eu(tta)_3]$ complex is incorporated into OIH material. Moreover, experiments in progress have shown that SiCO-$[Eu(tta)_3]$ can be used to produce cylindrical LSCs. Which, are more efficient than planar ones. All the results indicate that the obtained material have a huge potential to be used as efficient luminescent solar concentrators and consequently improving PV cells energy conversion.

[†]Workshop on Advanced Solid-State NMR - 2023

Acidity modulation of mixed metal oxide catalysts probed with solid state ^{31}P-NMR analysis[‡]

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Spectroscopic techniques invoking the adsorption of probe molecules have been widely employed in determining the nature, strength, and concentration of acid sites in solid catalysts. Despite not much explored for metal oxides, trimethylphosphine oxide (TMPO) adsorption monitored by SS ^{31}P-NMR spectroscopy has been shown as a robust and reliable technique. The main benefit of this approach is the linear correlation that exists between the chemical shift of the adsorbed TMPO and the deprotonation energy of the TMPOH+ species formed over Brønsted acid sites (BAS); the higher the chemical shift, the stronger the adsorbed TMPO specie. Making use of these advantages, we employed this technique to probe the surface acidity modulation of Ti-Nb mixed metal oxides. We also used pyridine adsorption monitored by FTIR in a complementary way, once adsorbed-TMPO SS ^{31}P-NMR analysis is less sensitive to Lewis acid sites (LAS).

[‡]Workshop on Advanced Solid-State NMR - 2023

Solid-state NMR and Dynamic Nuclear Polarization of Functional Materials: Basic Principles and Applications[§]

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Solid-state nuclear magnetic resonance (NMR) and hyperpolarization techniques like dynamic nuclear polarization (DNP), combined with molecular modelling or quantum chemical calculations are among the most powerful characterization techniques of functional materials on the atomic level. The first part of the presentation gives an overview about solid-state NMR and DNP techniques and their application potential in materials sciences applications. The second part of the presentation shows several applications of these techniques, which were performed in recent years in our lab. First, we show examples of the functionalization of large specific surface area materials with catalytic groups and the monitoring of the reaction progress by SSNMR. Next, we reports studies on mixed metal oxides such as V-Mo-W oxides, which are employed as heterogeneous catalyst in bulk-scale production of basic chemicals. Then we discuss recent results on the behavior of small guest molecules in confinement. Finally, we report results on the characterization of modern electric function materials.

[§]Workshop on Advanced Solid-State NMR - 2023

Magnetocaloric Effect in geometrically frustrated Kagome cluster systems[¶]

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In this work, we study the magnetocaloric effect by adopting the Ising spin model in the kagome lattice with antiferromagnetic interactions. The magnetocaloric effect consists in a temperature change of magnetic materials under adiabatic magnetization conditions, which can be an eco-friendly alternative for conventional cooling or heating systems. A correlated cluster mean-field method is used in order to obtain an effective cluster problem, which can be solved self-consistently by an exact diagonalization method. This method is able to account for frustration coming from the finite clusters interactions. As a result, we analyze the isothermal entropy change for different sets of external magnetic fields. These findings show that an enhancement of the magnetocaloric potential is obtained in a low range of magnetic fields, due to the presence of high geometrical frustration.

[¶]Workshop on Advanced Solid-State NMR - 2023

Synthesis of Niobium Phosphate Glasses and Structural Characterization by Solid State Nuclear Magnetic Resonance[‖]

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Phosphate glasses are widely used in optical communications and solid-state lasers owing to the high solubility of photonically active metal ions in them (1). The incorporation of transition metal ions, such as Nb_2O_5, not only improves the chemical durability of phosphate glasses, but also significantly contributes to increase both their linear and non-linear indexes of refraction (2). However, a fundamental understanding of the structural role of niobium, which can serve either as a network modifier or as a network former, in these glasses has not been achieved. Solid-state nuclear magnetic resonance (NMR) has been proven to be a powerful tool for structural elucidation of glasses, due to its element-selectivity, inherently quantitative character, and its focus on local order (1). From the NMR point of view, niobium features one of the most NMR-sensitive nuclei ^{93}Nb which is 100% natural abundant. Nevertheless, it suffers from a large nuclear quadrupolar moment, and the 93Nb NMR spectra are dominated by strong quadrupolar interactions, resulting in excessive line broadening and poor resolution. These challenges can be addressed by techniques involving fast MAS, wideband excitation methods and dipolar recoupling techniques (3). Here, we report results on glasses in the system Na_2O-Nb_2O_5-P_2O_5 from two compositional series. Advanced NMR experiments have been used to characterize the local environments of sodium, phosphorus and niobium with the aim of obtaining new structural insight towards the development of new structure-function correlations.

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[‖]Workshop on Advanced Solid-State NMR - 2023

Solid state NMR investigation of structural changes in borophosphate glasses due to the addition of ZnO**

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In this work, the influence of ZnO in the structural parameters of Zinc Borophosphate glasses was studied for the system (x)ZnO-(85-x)P_2O_5-(15)B_2O_3, (x = 30, 40, 50, 60 and 70 mol%). The structural analyses have been carried out using XRD, Raman spectroscopy and solid state NMR. A multiple NMR approach was applied for the characterization of the samples, combining ^{31}P and ^{11}B single-pulse experiments with double quantum filtered ^{31}P experiments and ^{31}P-^{11}B double-resonance experiments. The results reveal changes in the structural characteristics with composition, associated with a replacement of BO_4 units by BO_3 units in the boron structure as well as the replacement of Q^3 phosphorous units by Q^2 and Q^1 units, which is translated as an increase in the average number of non-bridging oxygen (NBO). These changes were finally correlated with radiation shielding properties for these glasses.

**Workshop on Advanced Solid-State NMR - 2023

Structural control on the dissolution behavior of borophosphate glasses for wound healing: insight from NMR[††]

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Bioactive glasses are a class of biomaterials with diverse medical applications including soft- and hard-tissue regeneration. While silicate-based glasses have been commercialized for bone- and dental-related trauma, borate and borophosphate glasses are frontrunners for soft-tissue wound healing, as they dissolve on a timescale appropriate for delivering therapeutic ions to the injury site. Establishing a relationship between the borophosphate glass structure and dissolution behaviour is essential to enable researchers and engineers to design glasses with controllable degradation rates for various applications. We have characterized a series of sodium borophosphate glasses before and after standardized dissolution tests using 31P and 11B magic-angle spinning nuclear magnetic resonance (NMR) spectroscopy. The NMR data are interpreted using Pauling bond strengths and charge-compensation arguments to conclude that P^3_{1B} and P^3_{0B} dominate in glasses rich in phosphorus, while boron-rich glasses comprise mainly P^3_{2B} and P^2_{1B} species. Solution ^{31}P NMR provides real-time information about the phosphate species released into solution, revealing that the balance of B – O – B and P – O – B linkages is a determining factor in the degradation rate of borophosphate glasses.

[††]Workshop on Advanced Solid-State NMR - 2023

Solid-State NMR as a tool to understand amyloid fibril structure[‡‡]

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Amyloidosis is a clinical disorder caused by extracellular deposition of proteins that are normally soluble in their native conformation, but suffer conformational modifications resulting in insoluble, abnormal fibrils that impair organ function. Parkinson's disease (PD) and Alzheimer's disease (AD) are the two major common neurodegenerative diseases. In our group we are working with four different proteins: Transthyretin (TTR) that is linked to the systemic amyloidosis, α-synuclein that is linked to Parkinson disease, Amyoid β peptide (Aβ_{1-40}) related to Alzheimer disease and PrP protein that causes prion diseases. Beside, amyloid fibrils are also linked to physiological conditions and can be applied as a nanotechnological tool. Here we will present some strategies applied to study the architecture of amyloid fibrils in order to have more insights about its formation and stability.

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[‡‡]Workshop on Advanced Solid-State NMR - 2023

Hyperfine coupling as probe of orbital anisotropy in heavy fermions[§§]

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Heavy-fermion (HF) metals are described by strong electron-electron interactions that can be tuned across a quantum phase transition between localized f-electron magnetism and itinerant heavy-mass Fermi liquid behavior. Therefore, the overlap between neighboring atomic wave functions is a central feature and gives rise to a range of emergent phenomena, including anti-ferromagnetism, unconventional superconductivity, and the ability to tune from one ground state to the other in this class of materials. Nevertheless, despite important recent improvements in the field, measuring the degree of this hybridization by conventional methods is challenging and indirect. We, thus, provide an approach using NMR to determine the magnetic couplings between the f-electrons and neighboring nuclear spins in a series of Kondo lattice materials and find that the hybridization is strongly direction dependent in this significant class of superconducting HF materials. The experimental data are discussed in terms of a change in Ce's 4f orbitals that arises from evolution of crystal-electric field (CEF) energy levels upon doping/pressure. We demonstrate that the hyperfine coupling probed by NMR provides a quantitative measure of orbital anisotropy.

[§§]Workshop on Advanced Solid-State NMR - 2023

Two-dimensional exchange NMR spectroscopy (2D EXSY): An approach for hybrid material study[¶¶]

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Hybrid materials are homogeneously formed by the synergistic combination of organic and inorganic components at the nanometer or molecular level. The solid-state NMR technique can be an important approach for understanding and/or elucidating the structure formed and to correlate with its properties. With the evolution of the NMR spectrometers (high-speed spinner frequency and field), the use of ^{1}H-^{1}H 2D-exchange experiments growing for study in different materials, such as polymers, protein, and hybrid materials. Two-dimensional exchange NMR spectroscopy (2D-EXSY) can provide important information for understanding the structure formed by gelatinization process and the cross-link between inorganic-organic networks formed by photopolymerization. A variety of selective excitation experiments can be carried out, and the signals that are sensitive to the motions that occur on the slowly dynamic processes and give rise to off-diagonal cross-peaks are observed in the 2D spectrum between the resonances of the sites involved in the exchange. The distance of the inorganic domain can be extracted and calculated from ^{1}H-^{1}H correlation observed at a different time (τc) in the 2D EXYS spectra.

[¶¶]Workshop on Advanced Solid-State NMR - 2023

^{19}F and ^{23}Na relaxation processes in pseudo-cubic $NaYF_4$ nanoparticles: NMR as a tool to investigate surface and paramagnetic effects.***

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$NaYF_4$ crystals and nanocrystals have attracted great attention in optical applications because it can host rare-earth (RE) emitting ions in a very beneficial lattice. It also shows good RE solubility since they replace their chemically similar Y ions. The α-$NaYF_4$ phase has a pseudo-cubic structure, i.e., locally, the cubic structure is distorted since Y and Na are statistically distributed in the face-centered cell. It leads to a quite representative heterogeneous broadening of ^{19}F and ^{23}Na NMR spectra, reducing the structural information that can be obtained by high resolution solid state NMR. For instance, bulk sites and defects or surface sites are indistinguishable by magic angle spinning NMR. However, relaxation processes are mostly due to fluctuations of the dipolar coupling and/or quadrupolar coupling to the time-modulated electrical field gradient (EFG). Thus, for ^{23}Na NMR, relaxation processes are highly sensitive to local distortions. We demonstrate that in this case one can associate spectroscopy to relaxation measurements to resolve such structural regions.[1] Another issue arises when one wants to characterize the RE distribution in the $NaYF_4$ lattice, which is a routine NMR task. Usually, the ^{19}F and ^{23}Na NMR line broadening can be rationalized in terms of van Vleck's second moment theory, i.e., $(M_2)^{1/2} \sim \sigma(\text{ppm}) \sim \mu_{eff}(RE^{3+})$. A statistical distribution of RE in the lattice as a function of concentration leads to a linear line broadening behavior whereas saturation means RE clustering. But in such a case where there is a superposition of paramagnetic and heterogeneous broadening, this approach is obscured. We show that this investigation can be also done by associating spectroscopy with relaxation measurements. However, it is of ultimate importance to take into consideration the competition between dipolar, quadrupolar and Solomon's relaxation mechanisms in order to weight the paramagnetic contribution.

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***Workshop on Advanced Solid-State NMR - 2023

Incorporation of Gallium Into Bioactive Glasses: New Structure/Function Relations Uncovered by Solid State NMR Techniques†††

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Since the pioneering publication reporting the ability of certain glasses in the SiO_2-CaO-Na_2O-P_2O_5 composition diagram to join bone material without forming fibrous tissue around them or promoting inflation or toxicity (1), research and development of bioactive glasses and glass-ceramics have promoted better quality of life. In bioglasses, gallium stands out for its antibacterial potential, due to the similarity between its Ga^{3+} ions and Fe^{3+} ions (2); so far, however, there is little knowledge about the relation between the details of its structural incorporation and bioactive properties. The present work aimed to study gallium-doped bioactive glasses, melt-quenching and sol-gel process derived, using NMR techniques and additional characterizations. For the melt-derived glasses, seven samples of Biosilicate® doped with Gallium were produced, with composition [(49,16-x)SiO_2–(23,33)Na_2O–(25,79)CaO–(1,72)P_2O_5–(x)Ga_2O_3], where x= 0,1,2,4,6,8,10 mol%. DSC results show an increase in the glass transition temperature regarding Ga content, indicating there's an increase in network connectivity with the presence of gallium. The NMR spectra indicate that gallium is 4-coordinated and that there is formation of Ga-O-Si linkages with the increase of gallium content in the sample, as well as a proximity/interaction effect of P and Ga atoms. For the sol-gel derived glasses, samples of composition [(80-x)SiO_2–(15)CaO–(5)P_2O_5–(x)Ga_2O_3] and x=0,2,4,6,8,10 mol% were prepared. The NMR results indicate that, as in the previous set of samples, there may be a formation of Ga-O-Si linkages, since there is a decrease in high-coordinated ^{29}Si and a proportional increase in the lower coordinations. Something curious observed in the ^{29}Si spectra is that there is a stabilization of the components between the 6%, 8% and 10% samples — the spectra are very similar. This may indicate that 6% is an upper bound for gallium incorporated in the sample. In this case, a change in gallium environment should be expected, which will be explored further through ^{71}Ga measurements. This is the focus of the present phase of the research, as well as BET characterization of the other samples. In the future, it is intended to focus on the insertion of sodium in samples derived from sol-gel, on new characterizations and on bioactivity studies (dissolution kinetics in SBF), in order to compare the properties of the different sets of samples.

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