



Synthesis of the Metavanadate CaV_2O_6 by the Sol-Gel Method and the Characterization by X-Ray Diffraction and Time-Differential Perturbed Gamma-Gamma Angular Correlation Techniques

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1. Introduction

With the increasing global demand for sustainable energy sources, the study of their production and storage methods has been prominent in the academic community. In this regard, the production of new materials for sustainable batteries with improved performance are relevant in this scenario.

Lithium, used as a key element in energy storage devices presents extraction challenges, scarcity, and a global demand which can significantly elevate its cost and availability in the market - especially for countries like Brazil. In this perspective, the study of new materials with potential for energy storage becomes necessary.

Vanadates are relevant in this context due to their physicochemical characteristics and low cost, demonstrating enormous potential for application in rechargeable aqueous batteries [1]. The spacing between their crystallographic planes stands out. This spacing allows for the insertion or de-insertion of elements with larger atomic radii, such as divalent charge ions, can carry larger electronic charges than lithium and thus serve as substitutes for this metal in batteries.

The choice to study the synthesis and characterization of calcium vanadates, particularly in their metavanadate form (CaV_2O_6), is due to the lack of literature on the sol-gel synthesis route for calcium metavanadate. Additionally, calcium proves to be an interesting candidate because it is readily obtainable, abundant in minerals, cost-effective, and easy to handle.

In this manner, the study of this synthesis approach will be accompanied by volumetric structural characterization using X-ray Diffraction and *in-situ* (and at the neighborhood) crystalline analysis through the insertion of a radioactive isotope via thermal diffusion—specifically, ^{111}In (^{111}Cd)—in order to measure hyperfine interactions via the Perturbed Gamma-Gamma Angular Correlation (PAC), a non-usual nuclear technique. This work was conducted at IPEN, within the facilities of the Hyperfine Interactions Group, located at the Research Reactor Center. The aim is to achieve not only satisfactory results through sol-gel

synthesis but also to employ nuclear techniques that aid in identifying material properties and provide applications for the industry.

2. Methodology

The sample of calcium metavanadate was synthesized using the well-known Pechini sol-gel method. The following reagents were employed: vanadium pentoxide (99% Fluka), calcium chloride (97% Merck), hydrochloric acid (P.A. Anhydrous), ammonium hydroxide (P.A. CRQ), monoethylene glycol (P.A. NEON), anhydrous citric acid (P.A. Dinâmica).

Using masses with corresponding stoichiometric proportion, vanadium pentoxide was diluted in hydrochloric acid at 70°C while calcium chloride was separately diluted in the same acid and combined with the initial mixture. This was followed by addition of dilute citric acid in distilled water, monoethylene glycol and a basic component that stabilized the pH above 7. Once formed, the gel underwent a calcination process at temperatures ranging from 250°C to 400°C, followed by thermal treatment at temperatures between 600°C and 800°C. The characterization techniques employed included X-ray diffraction (XRD) and time-differential perturbed gamma-gamma angular correlation (PAC). XRD provides data related to the number of phases present in the sample and the crystallographic characteristics [2,3].

By placing a small volume on the surface of samples and allowing it to diffuse at temperatures of about 600°C for four hours, radioactive nuclei, specifically ¹¹¹In (radioactive indium in the form of InCl₃ dissolved in an aqueous solution), were inserted into samples through thermal diffusion. Once the isotope becomes part of the crystal lattice, the PAC technique can analyze the perturbation caused by the electrons within a neighboring crystal site to the energy levels of this radioactive nucleus. This analysis is based on gamma rays emitted during the nucleus's decay and captured in coincidence by a pair of detectors over a period of time, commonly referred to as delayed gamma-gamma coincidences[3].

3. Results and discussion

The experimental method applied to the synthesis of calcium metavanadate (CaV₂O₆) demonstrated satisfactory results in both preparation and characterization using XRD and PAC. This is particularly noteworthy considering the usual challenges in obtaining a stabilized oxide in a single crystalline phase using the sol-gel technique. From the synthesis process, XRD results show a phase predominantly (approximately 99.2%) composed of alpha vanadate (α -CaV₂O₆) and a secondary phase, CaV₂O₅. These phases exhibit distinct vanadium geometries and oxidation states: 5+ and 4+, respectively. Data processing was performed using the GSAS-II[4] and VESTA[5] software tools to identify and characterize the crystalline phases formed. Fig. 1 presents the unit cells of the primary (C2/m group) and secondary phase (Pmmn).

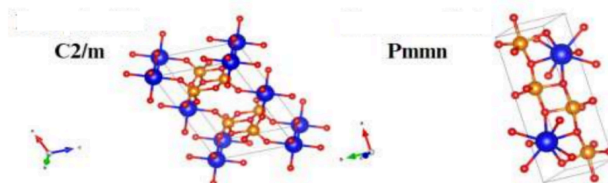


Figure 1: Unit cell representation of the primary and secondary phases obtained from the Rietveld fit of XRD data. Blue, orange, and red spheres represent calcium, vanadium, and oxygen atoms, respectively.

Fig. 2 presents the X-ray diffraction pattern of the CaV₂O₆ sample. By refining this diffraction pattern, especially for the primary phase, we can observe the peaks registered by the green line, representing both the primary and secondary phases. The significant peaks for each phase are indicated by red traces for the

secondary phase (CaV_2O_5) and blue for CaV_2O_6 . The black line represents the difference between the observed (blue peaks) and calculated (green) data.

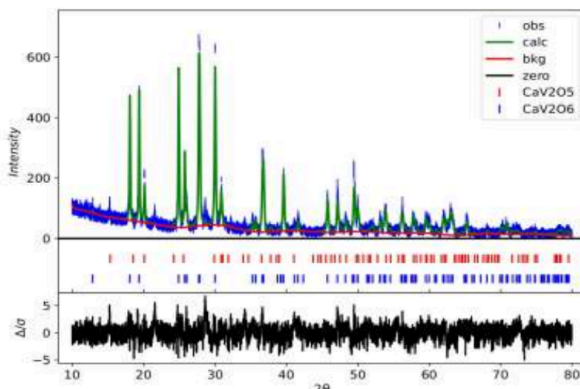


Figure 2: XRD pattern for CaV_2O_6 samples resulting from the fit using GSAS II software.

The chosen nucleus for PAC analysis, ^{111}In , has a half-life of 2.8 days and undergoes beta decay through electron capture, resulting in the excited state of ^{111}Cd . This $^{111}\text{In} \rightarrow ^{111}\text{Cd}$ decay is appropriated for PAC because, after the decay, the excited state of ^{111}Cd decays to the ground state by emitting two gamma rays (γ_1 and γ_2) through an intermediate level with a half-life of 84 ns large enough to allow the nucleus to be affected by the hyperfine interactions with the electrons in its vicinity. These gamma rays are subsequently detected by the four detectors of the spectrometer, generating twelve delayed γ_1 - γ_2 coincidence spectra.

The resulting $R(t)$ function (Fig. 3) from PAC data collected at room temperature, revealed a quadrupolar interaction with two distinct site fractions occupied by probe nuclei in the sample. These site fractions are represented by the red and green lines in the graph. The red-marked fraction predominates, accounting for 66% of probe population in the sample. It exhibits a quadrupole frequency of 65 MHz and an asymmetry parameter (related to the charge symmetry around the probe nuclei) of $\eta = 0.520$, indicating non-isotropy in the charge distribution within the crystal plane. The delta value of 0.07 MHz suggests that the ^{111}Cd atoms are immersed in a well-defined electric field gradient throughout the site. These atoms can occupy three possible positions: Vanadium or calcium (most likely) point groups, as well as cationic or anionic vacancies in cases of structural asymmetry.

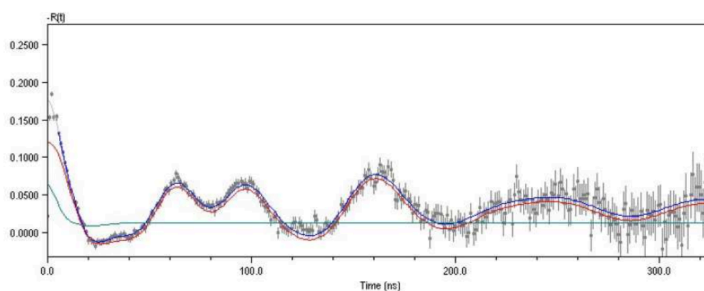


Figure 3: $R(t)$ function obtained from PAC measurements with $^{111}\text{In}(^{111}\text{Cd})$ probe nuclei in CaV_2O_6 at room temperature.

The second fraction, represented by the green line and constituting 34% of the probe population in the sample, exhibits a higher quadrupole frequency of 113 MHz, a null η , and a delta value of 0.71. These values indicate that only a minor portion of the PAC probe nuclei are occupying this site fraction in the sample, probably interstitial positions, near the surface, or close to defects. The high value of delta indicates that the electric field gradient here varies, resulting from distinct electronic densities in different parts of the probe (it's worth noting that the number of probes consists of a set of nuclei, which can number in the order of 10^{11}).

Therefore, the synthesis by the sol-gel method, besides producing the expected stoichiometry (CaV_2O_6) with the correct structure measured by XRD, establish the viability of the synthesis method as well as it yielded PAC results, a very sensitive nuclear technique, with well-defined hyperfine parameters.

Conclusions

With this work, it was possible to conclude and achieve the following objectives: the sol-gel method was successful used to synthesize CaV_2O_6 samples, as the primary phase revealed by XRD constitutes more than 95%, the primary phase exhibits a monoclinic structure and the secondary one an orthorhombic structure. The PAC spectrum fit revealed that the ^{111}Cd nucleus occupied two distinct crystallographic sites, indicating two different hyperfine interactions (HI). This demonstrates that the crystal lattice of this vanadate can accommodate the insertion or removal of atoms larger than lithium (potentially during aqueous battery charging and discharging). In the HI, ^{111}Cd replaces ions in the crystal lattice—specifically, a regular cationic position within the lattice. Also, the sol-gel method showed up as cost effective and reproducible considering materials for battery production.

Considering the insights provided by this work regarding metavanadates in general—especially CaV_2O_6 —future studies could include: Investigating the synthesis of CaV_2O_6 and other metavanadates using alternative methods such as co-precipitation and hydrothermal techniques, conducting PAC analysis of CaV_2O_6 at different temperatures to study its thermal stability and behavior under varying atmospheres.

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