Measuring Positronium Lifetimes: More Advantages of Digital Spectrometers

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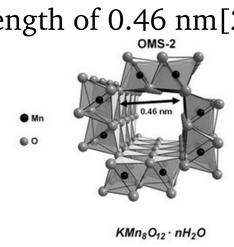
Measuring nano-voids in K-OMS-2 with digital positron lifetime spectroscopy

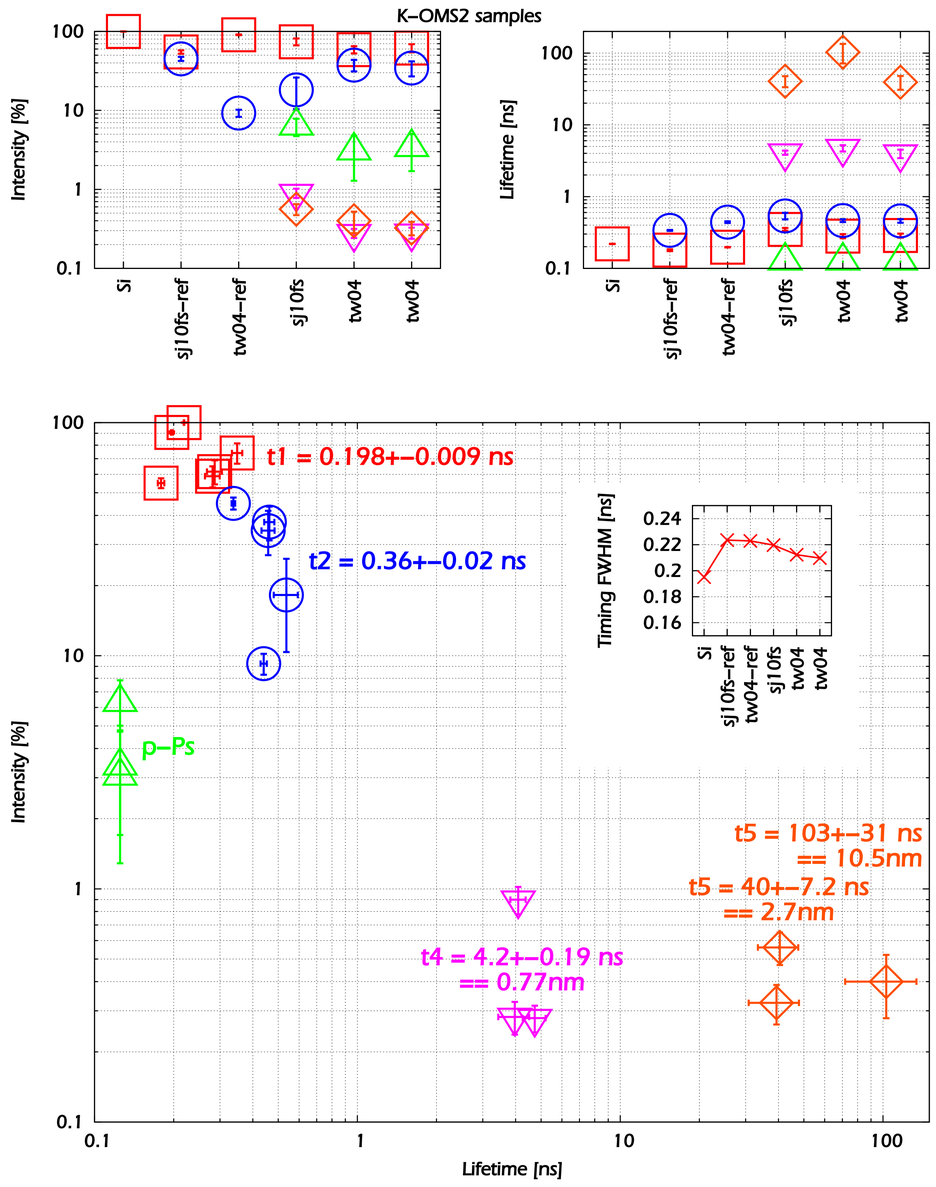
Octahedral Molecular Sieves (K-OMS-2) are micro-porous, crystalline transition metal oxides with MnO6 octahedra as the primary building units [1]. Typically, these materials have a one-dimensional, square-shaped pore structure with an edge length of 0.46 nm[2]:



Potassium acts as structure directing agent and stabilises the tunnel structure. Due to the existence of manganese in different oxidation states (Mn2+, Mn3+ and mainly Mn4+) inside of the frame-work, these materials are interesting catalysts for selective oxidation reactions.

K-OMS-2 are prepared via two different routes: (i) oxidation in aqueous solution (sample TW04) or (ii) oxidation in solid-state-reaction (sample SJ01FS) of Mn2+ with KMnO4 [3].

The reference samples where produced by a 6h 1000°C treatment followed by compacting with 2kPa.



K-OMS-2 Results from PLS: The upper graphs show the traditional plots of intensities and lifetimes for each sample, the lower graph shows the intensity plotted versus the lifetime to spot clusters. Both axes are logarithmic for better clarity.

There are two lifetime components of ~200ps and ~360ps. Unfortunately these components are not the same for the porous samples and the "reference" samples, still we attribute them to the bulk of the samples.

Additionally the p-Ps component and two long lifetime components where found in the porous samples. These long components are ~4.2ns and between 40ns and 103ns. Using the extended Tao-Eldrup models and the calibration-curve of [4, 5], these conform to 0.77nm and 2.7-10.5nm pore-size.

As the intensities of both of these components are rather low, the longest component could also very well show a distribution of pore-sizes and relate to the pores measured in Nitrogen-absorption.

A bit more difficult is the interpretation of the pores of 0.77nm. They have the right size for the internal openings of the OMS-2 structure. But with the K-ion the space should be invisible or much reduced for positrons.

Positronium lifetime

Many general advantages of digital positron spectrometers have been given in the past [7, 8]. Yet a special advantage for Positronium spectroscopy hasn't gotten that much attention so far.

Analogue set-ups are limited by the number of bins the multi-channel-analyser (MCA) provides. For lifetime spectra with long components this usually involves a trade-off, as the input-range of the MCA has to fit across a wider time-span. This reduces the timing-resolution in general and limits the fine grained size of one bin with respect to time.

With standard 2^14 bins and a time-window of 1μs, the resulting 61ps per bin make it hard to determine the p-Ps lifetime of 125ps.

Digital to the rescue

With digital set-ups this does not apply. As the number of bins in the spectrum is virtually un-limited, the time per bin in the spectrum is not limited and can be chosen freely.

This allows for measurements of the long lifetime components of o-Ps together with accurate measurements of p-Ps while retaining the spectrometers good timing resolution.

The measurements on this posters show results of real-world measurements. Apart from the covered time-span the set-up of the spectrometer was not changed from semi-conductor to porous-material measurements. The timing resolution stays the same for the Si-reference and the porous materials.

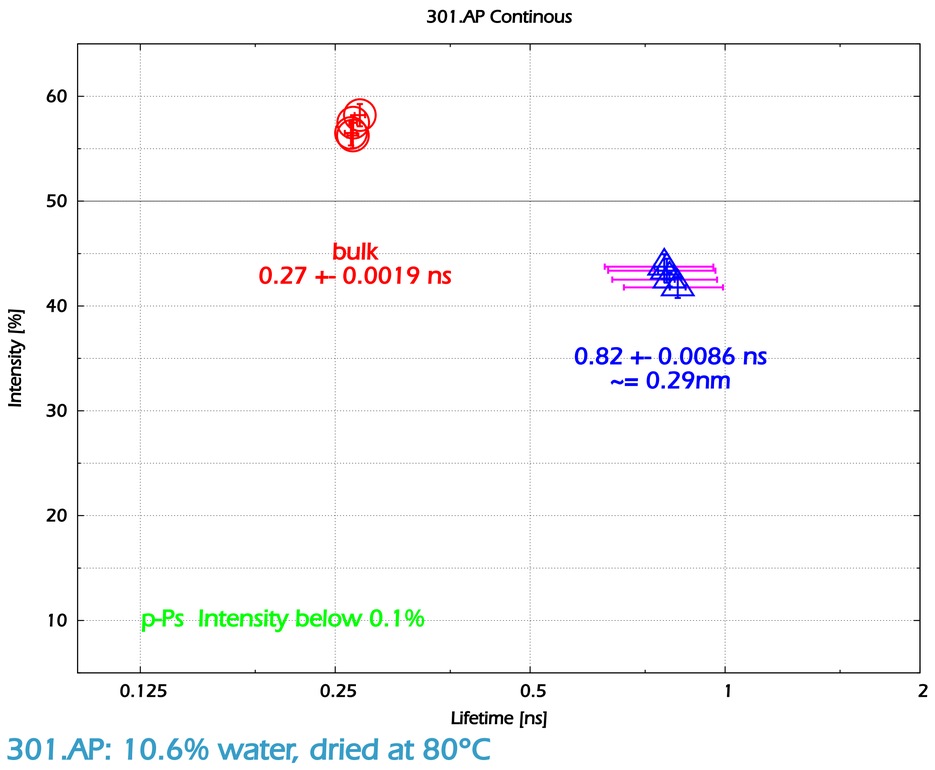
Finding colloides while searching for nano-voids in sodium silicate solutions

Other materials of interest are dried sodium silicate sols. Prepared by dissolving sodium silicate glasses they contain colloids of different size classes starting with primary particles having a radius of 0.5nm. Larger particles are probably aggregates of the primary particles. The internal structure of the colloids is though to resemble the structure of silicate glass. Some authors suggest a cubic octamer as smallest possible colloid.

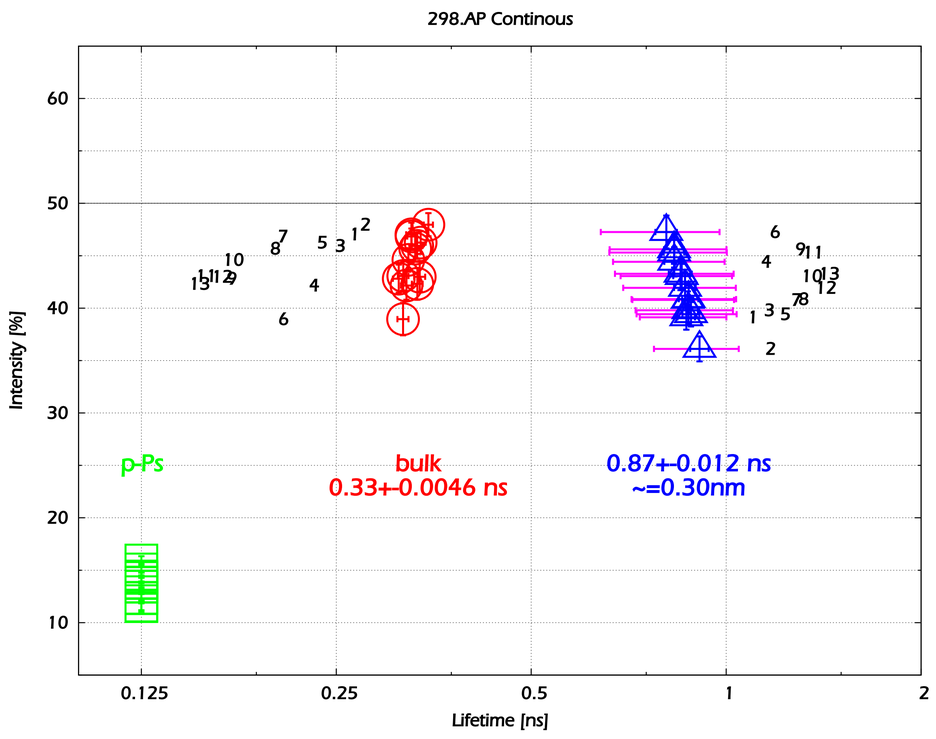
These solutions form transparent amorphous solids by simple drying.

Two samples with a molar SiO2:Na2O ratio of 3.3 where provided. Sample 298.AP was dried at 80°C to 10.6% wetness. The second sample 301.AP was tried at 40°C to ~30% wetness.

While the original quest was to search for the size and distribution of colloids and colloid-aggregates, these can not be found by positrons. But we measure a Ps lifetime:



301.AP: 10.6% water, dried at 80°C
Several measurements without a visible time dependency.



298.AP: 10.6% water, dried at 80°C
Several measurements where done, the numbers displayed indicate the measurement. There is no time dependence visible for the bulk- and the void-components.

Both samples show a high porosity with Ps intensity well above 40%. The bulk lifetime of 270ps and 330ps is not yet evaluated in detail. It might well be a mixture of SiO2, Na2O, water and (in sample 301) p-Ps. Sample 298.AP seems to show a p-Ps:o-Ps ratio of roughly 4:1.

The positronium component of 0.82ns and 0.87ns is showing a distribution of 0.3ns to 0.35ns. Using the calibration curve of [5] this results in pore-sizes of 0.29nm to 0.3nm. This coincides with the dimensions of the basic colloid structure according to [6].

References

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[8] doi:10.1016/j.apsusc.2008.05.215

We wish to thank Ms. Jank from the department of technical chemistry of the university Leipzig for providing the K-OMS-2 samples.
Thanks also to Mr. Roggendorf from department of physics of the university Halle for providing the sodium silicate samples.
The work is founded by the German Federal Ministry of Education and Research under the project 05KK7NH1.

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