NMR INVESTIGATION OF ZIRCONIUM PHOSPHATES

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Zirconium phosphates (ZrP) are a family of materials used in variety of applications including batteries, super-capacitors, catalysis and medicine as drug carriers [1, 2]. They are 2D materials, which, due to their polymorphic structure, are classified as α-, γ- and λ- ZrP. These compounds are suitable for intercalation with various ions (Na^+, K^+, NH_4^+, Cl^- and others), enabling tailoring for a wide range of applications [3].

In this study solid-state Nuclear Magnetic Resonance (ssNMR) was used to characterize α- and γ- ZrP polymorphs doped with NH_4^+, K^+ and Na^+ ions. ^{31}P and ^{23}Na MAS NMR methods were used to determine the composition of the samples. Alongside 2D NMR techniques, such as ^{31}P-^{31}P 1Q-2Q and ^{23}Na MQMAS NMR, it was possible to assign ^{31}P MAS NMR spectral lines to different crystal motifs of ZrP polymorphs and determine number of distinct ^{23}Na environments present in the samples.

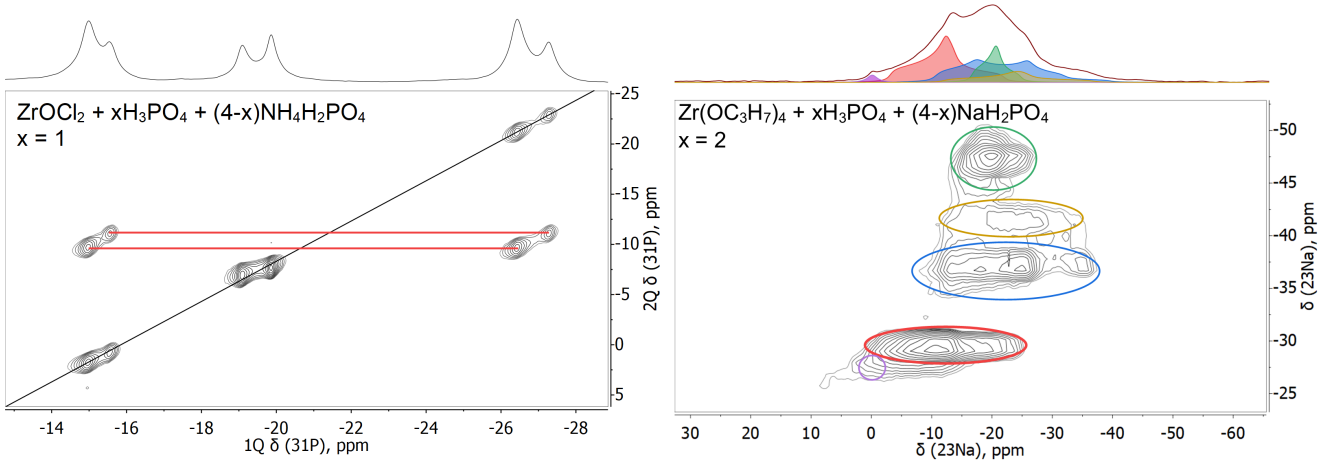

Fig. 1. ^{31}P-^{31}P 1Q-2Q (left) and ^{23}Na MQMAS (right) NMR spectra of α- and γ- ZrP polymorphs. Horizontal projections of 2D spectra correspond to 1D ^{31}P and ^{23}Na MAS NMR spectra.

It was found that α- and γ- polymorphs intercalated with NH_4^+, K^+ and Na^+ were formed during synthesis procedure. Additional ion exchange with hydrochloric acid (HCl) was performed to remove intercalated ions and confirm previous results. The ^{31}P-^{31}P 1Q-2Q NMR data enabled the identification of two structural phases of NH_4ZrP polymorphs and explanation of crystal structure of α-KZrP. Furthermore, intercalation with Na^+ ions yielded products with four distinct ^{23}Na chemical environments of NaZrP.

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