

MS21 O1

Structural characterisation of layered mixed titanium zirconium phosphates Jennifer E. Readman, Victoria Burnell and Joseph A. Hriljac, *School of Chemistry, University of Birmingham, Edgbaston, Birmingham, B15 2TT, United Kingdom.*

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There has been a considerable amount of interest in the ion-exchange properties of layered zirconium phosphates [1, 2]. This interest has been renewed due to potential application in the remediation of nuclear waste. To date there has been two reports in the literature of a layered mixed titanium zirconium phosphate, which was poorly crystalline [3, 4]. The authors believed that these materials would have enhanced ion-exchange properties due to the presence of titanium. Here we present the hydrothermal synthesis of a series of crystalline layered mixed titanium zirconium phosphates and their structural characterisation. Structural characterisation was carried out using both Rietveld and Le Bail methods and also pair distribution function analysis (PDF) of powder X-ray diffraction data [5]. To our knowledge, it is the first time PDF studies have been carried out on these type of materials. It was found that the materials are similar in structure to α -zirconium phosphate [6], and no ordering of the titanium or zirconium was found. The thermal properties of the materials were investigated using both TGA and in-situ powder X-ray diffraction. It was found that the materials lose crystallinity upon the loss of the water intercalated between the layers. At higher temperatures, the samples decompose further, with the loss of water to form a dense phase. The behaviour was found to be similar to that of α -titanium phosphate, rather than α -zirconium phosphate (which forms a crystalline intermediate phase). A mixture of titanium pyrophosphate and zirconium pyrophosphate, rather than a single pyrophosphate of a solid solution was formed at high temperatures Initial ion-exchange results will also be discussed.

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MS21 O2

Structural effects of electric fields - AlPO_4 and other piezoelectric α -quartz isotypes. N.K. Hansen^a, P. Allé^a, P. Fertey^{b,a}, O. Cambon^c, J. Haines^c ^a *Laboratoire de Cristallographie et Modélisation des Matériaux Minéraux et Biologiques, Nancy Université, France.* ^b *Synchrotron Soleil, France,* ^c *Institut Charles Gerhardt, Université Montpellier 2, France.*

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The effects of applying electric fields to crystals are well described on a macroscopic scale by, among others, the dielectric and piezoelectric coefficients. Nevertheless the origin of these phenomena (polarization and strain) is not yet understood at an atomic level.

When applying a pseudo-static strong electric field to a crystal during a diffraction experiment [1], we observe induced changes in Bragg angles and intensities. The former has a simple relationship to the piezoelectric constants, and from the latter, having measured a sufficient number of reflections, we may obtain the structural changes resulting from the field.

The aim of the studies reported here is to improve our understanding of the mechanisms responsible of the piezoelectric behaviour in crystals, which may be of help for finding better materials for technological applications. In the past we have carried out this type of experiment for α -quartz [2], and very recently for berlinite (AlPO_4). These results may be compared with measurements realized on a third compound GaPO_4 independently performed by our group [3], although in a less complete study, and by Gorfman *et al.* [4].

The piezoelectric constants obtained from the diffraction measurements all agree closely with the known values. This is important for ensuring that the applied field is homogeneous and has the expected strength throughout the diffracting volume of the sample.

The structure of these compounds can be thought of as a three-dimensional network of corner sharing tetrahedra (the corners are the oxygen atoms). For all the compounds the main effect is changes in bond angles, within the tetrahedra as well as the bond angle at the oxygen atoms corresponding to the angle between to neighbouring tetrahedra. For a field of 30 kV/cm, the bond angle changes are at most a few tenth of a degree. The higher the (pseudo) dipole moment of a tetrahedron is, the larger the effect of the electric field. The tendency, as one could expect is a tendency rotate the tetrahedra so that the pseudo-moments will approach the direction of the field. These observations are consistent with the comparative studies of structure (in absence of a field) and piezoelectric properties.

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