CHARACTERISATION AND THERMAL BEHAVIOUR OF Ag_2PO_3F

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Monofluorophosphates(V) are important materials used as toothpaste additives, wood preservatives, corrosion inhibitors or as intermediates during biomineralisation of fluoroapatite. Possible preparation routes of these materials include solid state reactions using metalfluoride/-phosphate melts, or conversion of the readily soluble $(NH_4)_2PO_3F$ and metal salts in aqueous solutions. A more convenient method makes use of the metathesis reaction

$Ag_2PO_3F + 2\ M^{II}Cl / (M^{II}Cl_2) \rightarrow M^{I}_2PO_3F / (M^{II}PO_3F) + 2\ AgCl.$

However, no detailed structural information on the starting material Ag_2PO_3F is known so far. Characterisation and thermal behaviour of this phase are presented here.

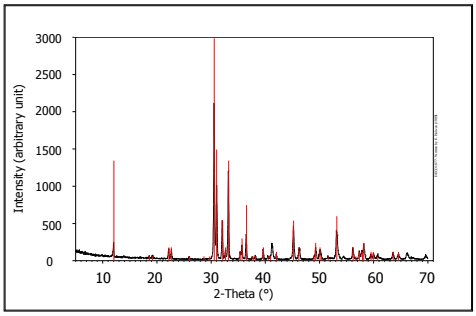

Figure 1: X-ray powder diffraction pattern of Ag_2PO_3F, red bars correspond to library data (PDF#18-1176)

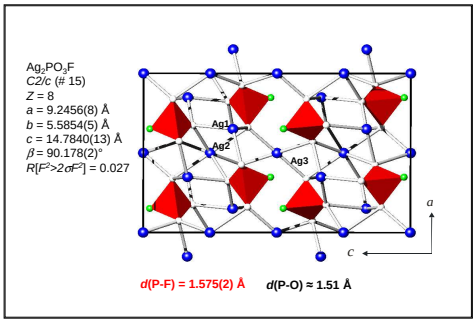

Figure 2: Crystal structure of Ag_2PO_3F

Single crystals of Ag_2PO_3F were grown by slow evaporation of a diluted aqueous solution of $(NH_4)_2PO_3F$ and $AgNO_3$. The crystal structure is made up of PO_3F tetrahedra and distorted $[AgO_4]$ and $[AgO_6]$ polyhedra as the main building units (Figures 1 and 2).

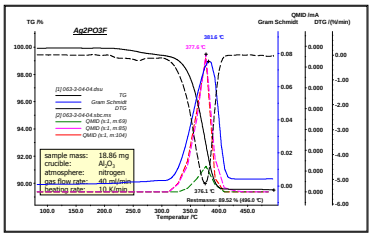

Figure 3: Relative mass change of Ag_2PO_3F investigated with TG-FTIR-MS

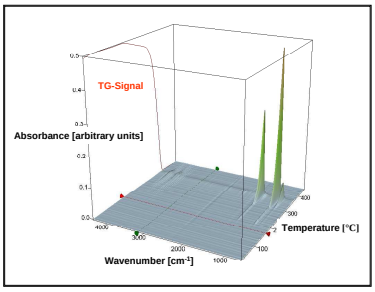

Figure 4: 3-D view of all IR-spectra versus temperature with TG-signal

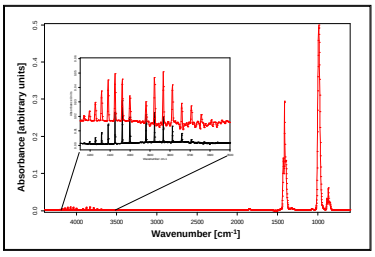

Figure 5: Extracted single spectrum at 377°C (red) comparison with library data of HF (black)

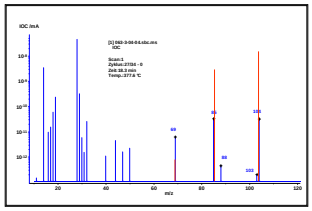

Figure 6: Detected MS data at 377°C (blue), red bars correspond to library MS data for POF_3 (NIST Chemistry WebBook)

A simultaneous TG-FTIR-MS measurement of Ag_2PO_3F (Figure 3) indicates a mass loss step of 10% at 375°C (DTG). The gaseous decomposition products formed are identified to be mainly POF_3 (Figures 4 to 6) and small amounts of HF (Figures 4 and 5). The solid reaction products are $Ag_4P_2O_7$ and Ag_3PO_4 according to the following equation.

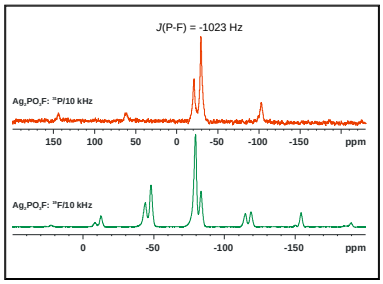

Figure 8: Solid state ^{19}F- and ^{31}P-NMR Spectra

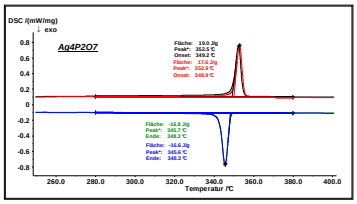

Figure 7: DSC results for $Ag_4P_2O_7$ 2 heating and cooling cycles

$4\ Ag_2PO_3F_{(s)} \rightarrow$

$Ag_4P_2O_{7(s)} + Ag_3PO_{4(s)} + AgF_{(l)} + POF_{3(g)}\uparrow$

Single phase $Ag_4P_2O_7$ was investigated by means of DSC. The reversible phase transition at 350°C is presented at Figure 7.

Structure data of Ag_2PO_3F are consistent with solid state NMR spectra (Figure 8).