

# CHARACTERISATION AND THERMAL BEHAVIOUR OF $\text{Ag}_2\text{PO}_3\text{F}$



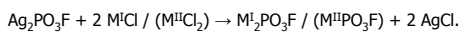
Matthias Weil and Ekkehard Füglein



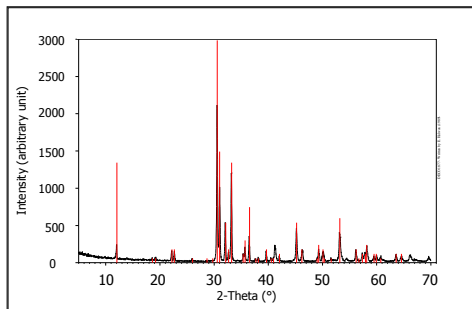
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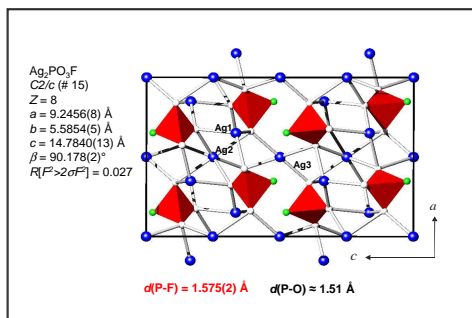
Monofluorophosphates(V) are important materials used as toothpaste additives, wood preservatives, corrosion inhibitors or as intermediates during biomineralisation of fluoroapatite. Possible preparation routes of these materials include solid state reactions using metalfluoride/-phosphate melts, or conversion of the readily soluble  $(\text{NH}_4)_2\text{PO}_3\text{F}$  and metal salts in aqueous solutions. A more convenient method makes use of the metathesis reaction



However, no detailed structural information on the starting material  $\text{Ag}_2\text{PO}_3\text{F}$  is known so far. Characterisation and thermal behaviour of this phase are presented here.

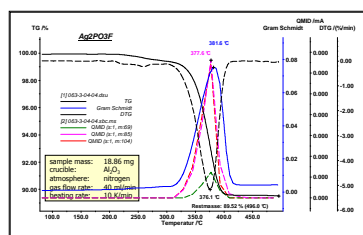


**Figure 1:** X-ray powder diffraction pattern of  $\text{Ag}_2\text{PO}_3\text{F}$ , red bars correspond to library data (PDF#18-1176)

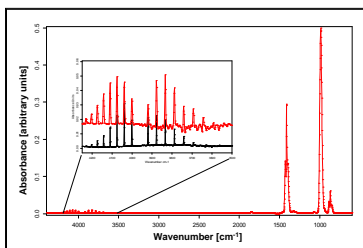


**Figure 2:** Crystal structure of  $\text{Ag}_2\text{PO}_3\text{F}$

Single crystals of  $\text{Ag}_2\text{PO}_3\text{F}$  were grown by slow evaporation of a diluted aqueous solution of  $(\text{NH}_4)_2\text{PO}_3\text{F}$  and  $\text{AgNO}_3$ . The crystal structure is made up of  $\text{PO}_3\text{F}$  tetrahedra and distorted  $[\text{AgO}_4]$  and  $[\text{AgO}_6]$  polyhedra as the main building units (Figures 1 and 2).

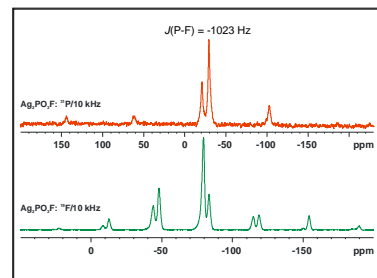


**Figure 3:** Relative mass change of  $\text{Ag}_2\text{PO}_3\text{F}$  investigated with TG-FTIR-MS

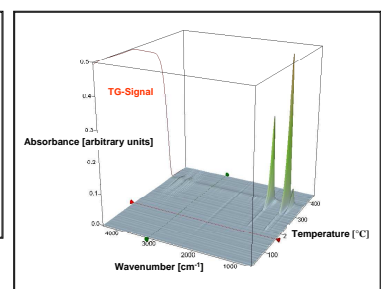


**Figure 5:** Extracted single spectrum at 377°C (red) comparison with library data of HF (black)

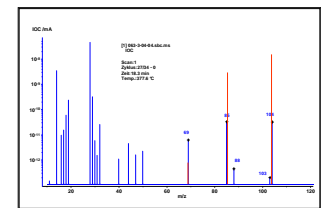
A simultaneous TG-FTIR-MS measurement of  $\text{Ag}_2\text{PO}_3\text{F}$  (Figure 3) indicates a mass loss step of 10% at 375°C (DTG). The gaseous decomposition products formed are identified to be mainly  $\text{POF}_3$  (Figures 4 to 6) and small amounts of HF (Figures 4 and 5). The solid reaction products are  $\text{Ag}_4\text{P}_2\text{O}_7$  and  $\text{Ag}_3\text{PO}_4$  according to the following equation.



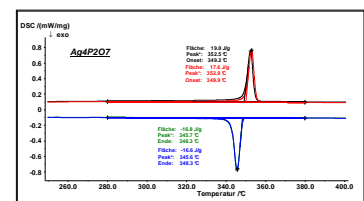
**Figure 8:** Solid state  $^{19}\text{F}$ - and  $^{31}\text{P}$ -NMR Spectra



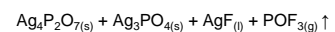
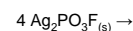
**Figure 4:** 3-D view of all IR-spectra versus temperature with TG-signal



**Figure 6:** Detected MS data at 377°C (blue), red bars correspond to library MS data for  $\text{POF}_3$  (NIST Chemistry WebBook)



**Figure 7:** DSC results for  $\text{Ag}_4\text{P}_2\text{O}_7$  2 heating and cooling cycles



Single phase  $\text{Ag}_4\text{P}_2\text{O}_7$  was investigated by means of DSC. The reversible phase transition at 350°C is presented at Figure 7.

Structure data of  $\text{Ag}_2\text{PO}_3\text{F}$  are consistent with solid state NMR spectra (Figure 8).