PLENARY 1

FORTY YEARS OF METAL FLUORIDES – AND NO END?

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The modern chemistry of metal fluorides, specially polynary ones starts with the work of HENRY EMELÉUS (1948)

(1a) $CoCl_2 + BrF_3 \longrightarrow CoF_3$

and WILHELM KLEMM (1949)

(1b) $2\,KCl + NiCl_2 + F_2 \longrightarrow K_2[NiF_6]$

More than 1000 new fluorides have been synthesized using these pathways. What did we do? Where did we fail? What should be done?

(A) Both pathways led to higher oxidations states, - lower oxidation states were more or less omitted.

(B) The new compounds were obtained mainly as powders, - single crystals for structural elucidations were not available.

So within the past, cultivation of both trails took place:

(Ca) HIGH PRESSURE SYNTHESIS created single crystals of e.g. MnF_4, and

(Cb) SOLUTION CHEMISTRY with aqueous/pure HF enabled one to grow single crystals (of e.g. K_2MF_6 with M=Pt etc.) and powder of metastable fluorides (like e.g. PrF_4).

To break into parts the remaining jungle we studied new 'in situ' syntheses:

(D) THE REACTION WITH 'THE WALL', e.g.

$Cs_2[TiF_6] + NaF$ (in Ti-tubes) = $Cs_2Na[TiF_6]$, single crystals

(E) FLUORINATION BY A 'LIFT', e.g.

$3\,CsF + Ge + 2\,CuF_2 = 2Cu + Cs_3F[GeF_6]$, single crystals

Both new methods are of general application. Numerous examples will be given.