(MV)[$M^{III}X_5$] (MV: methylviologen; M: Bi, Sb; X: Cl, Br, I): A New Family of Ferroelectrics

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The ns^2 elements of groups 14 et 15 are well known to give materials with ferroelectric properties, as in $BiFeO_3$, for which the bismuth(III) lone pair stereoactivity is clearly correlated to the dielectric properties.

We found that the the methylviologen dication, has stabilized unprecedented $M^{III}X_5$ chains (M= Bi, Sb) of trans-connected MX_6 octahedra (the much more common isomer (M= Bi, Sb, X= I, Br, Cl) corresponds to the chain of cis-connected octahedra,), and this can be correlated to the electron acceptor behavior of the organic entitites which consequently modulates the charge density at the organic-inorganic interface.[1] The first characterized compound, (MV)[$BiBr_5$], is centrosymmetric at ambient temperature, and built from regular chains of octahedra (stereo-inactivity of the lone pair). At -30°C, the material undergoes a ferroelectric transition, due to the stereo-activation of the bismuth(III) lone pair and the presence of polar chains ($P2_1$ polar structure)[2] (Figure). The ferroelectric behavior of (MV)[$BiBr_5$] has been confirmed by pyroelectricity measurements.

In this communication, we will present a series of new compounds recently achieved, and belonging to either the (MV)[$M^{(III)}X_5$] type, or the mixed halide (MV)[$M^{(III)}X_{5-x}X'_x$] type (M= Bi, Sb, X= I, Br, Cl). Their general structural layout is alike, but the structures can differ one from each other due to the nature of the MX_5 chains, polar or apolar, regular (M-$X_{bridging}$-M bond angle close to 180°) or distorted (M-$X_{bridging}$-M bond angle close to 130°), the coupling between chains (in case of polar chains), the nature of the intermediate phases (case of mixed halide salts), either defined compounds or compounds belonging to a solid solution. The majority of these (MV)[MX_5] compounds form a new family of ferroelectrics. The synthesis, crystal structures and dielectric properties investigations will be described.

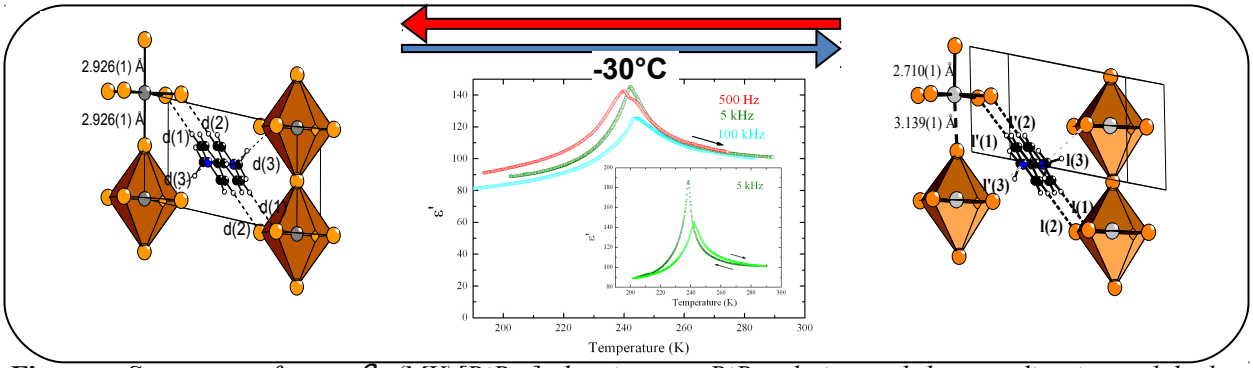

Figure – *Structures of α- et β- (MV)[$BiBr_5$] showing two $BiBr_5$ chains and the coordination polyhedron around Bi^{3+}, octahedral (β- phase - left), and distorted octahedral leading to polar $BiBr_5$ chains (α-phase - right). Graph : Dielectric constant ε' versus T for different applied frequencies (Inset: thermal cycling of the dielectric constant at a fixed frequency ε').*

[1] N. Mercier, N. Louvain , W. Bi ***CrystEngComm* 2009, 11, 720-734.**

[2] W. Bi, N. Leblanc, N. Mercier, P. Auban-Senzier and C. Pasquier ***Chem Mater*** **2009, 21, 4099-4101.**