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THE NEW Fe₄A₂O₉ (A=NB OR TA) MAGNETOELECTRIC OXIDES: ON THE PECULIAR ROLE OF DIVALENT IRON IN THE "429" CORUNDUM DERIVATIVES[*]

In transition metal oxides of ABO_3 formulas, the close packing of oxygen atoms is either cubic or hexagonal. For instance, this allows to describe the two possible polytypes of the $ACoO_3$ cobalt perovskites, derived from cubic or hexagonal structures. This ABO_3 formula (or A_2O_3 if A=B) also includes the corundum derivatives in which the oxygen close packing is hexagonal, their trigonal structures being either centro- ($R\bar{3}c$ or $P\bar{3}c1$) or non centrosymmetric (like $R3c$). In fact, all corundum compounds can be written $A1A2(BB')O_6$ offering for the chemists a large choice of cation combinations.

One common feature of perovskite and corundum compounds lies in their functionality richness, as illustrated by their use in solid oxide fuel cells and their hardness for the former and the latter, respectively.

In the search for multifunctional materials, multiferroics have been the focus of many studies especially for those showing coupled ferroelectric and magnetic properties, which interest relies in the possibly to command the electrical polarization P (or magnetization M) by magnetic field H (or electrical field E) application (or vice versa). Again, for this research field, the $A1A2(BB')O_6$ magnetic compounds, including some perovskites, have produced many multiferroic compounds. For the corundum derivatives, the polar ones have also attracted much attention; the origin of their large P is not coming from the off-centring of d^0 cations as in PZT but rather from the cationic repulsion in dimers formed by edge-shared BO_6 and $B'O_6$ octahedrons. When these B and B' cations are magnetic and crystal ordered (in the polar corundum) then

a spontaneous P is observed and its magnitude can be tuned by external field magnetic field application leading to linear magnetoelectric (LME) effect.

In the centrosymmetric corundum, like the prototypical α-Cr_2O_3, no net spontaneous P exists but, in the antiferromagnetic state (AF), for applied H values beyond the magnetic field of the spin flipping transition, P is authorized by symmetry with values linear in H (LME). Thus, for these compounds, their AF structure determines whether or not they belong to LME. Among other LMEs, the $A_4M_2O_9$ have been investigated as their frustrated AF structure permits LME effect for A=Co, Mn and B=Nb, Ta. Only very recently, we have shown that this structural type ($P\bar{3}c1$ SG) could also be stabilized for A=Fe. These only recent reports for Fe [1–3] may be explained by the difficulty to stabilize the divalent oxidation state for that element in oxides.

In this presentation, the synthesis and structural characterizations of these compounds will be given. The main difference of ME properties with those of other isostructural A=Co or Mn 429 will be reviewed, including their higher Neel temperatures and their more complex phase diagrams. Also, the improvement of the H-induced P values resulting from A site Fe/Co disordering will be presented ([4] and figure).

The lack of LME in the A=Ni compound will also be discussed in connection to its orthorhombic structure and its revisited ferrimagnetic structure [5, 6]. Finally, an example of another trigonal compound containing divalent manganese, Mn_3WO_6, a recently discovered new multiferroic, synthesized at ambient pressure and isostructural to Mg_3TeO_6, will allow to show that new structural types among trigonal compounds are still worth studying.
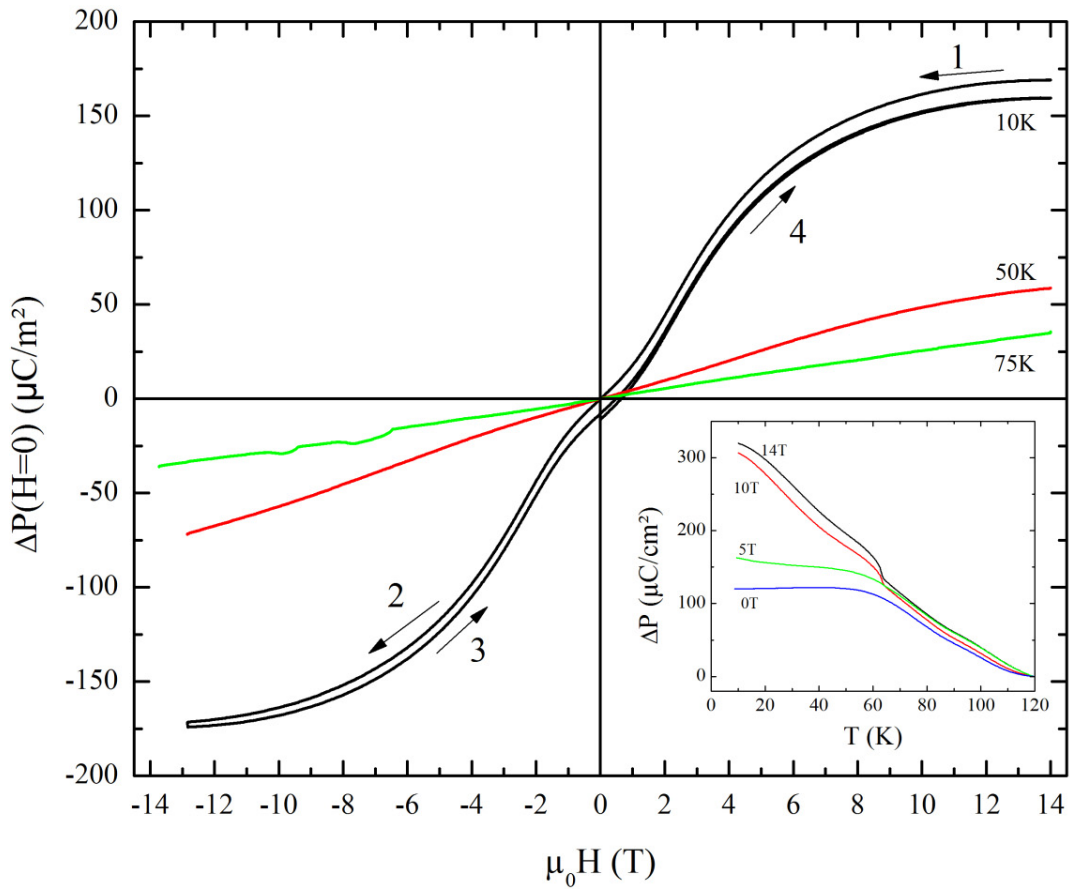
Fig. 1. Isothermal electrical polarization P of $Fe_2Co_2Nb_2O_9$ as a function of magnetic field H. Inset: T dependence of P collected for different H values. At T = 10K, P is clearly no longer linear in H reflecting the more ferromagnetic like behaviour induced by Fe/Co cation disordering at the A site of this 429 phase

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