Controlling magnetic sublattices in heterometallic ludwigite Fe3-xMnxBO5

Françoise Damay1, Fabien Lainé2, Anne Guesdon2, Sylvain Petit1, François Fauth3, Premysl Baran4, Antoine Maignan2, Christine Martin2

1Laboratoire Léon Brillouin, Gif Sur Yvette Cedex, France, 2CRISMAT, Caen, France, 3ALBA Synchrotron, Barcelona, Spain, 4Nuclear Physics Institute, Rez near Prague, Czech Republic
E-mail: francoise.damay@cea.fr

Ludwigite oxyborates M2M′BO5, where M and M′ are divalent and trivalent 3d metal ions, respectively, have an intriguing orthorhombic (SG : Pbam) crystal structure made of interconnected low dimensional units in the form of three-leg (3LL) ladders, 3LL1 and 3LL2 [1] (Figure 1). 3LL1 is made of three edge-sharing octahedra, while 3LL2 is made of three corner-sharing octahedra, in the ab plane. These three-octahedra units, or triads, share edges along c to form square ladder sublattices. The existence of two crystallographically distinct sublattices is actually not anodyne : in vonsenite Fe3BO5, Mössbauer and X-ray diffraction studies at room temperature have evidenced that Fe3+ species occupy preferentially 3LL1, while 3LL2 is occupied by Fe2+ [2]. In addition, a charge ordering transition has also been observed at TCO = 283 K [1], [4], resulting from the ordering on 3LL1 of the extra itinerant electron within each Fe3+ triad. This also impacts the magnetic properties : according to neutron diffraction results, 3LL1 and 3LL2 magnetically order, but independently, at TN1 = 112 K and TN2 = 70 K, with different propagation vectors, k1 = (0 0 ½) for 3LL1, and k2 = (0 0 0) for 3LL2.

To investigate the origin of this behavior, the isostructural system Fe3-xMnxBO5 has been studied by electron microscopy and low temperature neutron powder diffraction, combined with physical properties measurements. A decrease of both TN’s, more pronounced for TN2, along with a reduced ordered moment, are observed with increasing x, up to x = 1. Interestingly, results show that Mn is substituted preferentially on 3LL2 : for x = 1, in addition to the disappearance of charge ordering features, only short-range magnetic ordering is observed on 3LL2, leading to superparamagnetic ac susceptibility response [3]. Relaxor type ferroelectric properties are observed up to x = 1 at low temperature. Surprisingly, for x = 1.5, 3D long-range ordering below TN = 100 K is observed, which couples both 3LLs within a collinear k = 0 0 0 structure, without any sign of magnetic disorder.

The existence of two magnetic sublattices, whose composition and coupling can be tuned through preferential substitution, make of this ludwigite system a promising one to study the effect of controlled magnetic disorder in transition metal compounds.


Keywords: ludwigite, magnetic structure, disorder