Controlling magnetic sublattices in heterometallic ludwigite Fe$_{3-x}$Mn$_x$BO$_5$

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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 Fe$_{3-x}$Mn$_x$BO$_5$ 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.


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