

Breaking the geometric magnetic frustration in controlled off-stoichiometric LuMn_{1+z}O_{3+o} compounds

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TITLE

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3 **Breaking the Geometric Magnetic Frustration**
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7 **in LuMn_{1+z}O_{3+δ} controlled off-Stoichiometry**
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ABSTRACT

This study explores controlled off-stoichiometric $\text{LuMn}_{1+z}\text{O}_{3+\delta}$ ($|z| < 0.1$) compounds, intended to retain the utter LuMnO_3 intrinsic hexagonal symmetry and ferroelectric properties. X-ray powder diffraction measurements evidenced single phase $P6_3cm$ structure. Thermo-gravimetric experiments show a narrow impact of oxygen vacancies while distinguish a gas exchange $\sim 700\text{K}$, surprisingly lower temperature when comparing to perovskite systems. Comparison of different nominal ceramics revealed pertinent structural and magnetic properties variations owing to subtle self-doping effects. Deviations from the archetypal antiferromagnetic state were detected below $\sim 90\text{K}$ suggesting local rearrangements of the nominal Mn^{3+} ions matrix, breaking the ideal geometrical spins frustration, leading to non-compensated magnetic structure.

KEYWORDS:

ferroelectric ceramics,

thermogravimetric analysis,

crystal structure,

magnetic frustration

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The relevant scientific and technological interest over multiferroics [1, 2] leads to the study of a diversity of extrinsic composites and intrinsic materials, in particular based on lanthanide manganite systems (LnMnO_3) due to the strong spin-lattice coupling and the high sensitivity of the physical properties to doping [3]. Special attention has been given to complex magnetic ordering geometries, leading to a non-centrosymmetric crystal structures through the spin-lattice coupling, which can give rise to magnetically induced ferroelectricity, with strong magnetoelectric effect [4]. Previous studies on self-doped manganites have evidenced the subtle modification of the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio, crystal structure and transport properties, including magnetic and conductive behavior, besides shifting critical transitions temperatures [3]. Off-stoichiometry within a restricted amount of cationic or anionic vacancies (well below percolation threshold) has the advantage of introducing controlled electric charge doping, while minimizing ionic radius variance and preserving the same elemental chemistry, and retaining the overall structural symmetry of the stoichiometric compound. In this context, we explore the hexagonal LuMnO_3 system which exhibit multiferroic behavior below the Néel temperature ($T_N \sim 90$ K) where ferroelectricity coexists with a canted antiferromagnetic (c-AFM) structure arising from the geometrical frustration of the triangular lattices of Mn^{3+} ions [3]. The study of $\text{LuMn}_{1+z}\text{O}_{3+\delta}$, here reported is mainly focused on the effects of scarce cation vacancies ($-0.06 \leq z \leq 0.01$), preventing percolation defects and preserving the original structural symmetry and intrinsic ferroelectric (FE) properties of the stoichiometric compound. The minor off-stoichiometry is intended to originate cation vacancies and promote subtle oxidation of neighboring Mn^{3+} ions, originating charge inhomogeneities and redistribution. These perturbations are anticipated to induce local irregularities in geometrical c-AFM frustration, as it is found in the stoichiometric compound [5]. According to Bulaevskii

1 model [7], an electric polarization contribution can be predicted from uncompensated
2 triangular spins geometry; consequently, a suitable break of the ideal geometrical AFM
3 frustration can eventually enhance multiferroic and magnetoelectric effect in the
4 material. In order to support this idea, a more specific study of samples with nominal
5 compositions $\text{LuMn}_{1.01}\text{O}_3$ (LuM101), $\text{LuMn}_{1.00}\text{O}_3$ (LuM100), $\text{LuMn}_{0.99}\text{O}_3$ (LuM099),
6 $\text{LuMn}_{0.98}\text{O}_3$ (LuM098) and $\text{LuMn}_{0.94}\text{O}_3$ (LuM094) was carried out, comparing
7 experimental results with referenced data on LuMnO_3 manganite.
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10 Polycrystalline samples were prepared by sol-gel combustion method known to
11 produce powders with low grain size distribution and homogenous composition [8].
12 High grade Lu_2O_3 and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ compounds were used as precursors. Effective
13 formation of the hexagonal phase was achieved after calcination at $600\text{ }^\circ\text{C}$ for 4 h,
14 followed by grinding, sieving, pressing into pellets, sintering under air and quenched to
15 room temperature. Samples LuM100; LuM099 and LuM094 were sintered at $\sim 900\text{ }^\circ\text{C}$
16 during 96 h. Samples LuM101 and LuM098 were additionally sintered at $1300\text{ }^\circ\text{C}$
17 during 68 h, then recovering the $\sim 900\text{ }^\circ\text{C}$ annealing for 24 h. SEM observation and EDS
18 analysis were performed with a *FEI Quanta 400* (W filament) with an *EDS/EDAX*
19 detector. Rutherford Backscattering (RBS) and Proton Induced X-Ray Emission (PIXE)
20 spectrograms were simultaneously acquired. Samples were irradiated with 2 MeV
21 protons focused in $3 \times 4\text{ }\mu\text{m}^2$ and sweeping thru $1.5 \times 1.5\text{ mm}^2$, having found no
22 composition heterogeneities or contaminants. Thermogravimetric analyses (TGA) were
23 carried out using a *Setsys Evolution 1750* (*Setaram*) under O_2 flow from room
24 temperature to 400 K at 10 K/min, twice cycled up to 1150 K and once up to 1800 K at
25 2 K/min rate. Photoluminescence spectra were recorded at 12 and 300 K with a *Horiba*
26 *TRIAX 320* coupled in front face acquisition mode to a *Hamamatsu R928*
27 photomultiplier, using a 450 W Xe arc lamp as excitation source. X-ray diffraction was
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1 performed in a *Panalytical X'Pert Pro* equipped with *X'Celerator* detector and
2 secondary monochromator detector using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Rietveld
3 refinements were performed using *FullProf* software [9]. Magnetization measurements
4 from 5 to 300 K up to 10 Tesla used a *Cryogenic Ltd.* VSM system, whereas for
5 measurements up to 400 K a *Quantum Design MPMS-XL* SQUID system was used [10].
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11 The samples composition was checked by SEM/EDS and corroborated by
12 comparison with the results from RBS/PIXE techniques. No significant traces of
13 contaminants were found. The atomic ratio $|\text{Mn}|/|\text{Lu}|$ obtained is consistent with the
14 intended nominal composition expressed within the horizontal error bars expressed in
15 [figure 1a](#). XRD patterns reveal that presence of possible spurious phases like Lu₂MnO₅
16 or Mn₃O₄ are below accountable limit (<0.5%). Nevertheless, additional verification
17 using luminescence measurements evidence some residual traces of Lu₂O₃ phase in
18 samples LuM094 and LuM099. As such, for the same sintering conditions, the self-
19 doped LuM099 and LuM094 samples did not attained similar crystallographic quality
20 and chemical homogeneity as found in the LuM100 stoichiometric compound,
21 subsequently, samples LuM101 and LuM098 were subjected to additional sintering.
22 The Rietveld analysis of the obtained XRD data was successfully performed assuming
23 single phase structure for each compound, with the characteristic hexagonal space group
24 *P6₃cm* (185), as exemplified in [figure 1b](#), with typical quality factors $R_p < 5$, $R_{wp} < 7$
25 and $R_{exp} < 3$. Estimated mean crystallites size for the samples LuM101 and LuM098 is
26 ~93 nm, and for the samples LuM100, LuM099 and LuM094 is ~ 55 nm. The
27 comparison of the calculated *a* and *c* lattice parameters and unit cell volume of the
28 samples with several referenced data for nominal LuMnO₃ compounds [5, 11-21] is
29 shown in [figure 1](#). The dispersion of cell parameter values (~0.03 % variance in *a* and *c*)
30 published for this system can be understood from eventual slight off-stoichiometry (*z*,
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1 δ) which has not been considered, a normal consequence of the different synthesis
2 methods, precursors quality, sintering and annealing conditions.
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4 The cell parameters of the nominal LuMnO₃ compounds closer to stoichiometry as
5 LuM100 and LuMn099 are consistent with the values reported by Lee [5], Van Aken
6 [11] or Ghosh [12]. Sample LuM101 reveals some contraction, whereas for samples
7 LuM094 and LuM098 is perceptible a volume expansion of the unit cell due to a
8 pronounced extension of *a* parameter. This effect is compatible with the manifestation
9 of Mn vacancies and anionic repulsion, promoting a slight elongation of Mn–O bonds
10 located in the basal plane. Such interpretation is also plausible to elucidate the structural
11 spread found in several nominal compounds supposed as stoichiometric [13-21].
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24 The extensive work developed by Dabrowski *et al.* [22] supports the strong
25 decrease of the oxygen diffusion and intake in pseudo perovskite manganite systems
26 with the decrease of the A-site element ionic radius. For the extreme case of lutetium
27 manganite, the oxygen excess could be extrapolated to $\delta \approx +0.01$ for samples sintered at
28 1200 K and $\delta \approx -0.005$ for 1600 K [22]. However, more recent studies [23, 24] suggest
29 oxygen thermodynamics modeled for perovskite systems should differ significantly for
30 the hexagonal structures, due to the lower ionic density and layered MnO₅ bipyramidal
31 arrangements. In order to access the relative impact arising from anionic vacancies (δ)
32 in the LuMnO₃ system, thermogravimetry (TG) experiments were performed. Figure 2a
33 confirms that by cycling the sample up to 1150 K, the observed mass variations are
34 completely reversible and due to oxygen exchange. Figure 2b shows that quenching the
35 samples from above 1400 K can lead to a slight $\delta \approx -0.002$; also suggesting that δ
36 variations can be reversed after annealing treatments reaching 1300 K. These TG
37 experiments ultimately enable to constrain $|\delta| < 0.004$ for samples under study. Besides
38 the normal dehydration at 400-500 K, an additional and relevant feature to point out is
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the partial mass/oxygen exchange observed between 600 and 700 K, surprisingly ~200 K below the typical temperatures at which such ionic processes arise in perovskite manganite [22].

The Lu-Mn-O phase diagram [25] has some similarities to the perovskite manganite compounds [26] and can also tolerate a limited deficit of A or B-site vacancies well below percolation limit without compromising the stability of the hexagonal structure. The two main mechanisms to preserve charge neutrality of a doped system (\mathbf{z}) are considered: partial oxidation of Mn ions and/or formation of oxygen vacancies [27]. In particular, charge compensation mechanisms due to each Mn deficit lead up to 3 valence electrons deficit which, for $\delta \sim 0$, in the pseudo-perovskite systems can impinge three Mn^{4+} ions. However, for the hexagonal system, no volume contraction is evident as predictable from the occurrence of smaller $\text{Mn}^{4+}\text{-O}^{2-}$ bonds. In fact, the bipyramid crystal field (MnO_5) have a narrow splitting of the d-orbital energies, hence are less Jahn-Teller active and less prompt to form Mn^{4+} ions, than the octahedral cages (MnO_6) [28]. In addition to localized charge anomalies due crystallographic defects or grain boundaries, it is also conceivably that the new charge equilibrium could be unevenly dispersed through Mn^{3+} ions matrix; in fact, charges redistribution are not necessarily homogeneous, the $P6_3cm$ space group allows some subtle asymmetries for the six different Mn ions positions in the cell structure, each can slight differ in hybridization and intrinsic magnetic moment. These charges redistributions should reflect in the magnetic properties of the samples. In figure 3 and 4 is possible to compare some pertinent differences between the magnetic responses of the compounds. Albeit the small off-stoichiometry and spatial dispersion of cationic vacancies, the ensuing electronic perturbations are sufficient to modify the delicate balance of the compensated AFM matrix.

1 Magnetization measurements as function of temperature are represented in [figure 3](#);
2 the compounds with Mn deficit (LuM094, LuM098, LuM099) clearly exhibit a
3 smoothing of the anomaly of the M(T) curve at the expected AFM magnetic phase
4 transition, near $T_N \sim 90$ K, when compared to the more conventional behavior of the
5 LuM100 and LuM101 samples. Pronounced anomalies in the curves allow us to detect
6 the Néel temperature. Moreover, small anomalies observed between 25 and 50 K attest
7 additional magnetic rearrangements arising from complex competition between
8 antiferromagnetic interactions, as it was discussed by Das [\[29\]](#). For the paramagnetic
9 regime considered above 100 K, it is possible to perform (in the range 150-250 K) a
10 basic approach to the conventional Curie Weiss model $\{\chi = C/(T-\Theta)\}$ enabling the
11 calculation of the effective magnetic moment (μ_{eff}) and of parameter Θ , which denotes a
12 clue of the antiferromagnetic exchange interaction. For the compounds closer to
13 stoichiometry, LuM099, LuM100 and LuM101, the Θ values are very similar (~ -370
14 K) and $\mu_{eff} \sim 4.9 \mu_B/\text{Mn}$, which agrees with the expected value for high spin
15 configuration of Mn^{3+} , with $S = 2$ [\[30\]](#). For the sample designated LuM098 there is a
16 manifest deviation from the linear paramagnetic behavior, surprisingly, μ_{eff} approaching
17 $\sim 5.6 \mu_B/\text{Mn}$ ion at room temperature and, particularly, $\Theta < -550$ K, suggesting a notable
18 strengthening of antiferromagnetic interactions. The deviation from the linear expected
19 Curie-Weiss law evidence the stabilization of complex magnetic cluster-like behavior
20 well above T_{Neel} .

21 Magnetization measurements as function of external field shown in [figure 4](#),
22 revealed hysteresis loops in the self-doped samples with significant remanence and
23 coercive fields, reaching 0.005 emu/g and 0.02 T for sample LuM098 and 0.025 emu/g
24 and 0.1 T for sample LuM101; substantiating the presence of some weak ferromagnetic
25 component, not observable in the AFM stoichiometric LuM100 compound.

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In the present hexagonal manganite system, the polaronic exchange mechanism is lessened by the 120° angles in basal planes and is ruled out in the perpendicular axis. The super-exchange interaction is dominant in the regular spatial charge distribution of adjacent Mn^{3+} , dictating an antiferromagnetic order [5]. Nevertheless, slight off-stoichiometry overrides the strict overall symmetry rules, each vacancy imposes a local inhomogeneity and a slight redistribution of spatial charge, hence disturbing the conformed Mn^{3+} orbital clouds position and symmetry. Moreover the disseminated presence of vacancies can act simply as pinning dwells for domain walls [31] or even magnetic clusters [32, 33].

We observe that the LuMnO_3 hexagonal phase can be tolerant to a narrow cationic off-stoichiometry ($|\mathbf{z}| < 0.1$) and minor oxygen adjustments ($|\delta| < 0.005$) without substantial structural changes or phase segregation. In addition, TG experiments revealed an enhanced mass exchange at ~ 500 K, which is thermodynamically 300° lower than typically found in perovskite systems. Self-doping leads to a predictable ionic balance with slight oxidation of Mn^{3+} ions, resulting a noteworthy perturbation of magnetic triangular ordering, hence partially breaking the antiferromagnetic geometric frustration found below $T_{\text{Néel}}$ ascribed for the stoichiometric compound. Materials modification by self-doping suits a valid experimental approach to enhance multiferroic and magnetoelectric properties. Comparing several published works ascribed as LuMnO_3 , it becomes patent that the spread of structural and magnetic results can be understood within the high sensitivity of this system to very small composition variations.

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FIGURES CAPTIONS:

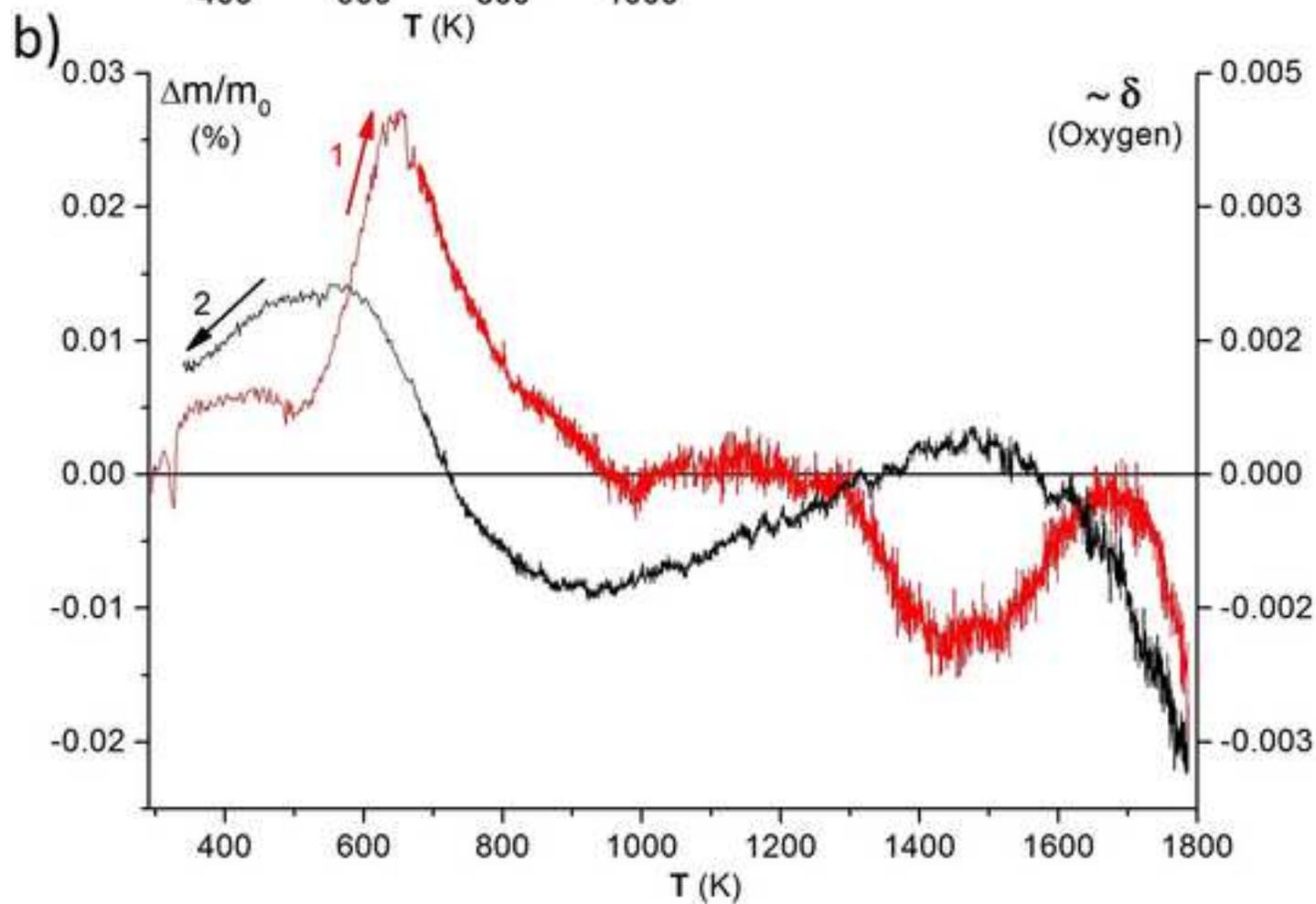
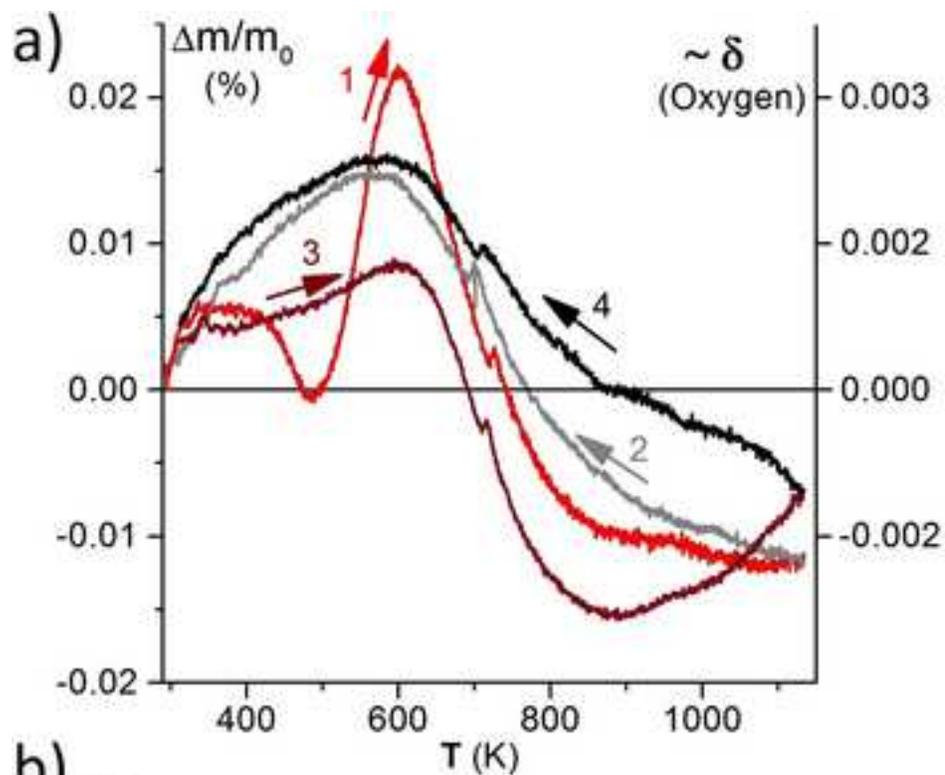
Figure 1: a) Comparison between samples composition and cell parameters obtained for the series of samples LuM- "094"; "098"; "099"; "100"; "101" respectively and from referenced data [5, 11-21]. **b)** Example of XRD and Rietveld refinement of sample LuM098.

Figure 2: TG measurements of sample LuM101 in low pressure O₂ atmosphere, **a)** double cycling to 1150 K; **b)** single cycle to 1800 K.

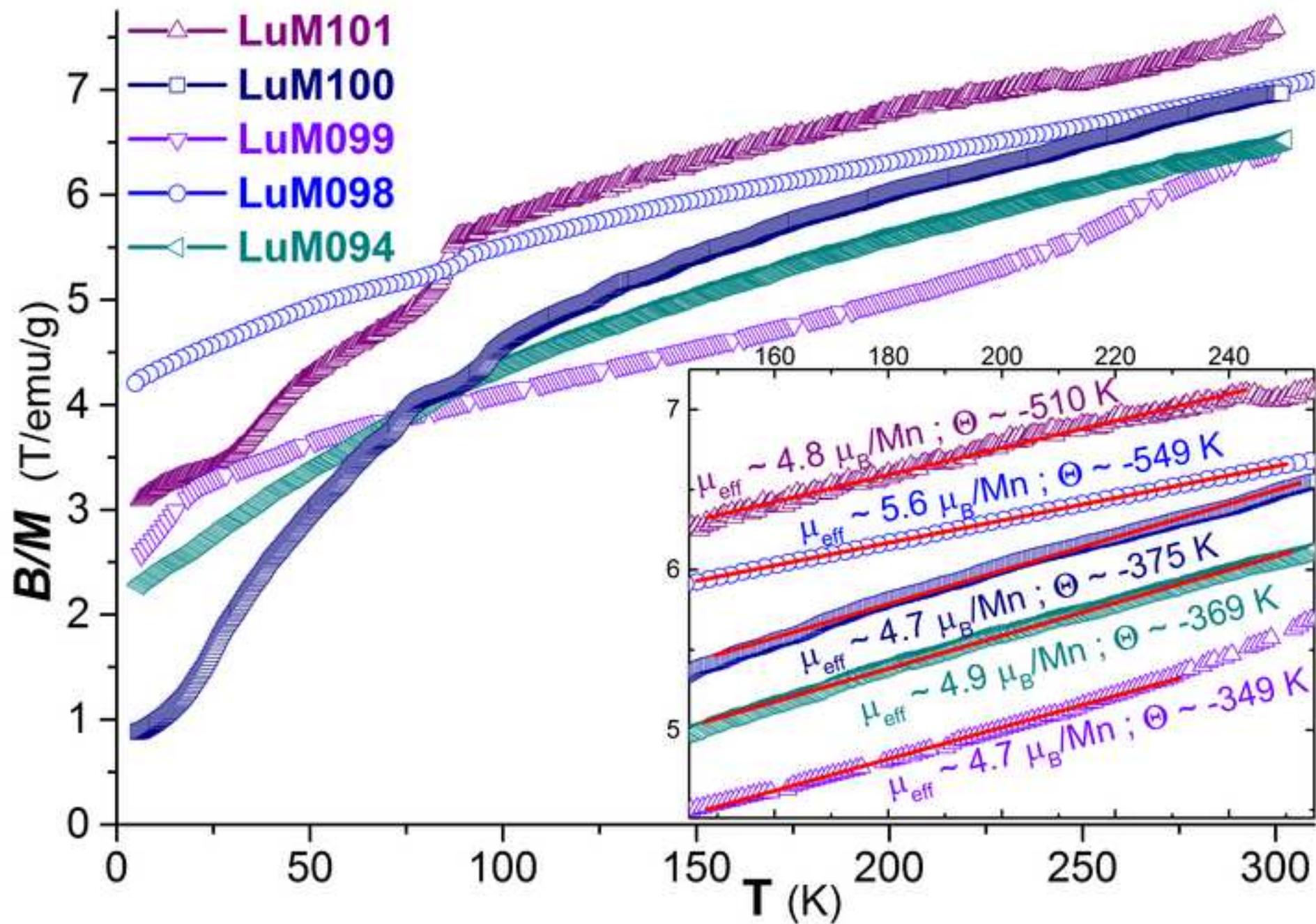
Figure 3: Magnetic measurements as function of temperature for the series of samples: a) B/M vs. T and b) dM/dT . Inset: Detail of Curie-Weiss fits and calculated parameters.

Figure 4: Comparison of magnetization (M) as function of magnetic field (B) at different temperatures for samples LuM **a)** -098, **b)** -100, **c)** -101. Respective insets zoom the behavior at low fields subtracted from the linear PM contribution.

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