Dielectric study of unexpected transitions in multiferroic Mn1-x(Mg,Zn)xWO4 ceramics

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ABSTRACT

The influence of magnetic field on the dielectric properties of several $Mn_{1-x}(Mg,Zn)_xWO_4$ multiferroic ceramics is investigated, and confirms an additional phase transition below the ferroelectric Curie temperature previously detected in this system in zero magnetic field. In highly doped samples an original plateau of the capacitance is observed between T_2 and this additional transition. Pyroelectric measurements in zero magnetic field for a $Mn_{0.85}Mg_{0.15}WO_4$ ceramic confirm the existence of this unexpected low temperature phase transition. The magnetic or structural origin of this transition is discussed.

1. Introduction

Magnetoelectric multiferroics are currently attracting a renewed interest, because of the superposition of magnetic and dielectric properties, the coupling of which may allows for new concepts in information storage. Magnetically induced ferroelectric states, observed in some compounds possessing geometrically frustrated spin lattices, or, as in $MnWO_4$, competing and frustrated interactions, are one promising path for highly efficient magnetoelectric coupling. $MnWO_4$ displays such a behavior, and is known to undergo three magnetic phase transitions below 14 K: the paramagnetic (PM) to the AF3 state at 13.5 K (T_N), the AF3 to the AF2 state at 12.3 K (T_2), and the AF2 to the AF1 state at 8.0 K (T_1) [1-3]. A spin-spiral order occurs in the incommensurate state AF2, and its non-centrosymetric nature induces a ferroelectric polarization along the b axis in $MnWO_4$ [4-6]. In the commensurate state AF1 the ferroelectric state is suppressed due to the collinear arrangement of the spins [2]. The spin spiral state in $MnWO_4$ originates from frustrated nearest and next-nearest neighbour superexchange interactions within the [MnO_4] chains, while the onset of 3D magnetic order depends on interchain interactions mediated by the diamagnetic [WO_4] chains [7]. Application of a magnetic field can affect the AF3 and AF1 non-polar states, as illustrated in the single-crystal studies of ref. [3] and [4]. In a recent study [8], the effect of diamagnetic substitutions at Mn site in ceramics belonging to the $Mn_{1-x}M_xWO_4$ (M = Mg, Zn) systems was investigated. It was found that the nonmagnetic doping destroys neither the three-dimensional nature of magnetic interactions nor the spin frustration, and that the phase-transition temperatures T_N and T_2 are reduced due to dilution effects. In several samples, an additional low temperature dielectric anomaly was observed, the temperature of which was referred to as T_1'. In this work we investigate the dielectric behavior of the $Mn_{1-x}M_xWO_4$ (M = Mg, Zn ; $0 < x < 0.30$) system under magnetic field, and report pyroelectric measurements in zero magnetic field on $MnWO_4$ and $Mn_{0.85}Mg_{0.15}WO_4$ ceramics, that were performed in order to investigate this dielectric anomaly.

2. Materials and methods

The details of the elaboration steps of $Mn_{1-x}Mg_xWO_4$ ceramic samples ($0 \leq x \leq 0.30$, individual samples will be referred to as Mgx or Znx, *e.g.*. Mg15), and of their chemical, structural and dielectric characterization were presented elsewhere [8].

The samples, after deposition of gold electrodes and attachment of silver wires for sake of electrical connection, were placed in a Quantum Design Physical Properties Measurement System (PPMS) from which a 9 T magnetic field can be applied.

The dielectric measurements were carried out in the frequency range of 10^2 - 10^3 kHz (the amplitude of the applied ac electric field being 1V) using an HP4194a impedance bridge, at heating and cooling rates of 0.2 K/min**.** No dielectric dispersion was observed, thus a single frequency of 788 kHz is presented, and all data were normalized at 16K for sake of comparison.

The measurement of pyroelectric currents was performed with a Keithley 6517B electrometer, the internal voltage source of which was used to pole samples. Pyrocurrents were measured with a heating rate of 2.0 K/min. Some perturbations related to the application of a 9T magnetic field did not allow us measuring pyroelectric currents in such conditions.

3. Results

Application of a magnetic field of 9 T induces a significant modification of the sharp peak associated with the AF3 to AF2 ferroelectric transition in both Mg and Zn substituted samples (Fig 1), which is in perfect agreement with those observed in pure $MnWO_4$ by Arkenbout et al [4]. The distorted shape of the peak at T_2, as seen in the inset of Fig 1(a), arises from the magnetic field induced reorientation of the polarization [4] and the related anisotropy of T_2 (in ref [4], under 9T, T_2 = 12,5K for H//x and H//z while T_2 = 11,5K for H//y). Low temperature anomalies (referred to as T_1') similar to those observed in zero magnetic field [8] were also detected in Mg substituted samples, the latter being visible in figure 1 and clearly distinct from the magnetic field effect on T_2. For Zn substituted ceramics however, such a low temperature anomaly is only confirmed in Zn30 sample, although it is likely present in Zn20 sample.

More startling is the evolution of the capacitance observed below T_2 in highly doped samples: Mg25, Mg30, Zn30, as it follows a plateau close to its maximum value. This feature is likely to be related to a continuous evolution of the ferroelectric state, and thus of its parent magnetic order. It should be noted that the low temperature anomaly in capacitance measurements for Mg15 and Mg20 is clearly distinct from the effect of magnetic field on T_2, thus allowing to ascribe the second peak following the capacitance plateau in Mg25, Mg30 and Zn30 to the low temperature anomaly at T_1'.

To further investigate the nature of the dielectric anomaly detected at T_1', we studied the pyroelectric properties of $MnWO_4$ and Mg15 ceramics. Figure 2 displays the pyroelectric properties of our $MnWO_4$ ceramic, and particularly the two pyrocurrents of opposite signs associated with AF1-AF2 and AF2-AF3 transitions. These pyrocurrents are consistent with the data reported in the literature for single crystals [4,5]. It is worth noticing the shift of the transition temperatures in pyroelectric measurements with respect to dielectric measurements, which accounts for the thermal inertia of our systems when using a 2 $K.min^{-1}$ thermal ramp.

As Figure 3 displays, a depolarization current appears in our Mg15 ceramic at T_1' and evolves continuously up to the ferroelectric transition at T_2, for which a maximum depolarization current of 10 pA is detected. A measurement (triangles on fig. 3) performed after i) cooling the sample down to 5K ii) poling the sample, confirms that the currents detected are actually depolarization currents and allows for a clear visualization of the baseline. Thus no inversion of the pyroelectric current associated to the two transitions at T_1' and T_2 was observed in our Mg15 ceramic, confirming this transition is not an AF2-AF1 transition, as the one observed in $MnWO_4$, and that our Mg15 sample remains ferroelectric below T_1'.

4. Discussion

Figure 4 displays the evolution of T_2 and T_1' upon Mg doping under a magnetic field of 0 or 9T and the dielectric state of the samples in the regions delimited by the transitions at T_2 and T_1'. It can be seen that a magnetic field of 9 T favors the mechanism responsible for the transition at T_1'.

The reproducible observation of the transition at T_1', its correlation with the nature and concentration of doping elements, its dependence upon magnetic field, and its confirmation by pyroelectric measurements, allows us to rule out an extrinsic perturbation (most of them (defects, interfaces…) being additionally several order of magnitude larger than the observed dielectric anomalies).

It is worth questioning the nature of the dielectric anomaly at T_1', which could be related to the AF2 to AF1 transition, observed in our reference $MnWO_4$ ceramic at 0T [8]. However no transition is detected at T_1' in magnetic susceptibility measurements at low field (0.1 T) on substituted samples [8], and no change of magnetic structure is detected in the powder neutron diffraction pattern of Mg15 between T_2 and 1.5K (H=0T) [8].

The anomaly observed at T_1' does not correspond to an AF2-to-AF1 transition since it would induce drastic changes of the magnetic diffraction pattern [2] and a pyroelectric signature (see Fig. 2)

which were not observed. Instead, pyroelectric measurements on Mg15 ceramic without magnetic field show that the sample remains ferroelectric down to 5K and through the transition at T_1'.

Before going any further, it must be recalled that an unexpected stabilization of the AF2 state down to 1.7K has been previously observed in a $MnWO_4$ powder sample "contaminated by small impurities of Mn_3O_4" [2, p6088], while the AF2-to-AF1 transition was affected by the presence of "a few mole percent of Mn_2O_3" in a flux-grown single-crystal [4, p184431]. These observations suggest that a departure from the ideal stoichiometry in $MnWO_4$, or a chemical substitution in our case, may destabilize the AF1 state.

In the following, we will consider the two possible nature of the transition detected at T_1' in substituted samples, *i.e.* a magnetic or structural nature.

On one hand, the transition observed at T_1' could be associated with an evolution of the ferroelectric state, as suggested by the capacitance plateau in highly doped samples. Since the ferroelectric state is directly related to the magnetic state in this system, its evolution could be directly related to an evolution of the magnetic state of our samples. Furthermore, one must bear in mind that representational analysis reveals that two spin configurations are allowed in the AF2 state, a spin spiral that yields ferroelectric properties and a non-polar sin-modulated magnetic structure [2,8]. This alternative sin-modulated structure may be involved in the transition detected at T_1' [2]. Of course a progressive magnetic ordering of the sample below T_2 ; *i.e.* a coexistence of AF2 and magnetically disordered zones in the sample between T_2 and T_1' could also account for the transition observed in substituted samples. In both cases (coexistence of two equivalent spin configuration of progressive ordering) the powder neutron diffraction pattern would not be modified, the transition would be hardly detectable from magnetic measurements, but the dielectric properties would be consistent with all our experimental observations. To be more specific, the coexistence of a ferroelectric and a paraelectric or disordered phase would yield a larger permittivity, and ultimately a capacitance plateau, and would also account for the pyrocurrents detected between T_1' and T_2 upon heating, in our Mg15 sample.

On the other hand, no transition at T_1' being detected by magnetic measurements or neutron diffraction, one may consider that this transition involve a modification of the crystal structure. It is worth to note that Chaudury & al. detected anisotropic lattice anomalies at T_1 in $MnWO_4$ during thermal expansion measurements [9]. They ascribed these anomalies to a magnetoelastic effect driven by the onset of the AF1 phase in $MnWO_4$. This assumption concerning the driving force of the transition is not fully consistent with our experimental observations, as the AF1 phase is not observed in our substituted samples. However a transition is actually observed at T_1', in a comparable temperature range. Thus, it should rather be envisaged that the driving force of the transitions detected at T_1 in $MnWO_4$ and T_1' in substituted samples is structural, and is the one triggering the onset of the AF1 state in $MnWO_4$. A structural modification would undoubtly account for the peaks detected at T_1' in substituted samples (as the modification of interatomic distances and bonding would affect the permittivity) and the persistence of the ferroelectric state through this transition (as it is related to the magnetic ordering). The evolution of the capacitance and pyrocurrents between T_2 and T_1' in substituted samples may be related to the corresponding evolution of the lattice strain (see ref [9]). As this transition is sensible to an external magnetic field (see Fig. 4), it could nonetheless involve magnetoelastic coupling.

Finally, it should be recalled that in Zn substituted samples, only the Zn30 sample displayed a transition at T_1', thus indicating significantly different behaviours upon Mg or Zn substitution. As both Mg and Zn yield divalent cations of similar radii [10], bonding modifications induced by these substitutions may be at the origin of our experimental observation.

With our current set of data from ceramic samples, the precise origin of the transition detected at T_1' can not be elucidated. However neutron diffraction on single crystal, as it would give access to both magnetic and nuclear structures, should provide relevant experimental elements to assess the nature of this transition.

3. Conclusion

Our dielectric and pyroelectric studies show that in the $Mn_{1-x}M_xWO_4$ (M = Mg, Zn ; $0 \leq x \leq 0.30$) system, the effect of a 9 T magnetic field on the ferroelectric AF3-to-AF2 transition is similar over the whole composition range. As in $MnWO_4$, a 9 T magnetic field induces a reorientation of the dielectric polarization. At low temperature, an additional anomaly is detected at T_1' in the capacitance measurements, and confirmed by subsequent pyroelectric measurements. In highly doped samples ($x \geq 0.25$) a plateau of the capacitance is observed, which suggest a continuous evolution of the ferroelectric state. Both a magnetic and a structural origin of the transition at T_1' are discussed, and both appear consistent with our experimental observation, thus no conclusion was reached on this point. The discrepancies between Mg and Zn substituted samples point towards bonding modifications as the origin the observed behaviours.

To discriminate between both mechanisms, single-crystal neutron diffraction experiments are planned. The intermediate state between T_2 and T_1' in this system, whatever its exact nature, may offer an interesting potential for magnetoelectric coupling.

ACKNOWLEDGMENT.

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REFERENCES

[1] Ehrenberg, H.; Weitzel, H.; Heid, C.; Fuess, H.; Wltschek, G.; Kroener, T.; van Tol, J.; Bonnet, M. J. Phys.: Cond. Mat. (1997), 9(15), 3189-3203.

[2] Lautenschlaeger, G.; Weitzel, H.; Vogt, T.; Hock, R.; Boehm, A.; Bonnet, M.; Fuess, H. Phys. Rev. B. (1993), 48(9), 6087-6098.

[3] Taniguchi, K.; Abe, N.; Takenobu, T.; Iwasa, Y.; Arima, T. Phys. Rev. Lett. (2006), 97(9), 097203/1-097203/4.

[4] Arkenbout, A. H.; Palstra, T. T. M.; Siegrist, T.; Kimura, T. Phys. Rev. B. (2006), 74(18), 184431/1-184431/7.

[5] Heyer, O.; Hollmann, N.; Klassen, I.; Jodlauk, S.; Bohaty, L.; Becker, P.; Mydosh, J. A.; Lorenz, T.; Khomskii, D. J. Phys.: Cond. Mat (2006), 18(39), L471-L475.

[6] Katsura, H.; Nagaosa, N.; Balatsky, V.A. Phys. Rev. Lett. (2005), 95, 057205-1–057205-4

[7] Tian C., Lee C., Xiang H., Zhang Y., Payen C., Jobic S., Whangbo M.-H., Phys. Rev. B (2009), 80, 104426/1-104426/8.

[8] Meddar L., Michael J., Deniard P., La C., André G., Damay F., Jobic S., Whangbo M.-H., Petricek V., Maglione M., and Payen C., Chem. Mater. (2009), 21, 5203–5214.

[9] Chaudhurya R.P., Yena F., dela Cruza C.R., Lorenza B., Wanga Y.Q., Suna Y.Y., Chu C.W., Physica B (2008), 403, 1428–1430

[10] Shannon, R.D.; Acta Crystallographica. 1976, A32, 751-767.

Figure captions

Figure 1: Normalized capacitance in the $Mn_{1-x}M_xWO4$, (M = Mg (a), Zn (b)) under 9T. The T_2, T_1 and T_1' transitions are indicated. The inset in (a) shows the modification of the transition at T_2 in Mg0 by a 9T magnetic field.

Figure 2. Pyroelectric properties of $MnWO_4$ (H=0T). The areas associated to pyrocurrents at T_1 and T_2 have been grayed to enlighten sign changes.

Figure 3. Pyroelectric properties of $Mn_{0.85}Mg_{0.15}WO_4$ (H=0T)

Figure 4. Evolution of T_2 and T_1' versus x in the $Mn_{1-x}Mg_xWO4$ system at 0 and 9T (the various stability regions are represented)

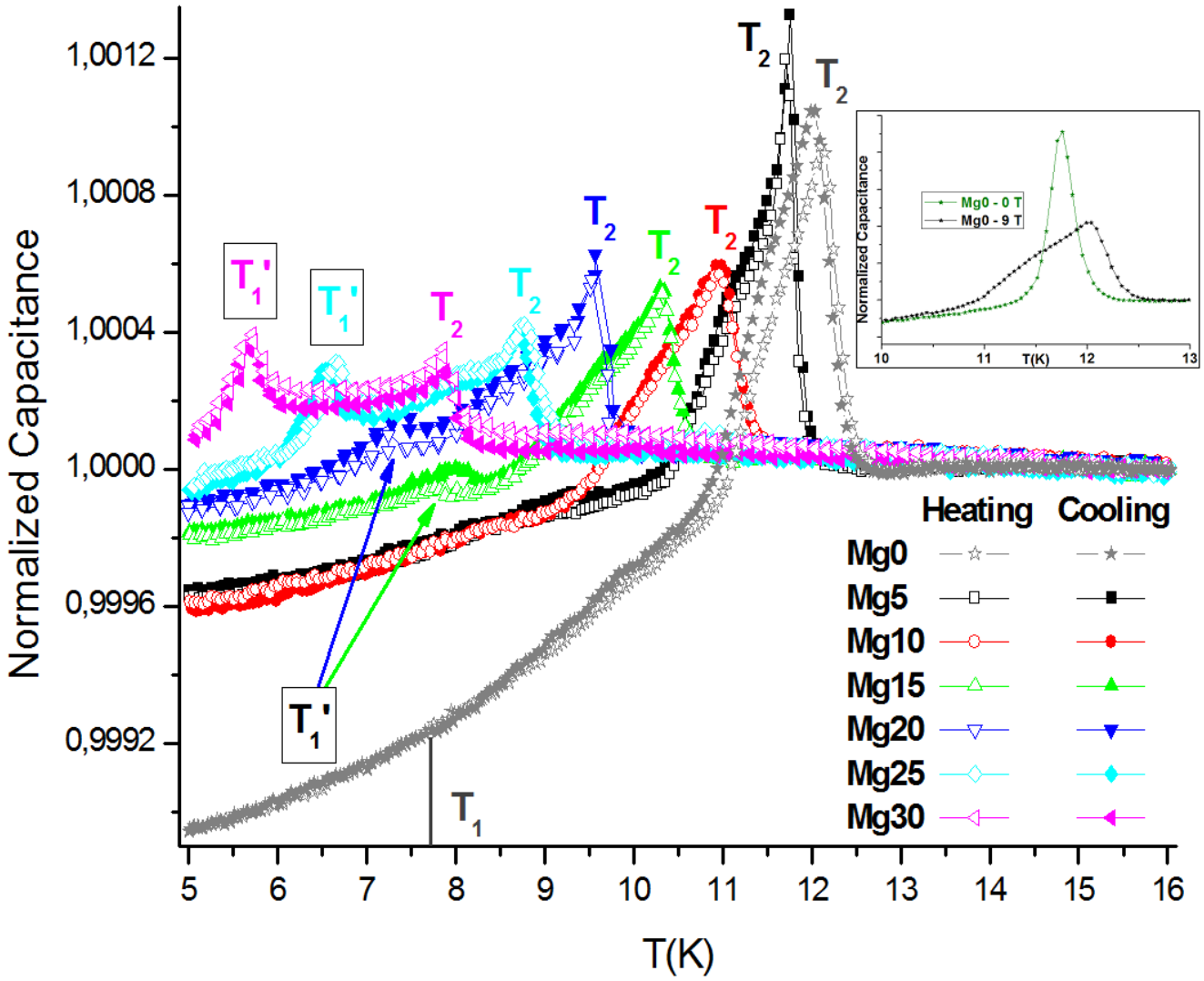
Normalized Capacitance
T(K)
1,0012
1,0008
1,0004
1,0000
0,9996
0,9992
5
6
7
8
9
10
11
12
13
14
15
16
T1'
T2
T1
Heating
Cooling
Mg0
Mg5
Mg10
Mg15
Mg20
Mg25
Mg30
Mg0 - 0 T
Mg0 - 9 T

Fig 1(a)

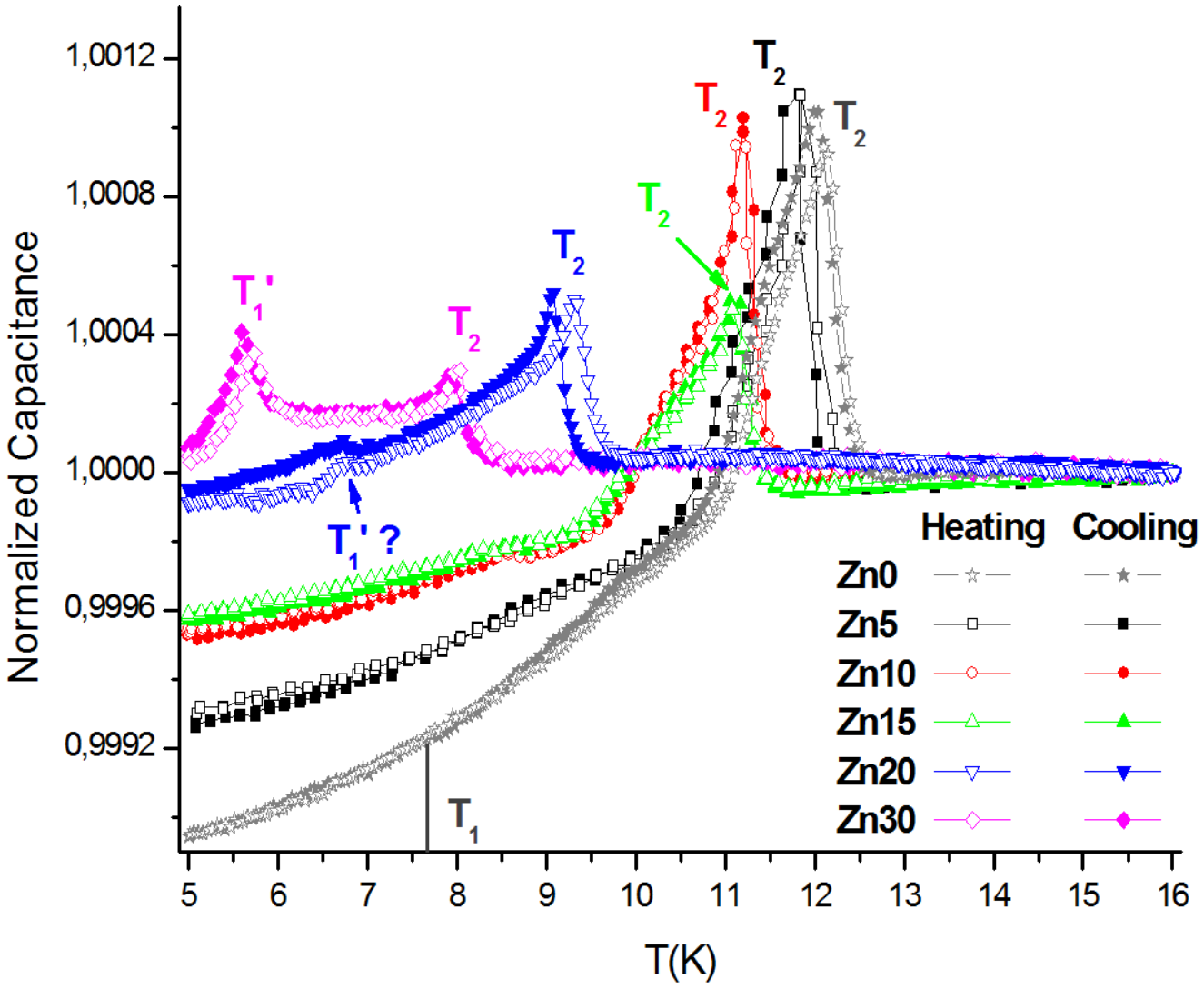
Normalized Capacitance
1,0012
1,0008
1,0004
1,0000
0,9996
0,9992
5
6
7
8
9
10
11
12
13
14
15
16
T(K)
T1'
T1' ?
T1
T2
Heating
Cooling
Zn0
Zn5
Zn10
Zn15
Zn20
Zn30

Fig 1(b)

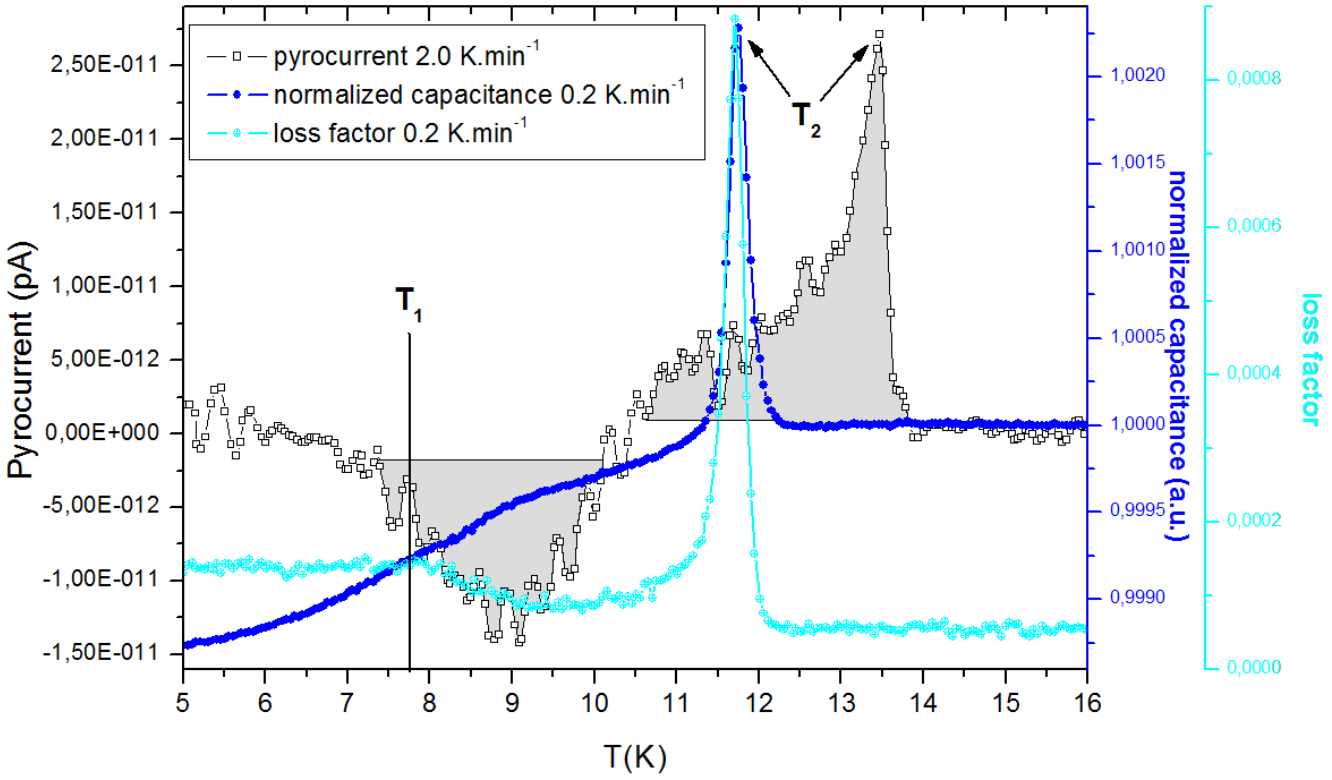
pyrocurrent 2.0 K.min-1
normalized capacitance 0.2 K.min-1
loss factor 0.2 K.min-1
T1
T2
Pyrocurrent (pA)
2,50E-011
2,00E-011
1,50E-011
1,00E-011
5,00E-012
0,00E+000
-5,00E-012
-1,00E-011
-1,50E-011
normalized capacitance (a.u.)
1,0020
1,0015
1,0010
1,0005
1,0000
0,9995
0,9990
loss factor
0,0008
0,0006
0,0004
0,0002
0,0000
5
6
7
8
9
10
11
12
13
14
15
16
T(K)

Fig 2

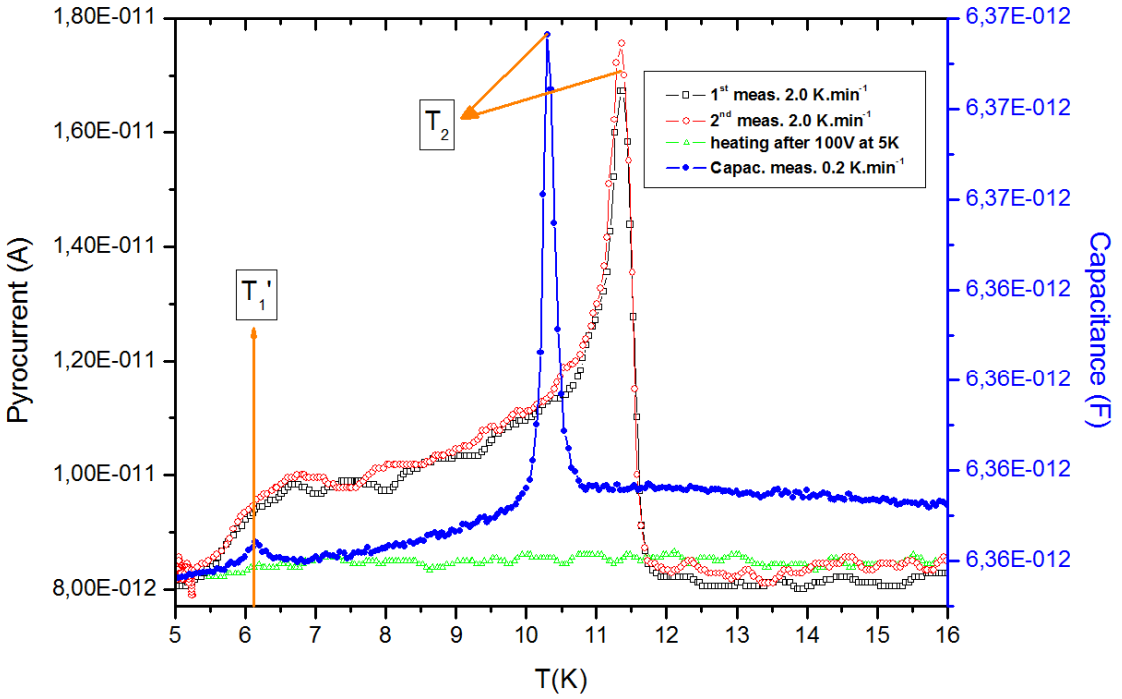
1,80E-011
1,60E-011
1,40E-011
1,20E-011
1,00E-011
8,00E-012
Pyrocurrent (A)
6,37E-012
6,37E-012
6,37E-012
6,36E-012
6,36E-012
6,36E-012
6,36E-012
Capacitance (F)
5
6
7
8
9
10
11
12
13
14
15
16
T(K)
T2
T1'
1st meas. 2.0 K.min-1
2nd meas. 2.0 K.min-1
heating after 100V at 5K
Capac. meas. 0.2 K.min-1

Fig 3

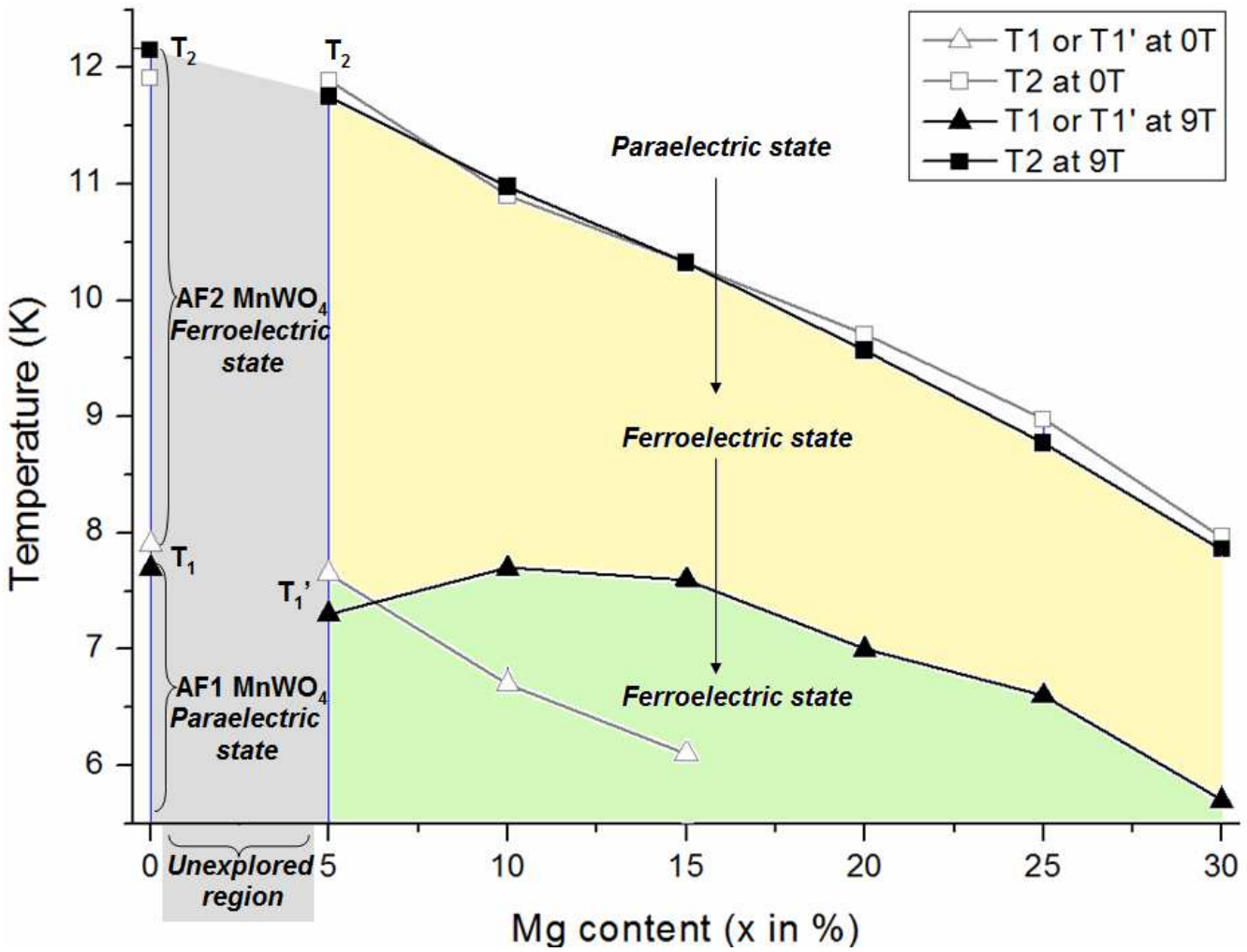
T1 or T1' at 0T
T2 at 0T
T1 or T1' at 9T
T2 at 9T
Paraelectric state
Ferroelectric state
Ferroelectric state
AF2 MnWO4
Ferroelectric
state
AF1 MnWO4
Paraelectric
state
T2
T2
T1
T1'
Unexplored
region
Temperature (K)
Mg content (x in %)
12
11
10
9
8
7
6
0
5
10
15
20
25
30

Fig 4

running head title

Unexpected transitions in $Mn_{1-x}(Mg,Zn)_xWO_4$ ceramics