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Comment on “The Origin of Magnetism in Mn-Doped $SrTiO_3$”

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Multiferroic materials, combining at least two of three properties: ferromagnetism, ferroelectricity, and ferroelasticity in the same phase, have been widely studied during the last years and have tremendous potential for multifunctional applications, despite difficulties to obtain intrinsic magnetoelectric multiferroics.[1] In view of this sparsity, weakly doped $Sr_{1-x}Mn_xTiO_3$ ceramics were found to be a particularly efficient exception. In addition to its enhanced antiferrodistortive elastic features,[2] it reveals both polar glass electric[3–5] and spin glass magnetic behavior,[4,5] thus representing the first ever multiglass. For $x = 0.02$, polar glass freezing due to the off-center displacement of Mn^{2+} ions on the Sr (“A”) sites[3,6] was found to trigger spin glass freezing.[4,5] Frequency dependent peaks in the temperature dependence of the magnetic susceptibility and magnetoelectric coupling were observed below 38 K and attributed to intrinsic spin coupling via frustrated antiferromagnetic superexchange.

Special attention was paid to the influence of the processing conditions such as the choice of the firing atmosphere on the structural, microstructural, dielectric, and electron spin resonance characteristics of Mn-doped $SrTiO_3$ ceramics.[2,7] Additional effects on the local structure and dc magnetic response of $Sr_{1-x}Mn_xTiO_3$ and $SrTi_{1-y}Mn_yO_3$ powders fired in O_2, air, and N_2 atmospheres were recently reported by Valant et al.,[8] while disputing the origin of magnetism in Mn-doped $SrTiO_3$. Their X-ray absorption near-edge structure (XANES) analysis has confirmed the statement of ref. [7] about the dominant occupancy of Sr sites by Mn in air-fired $Sr_{1-x}Mn_xTiO_3$, revealing a Mn^{2+}/Mn^{4+} ratio of 59/41[8] that is close to 56/44 obtained in ceramics.[6] Valant et al.[8] have also shown that the fraction of Mn^{2+} increases (decreases) by 23% under firing in N_2 (O_2), quantifying the increase of Mn^{2+}/Mn^{4+} ratio with decreasing O_2 content in the firing atmosphere, indicated also in ref. [7]. As for the $SrTi_{1-y}Mn_yO_3$ system, XANES data presented much smaller variations of the Mn^{2+}/Mn^{4+} ratio with the firing atmosphere from 9/91 for O_2- through 10/90 for air- to 13/87 for N_2-firing,[8] corresponding to the negligible change of dielectric response in ceramics.[7]

As for the magnetic characterization, no anomaly was observed by Valant et al.[8] on O_2-fired $SrTi_{0.97}Mn_{0.03}O_3$ and N_2-fired $Sr_{0.97}Mn_{0.03}TiO_3$ powders, while a deviation of the field-cooled (FC) magnetization from zero-field-cooled (ZFC) magnetization was claimed to appear below 42 K for air- and N_2-fired $SrTi_{0.97}Mn_{0.03}O_3$ and air- and O_2-fired $Sr_{0.97}Mn_{0.03}TiO_3$. Moreover, the ZFC curve of O_2-fired $Sr_{0.97}Mn_{0.03}TiO_3$ revealed a peak[8] at almost the same temperature as that previously reported on $Sr_{0.98}Mn_{0.02}TiO_3$ ceramics.[4,5] Although these two samples refer to different sources, states, processing conditions, and nominal Mn contents, the concentration of Mn^{2+} ions in both of them according to XANES[6,8] is of 1.10 ± 0.02% (0.03 × 36% and 0.02 × 56%, respectively), supporting the intrinsic multiglass scenario, induced by Mn^{2+} ions on the A sites.[4,5] The remaining Mn ions are in the 4+ state,[6,8] necessarily occupying the Ti (“B”) sites and creating a nonstoichiometric system with Ti excess that should segregate into a magnetically inactive second phase of TiO_2.[9] Leaving such mechanism of the ion redistribution “beyond the scope” of their paper but mentioning the “ferromagnetic” transition and magnetoelectric behavior observed in Mn_3O_4 below 43 K by Tackett et al.,[10] Valant et al.[8] have attributed all of the magnetic anomalies of Mn-doped $SrTiO_3$ to extrinsic origin like segregation of the Mn species into Mn_3O_4. However, in a subsequent paper, Tackett et al.[11] have additionally shown that down to the nanoparticle size the magnetic anomaly corresponding to the ferrimagnetic transition in Mn_3O_4[10] is frequency independent,[11] thus contrasting with that observed in $Sr_{0.98}Mn_{0.02}TiO_3$.[4,5] Obviously, the solely dc magnetic response reported by Valant et al.[8] is insufficient to identify the origin of the anomaly. In order to become convincing, at least the ac magnetic susceptibility should have been measured as well.

As an additional proof of the intrinsic magnetic coupling in $Sr_{1-x}Mn_xTiO_3$, we show in **Figure 1** the ZFC magnetization of air-fired ceramics, revealing sharp cusps at 35 K for $x = 0.020$[4] and at 43 K for $x = 0.025$. Thus, the magnetic anomaly depends

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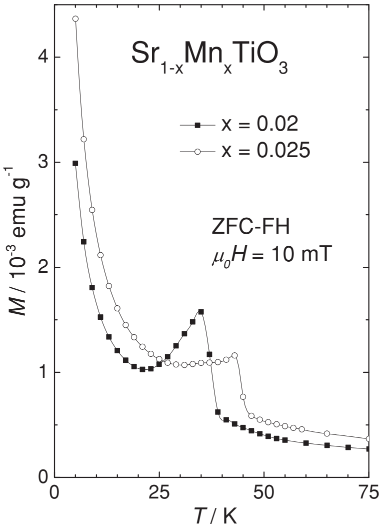

Figure 1. Temperature dependence of the magnetization of air-fired $Sr_{1-x}Mn_xTiO_3$ ceramics with $x = 0.02$ and 0.025, measured on heating in a magnetic field of 10 mT after zero-field cooling.

not only on the frequency, but crucially also on the Mn content. This confirms that the Mn dopant incorporates in the $SrTiO_3$ lattice, inducing the spin-glass transition. Unfortunately, Valant et al.[8] fail to show the magnetic responses for fully crystallized $Sr_{1-x}Mn_xTiO_3$ with different x values. They merely present data for $x = 0.03$ (Figure 6 in ref. [8]) and for incompletely crystallized powders after initial firing (Figure 4 in ref. [8]).

Concerning the "non-magnetic" N_2-fired $Sr_{1-x}Mn_xTiO_3$ powders, we would rather refer to them as to $Sr_{1-x}Mn_xTiO_{3-\delta}$, since high-temperature firing in the oxygen-deficient atmosphere leads first of all to the formation of oxygen vacancies especially in powders, which possess much larger surface area than ceramic pellets. Thus, despite that according to XANES the fraction of Mn^{2+} ions increases with N_2 content in the firing atmosphere, the antiferromagnetic superexchange coupling between two next-nearest neighbor Mn^{2+} cations through an O^{2-} anion,[12] suggested to be responsible for the magnetic anomaly in $Sr_{1-x}Mn_xTiO_3$,[4,5] becomes strongly suppressed. Hence, the magnetic anomaly of intrinsic origin was evidently eliminated in $Sr_{1-x}Mn_xTiO_{3-\delta}$ powders by breaking of the Mn–O bonds and distortion of the oxygen sublattice, resembling the suppression of purely intrinsic antiferrodistortive transition in N_2-fired Mn-doped $SrTiO_3$ ceramics.[2] However, consideration of the oxygen vacancy effect is missing in the discussion section of the paper by Valant et al.[8]

Regarding the $SrTi_{1-y}Mn_yO_3$ system, in contrast to what is written by Valant et al.[8] in their abstract, no magnetic anomaly was observed and, hence, reported yet for $SrTiO_3$ substituted with Mn on the B sites. Moreover, we find the magnetic responses as reported by Valant et al. for this system (Figure 5 in ref. [8]) to be uncorrelated with the XANES data (Table 1 in ref. [8]). From that table, the Mn^{4+} fraction in $SrTi_{1-y}Mn_yO_3$ is shown to be 89 ± 2% for all the final firing atmospheres, while 2% is claimed as the uncertainty of their XANES data.[8] Furthermore, for the nominal Mn content $y = 0.03$, the difference between, for instance, air- and O_2-fired samples would amount to below 300 ppm of "misplaced" Mn ions (i.e., on the level of uncontrolled impurities in the samples prepared by conventional mixed oxide method). However, the magnetic response differs much more significantly. This discrepancy between the structural and magnetic analyses of the paper by Valant et al.,[8] probably requires a cross-check of the magnetic characterization of their $SrTi_{1-y}Mn_yO_3$ samples.

Finally, apart from unconvincing magnetic indication there are no other evidences of the segregation of Mn ions into a Mn_3O_4-like phase at all. Neither X-ray diffraction nor the more powerful XANES technique do reveal the presence of Mn_3O_4.[8] For instance, the majority of the Mn ions in Mn_3O_4 is in the 3+ state, but XANES analysis did not trace any fraction of Mn^{3+} ions.[8] Only some "network of microstructural features resembling dislocations" was detected by transmission electron microscopy,[8] but in the absence of local chemical analysis this observation certainly does not provide enough evidence of Mn_3O_4 segregation.

In conclusion, doped oxide semiconductors are certainly of high scientific and technological interest, and the paper by Valant et al.,[8] despite some unsolved discrepancies shown above, represents a valuable contribution to this topic. Basically, we do not observe any considerable "conflict" between the data from ref. [4,5] and those of Valant et al.[8] However, we do not see also any need to refer to the extrinsic Mn_3O_4-related mechanism to explain the observed magnetic properties of Mn-doped $SrTiO_3$ unless i) local chemical and structural analysis proves the segregation of a distinct Mn-oxide and correlates with the magnetic results, ii) stoichiometry and oxygen vacancy effects are explicitly taken into consideration, and iii) the magnetic response is found to be reasonably independent of frequency up to the MHz regime and of the Mn content up to the solubility limit.

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