Response to "Comment on 'The Origin of Magnetism in Mn-Doped $SrTiO_3$'"

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We first summarize the main points of our disagreement with Tkach et al.[1] They claim that the magnetic peak observed at around 38 K in their essentially paramagnetic $Sr_{0.98}Mn_{0.02}TiO_3$ ceramic sample is caused by a spin glass ground state, which is an intrinsic property of the $Sr_{0.98}Mn_{0.02}TiO_3$ phase. They support their claim by providing ac magnetic data that shows weak frequency-dependence, and memory effects in the dc magnetic susceptibility, which are indeed consistent with the spin-glass model. In addition, they provide zero-field cooled magnetic data for the second sample in the $Sr_{1-x}Mn_xTiO_3$ series, namely, $Sr_{0.975}Mn_{0.025}TiO_3$ that shows a magnetic anomaly peak at around 43 K. In this way, they demonstrate that the temperature of the magnetic anomaly is dependent on the Mn concentration which serves as evidence that the magnetic anomaly is an intrinsic characteristic of the $Sr_{1-x}Mn_xTiO_3$.

In contrast, we have demonstrated in our previous studies[2,3] that the magnetic anomaly in $Sr_{1-x}Mn_xTiO_3$ and $K_{1-3x/2}Mn_xTaO_3$ perovskites (which was found in both systems at the surprisingly similar temperature of 43 K) strongly depends on the sample preparation conditions and, thus, has an extrinsic origin. In poorly processed samples this magnetic anomaly is superimposed on the paramagnetic behaviour of both $Sr_{1-x}Mn_xTiO_3$ and $K_{1-3x/2}Mn_xTaO_3$ perovskites. Therefore, we conclude that the magnetic peak at 43 K is a result of *magnetic phase separation*. The only origin of the magnetic phase separation is a *chemical phase separation*. The very characteristic temperature (T = 43 K) of the magnetic anomaly in both $Sr_{1-x}Mn_xTiO_3$ and $K_{1-3x/2}Mn_xTaO_3$ samples suggests that it is most likely caused by the very same secondary phase, namely, Mn_3O_4-based spinel with ferrimagnetic transition temperature of about 43 K.

The authors rightfully state that the *undoped* Mn_3O_4 spinel does not show frequency-dependent susceptibility in contrast to their magnetic data on $Sr_{0.98}Mn_{0.02}TiO_3$ sample. Also, the magnetic cusp in this sample is observed at 38 K, not 43 K, as would be expected for pure Mn_3O_4. First, we would like to mention that the notorious Mn_3O_4 phase has caused much confusion in the early days of 'diluted magnetic insulators' such as e.g., Mn-doped In_2O_3 and ZnO, etc.[4–6] In particular, its ability to partially accommodate foreign atoms, such as Zn and In may cause temperature shift of magnetic anomaly far below 43 K. It is also known that Mn_3O_4 phase can dissolve up to 10% TiO_2.[7] We argue that dilution of the Mn_3O_4 ferrimagnetic phase with non-magnetic Ti ions can alter the transition temperature in a manner similar to that observed in In-doped and Zn-doped Mn_3O_4. Furthermore, it is quite plausible that the same dilution with non-magnetic ions can alter magnetic interactions in Mn_3O_4 and induce a spin glass state that may be analogous to that observed in for Zn-doped Mn_3O_4.[8]

The authors write "Valant et al. fail to show the magnetic responses for fully crystallised $Sr_{1-x}Mn_xTiO_3$ with different x". Here, we would like to emphasize that our processing route differs from the processing route applied by Tkach et al. in one important step. For homogenization of the mixture of the initial reagents we use high-energy planetary milling, which is, for processing experts, known to significantly enhance reaction kinetics. In our case this resulted in a fast and complete reaction and crystallization at 1150 °C. We have already demonstrated this before in ref. [3] for Mn-doped $KTaO_3$. However, to be even more convincing we have performed additional experiment exactly as suggested by Tkach et al. **Figure 1** shows zero-field cooled (ZFC) and field cooled (FC) magnetic susceptibility of $Sr_{1-x}Mn_xTiO_3$ samples with x = 0.01 to 0.05, calcined twice at 950 and 1150 °C followed by sintering in air at 1500 °C for 5 h. This process has certainly yielded highly crystalline samples. In contrast to Tkach et al., we do not see magnetic anomalies in such $Sr_{1-x}Mn_xTiO_3$ ceramics. The FC data (open dots) are essentially overlapping the ZFC data (solid dots). The sample with the highest Mn concentration of x = 0.05 shows a very small magnetic anomaly manifested by slight divergence of the ZFC and FC data below 43 K (shown by arrow in Figure 1). We confirm, however, that our poorly processed samples in the $0.01 < x < 0.05$ concentration range show magnetic cusp at 43 ± 0.5 K. Therefore, we cannot confirm concentration-dependent temperature of the magnetic cusp in the well-processes $Sr_{1-x}Mn_xTiO_3$, as claimed by Tkach et al.[1]

The authors try to justify the absence of a magnetic anomaly in the properly processed A-site doped $SrTiO_3$ by formation of oxygen vacancies according to the formula $Sr_{1-x}Mn_xTiO_{3-\delta}$. Because the authors' theory of a spin glass state in $Sr_{1-x}Mn_xTiO_3$ is based on the "frustrated antiferromagnetic superexchange",

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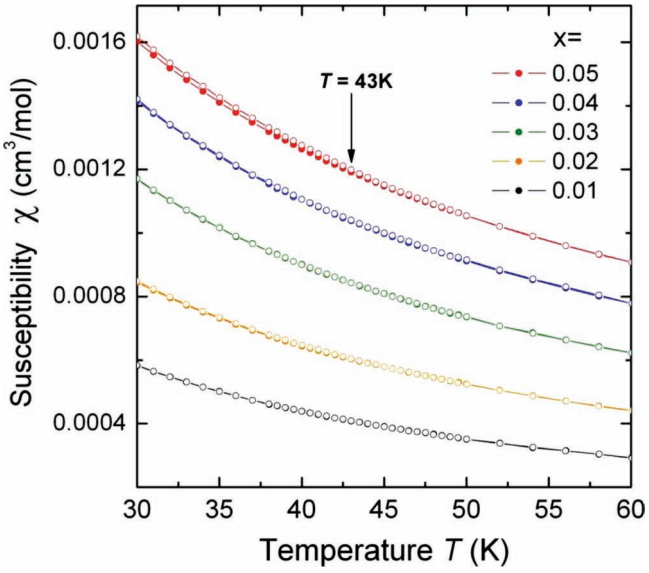

Figure 1. Magnetic susceptibility of $Sr_{1-x}Mn_xTiO_3$ samples with x = 0.01 to 0.05 calcined twice at 950 and 1150 °C followed by sintering in air at 1500 °C for 5 h. Solid circles are zero-field-cooled data and open circles are field-cooled data. ZFC data measured at 100 Oe were obtained upon heating the sample from 2 K after cooling in zero field. FC data were obtained upon heating the sample from 2 K after cooling in the field of 100 Oe.

the presence of oxygen vacancies is supposed to disrupt the magnetic interactions between the next neighbour Mn ions. In principle this is correct but the main question is whether δ is high enough to completely suppress the colossal "frustrated antiferromagnetic superexchange" between the two Mn ions in $Sr_{0.98}Mn_{0.02}TiO_3$. The authors themselves do not give any indication on the magnitude of δ that can destroy the magnetic interactions. Therefore, we tried to estimate it based on the literature data. First, the formation energies of dominant defects are under reducing conditions, in general, very similar for $BaTiO_3$ and $SrTiO_3$.[9] In the absence of data for $SrTiO_3$ this allows us to estimate them from data for $BaTiO_3$. For our experiment we used technical N_2 gas with p_{O2} of about 10^{-6} bar. Based on literature reports we can conclude that for such p_{O2} δ is lower than 10^{-3}.[10] In our opinion it is very difficult to suggest that such low oxygen deficiency would completely suppress antiferromagnetic superexchange if it still exists.

In conclusion, we confirm, once again, that the magnetic anomaly at 43 K in poorly processed $Sr_{1-x}Mn_xTiO_3$ samples originates from magnetic phase separation inevitably caused by chemical phase separation. Similar to the case of Mn-doped $KTaO_3$, we demonstrate that improvement of the sample processing and better homogenization of the powders can suppress or completely eliminate the extrinsic magnetic anomaly in $Sr_{1-x}Mn_xTiO_3$.

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