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Spin Ordering in Mn-Doped $KTaO_3$?

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The discovery of dilute magnetic semiconductor (DMS) behavior in Mn-doped GaAs[1] opened prospects of developing new magneto-opto and spintronic electronics based on DMS materials. A further intensive search for new semiconductors with a spin ordering has been driven by the vision of this new technology. Soon after the discovery of DMS, reports on diluted magnetic oxides, DMO, based on ZnO, SnO, TiO_2, In_2O_3, and so forth,[2−5] were published. Ferro- and antiferromagnetism in these materials was reported to be induced by doping 3d elements (such as Mn, Co, Cr, and Fe) into the host lattice. Such an existence of DMS/DMO in a wide band gap semiconducting oxide would be of a great technological importance given that the spin ordering is undoubtedly intrinsic (charge induced). Because the solubility of the magnetic ions in such oxides is small and kinetically hindered, the synthesis and proper characterization of these systems have become a topic of controversy, which resulted in a number of misinterpretations in published papers. After the initial "discovery" of DMS in oxide materials more careful work that involved much more comprehensive material processing studies called into question the existence of intrinsic DMS in many of the reported oxides.[6−8] Rather than an intrinsic phenomenon it was recognized as an extrinsic phenomenon due to the presence of ferromagnetic parasite phases or clustering/segregation of magnetic dopants.

Recently, similar investigations have been driven by the search not only for new DMS but also for new magnetoelectric materials. A number of new reports have been published on the existence of the magnetic ordering and spin glass behavior in doped perovskites such as $KTaO_3$, $BaTiO_3$, and $SrTiO_3$.[9−16] To avoid further misinterpretations, similar to those described above, we have undertaken detailed studies on the existence of the intrinsic magnetic ordering in these doped perovskites. Here we report a study performed on $KTaO_3$. The study is facilitated by our previous detailed analysis of chemistry, processing, and dielectric properties of Mn-doped $KTaO_3$.[17,18] We determined processing conditions for Mn incorporation onto the A-site of $KTaO_3$ lattice, the solid solubility of Mn to be $<4\%$ according to the $(K_{1-2x}Mn_x)TaO_3$ substitutional mechanism, and learned about the influence of processing conditions on the formation of Mn-doped $KTaO_3$. Here we show the influence of Mn concentration and different processing conditions on the low-temperature magnetic anomaly and disprove the existence of any intrinsic spin glass behavior in Mn-doped $KTaO_3$.

The first set of magnetic measurements was performed on the samples homogenized with a pestle and mortar and fired at 1000 °C. According to a detailed XRD analysis, the samples within the homogeneity range ($x \leq 0.03$) appeared to be single phase. Weak peaks of secondary tungsten bronze-type phase appeared for the $x > 0.03$ samples, for which the solid solubility limit is exceeded (Figure 1).

The molar magnetic susceptibility of pure $KTaO_3$ ($\chi_M = 1.03 \times 10^{-4}$ cm^3/mol) remains nearly temperature independent in the 10−300 K range with a slight upturn at $T < 10$ K due to the residual concentration of magnetic impurities. Mn-doped samples fired at 1000 °C show a

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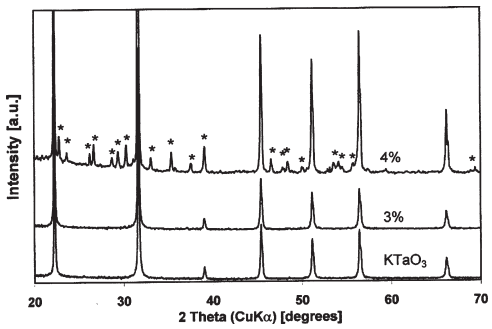

Figure 1. X-ray powder diffraction of Mn-doped $KTaO_3$ with 0, 3, and 4% of Mn, prepared by a homogenization with a pestle and mortar and heat treatment at 1000 °C. Asterisks denote tungsten bronze-type phase.

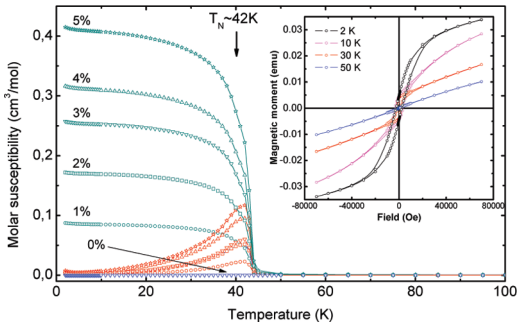

Figure 2. Molar magnetic susceptibility of zero-field cooled (red lines) and field cooled (B = 50 Oe) (green lines) Mn-doped $KTaO_3$ samples with Mn content from 0 to 5% (the lines for pure $KTaO_3$ are shown in blue). The samples were prepared by homogenization with a pestle and mortar and fired at 1000 °C. Note that no change in T_N with the Mn concentration can be observed. The inset shows the magnetic hysteresis loops for different temperatures for the 3% Mn sample.

strong magnetic anomaly with an onset temperature of $T \leq 44$ K (Figure 2). There is a similar anomaly in the $K_{0.97}Mn_{0.03}TaO_3$ sample with the onset temperature of around 44 K being reported in ref 9, where it was attributed to novel intrinsic spin glass behavior of Mn^{2+}-doped $KTaO_3$. A peculiar shape of the zero-field cooled magnetic susceptibility as well as an apparent absence of the frequency dependence of the magnetic susceptibility maximum seems to be difficult to reconcile with a spin-glass interpretation proposed by the authors [see Figure 4 of ref 9]. Also, the spin freezing temperature of 44K seems to be more characteristic of a concentrated rather than diluted magnetic compound.[19]

Our first step to unravel this mystery was to analyze the effect of Mn concentration. One of the most convincing items of evidence of genuine intrinsic DMS is the concentration dependence of the magnetic ordering temperature, $T_C(x)$, which usually varies as x or $x^{1/2}$.[20] For example, T_C in $(Ga_{1-x}Mn_x)As$ scales linearly with x, for example, $T_C \approx 2000x \pm 10$ K.[1,21] Our data shown in Figure 2 reveal that, although the magnitude of the magnetic anomaly in $(K_{1-2x}Mn_x)TaO_3$ increases with x,

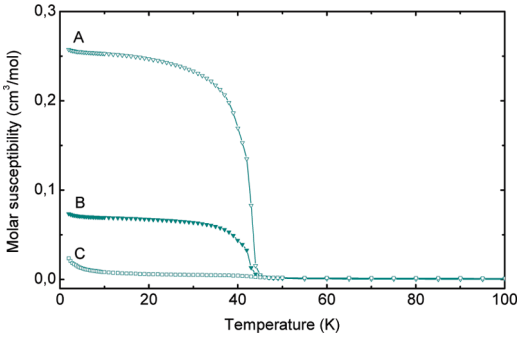

Figure 3. Molar magnetic susceptibility of field cooled (B = 50 Oe) Mn-doped $KTaO_3$ with 3% Mn. The samples were prepared by (A) homogenization with a pestle and mortar and firing at 1000 °C, (B) high-energy milling and firing at 1000 °C, and (C) second-step firing at 1350 °C.

its onset temperature (44 K) remains independent of Mn concentration. Furthermore, if the observed anomaly originates from the intrinsic magnetic interactions in Mn-doped $KTaO_3$ its magnitude would be expected to remain constant after exceeding the solid solubility limit. Our experiment does not confirm this. The magnitude of magnetic susceptibility continuously increases even for the samples that exceed the Mn solubility limit (4 and 5% of Mn). All these findings, therefore, make it difficult to attribute the magnetic anomaly at $T \leq 44$ K to the intrinsic spin glass behavior of $(K_{1-2x}Mn_x)TaO_3$.

Another set of variables that significantly influenced the magnitude of the magnetic susceptibility in our system was related to processing conditions. When we applied more energetic processing conditions the magnitude of the anomaly was significantly reduced. In Figure 3 we show molar susceptibility for 3% Mn-doped $KTaO_3$ for different processing conditions: (A) the mixture of starting powders was thoroughly homogenized with an agate mortar and pestle and fired in air at 1000 °C for 10 h; (B) the initial starting powder mixture was homogenized by high-energy milling in planetary mill at 300 rpm for 1/2 h. The firing was performed in air at 1000 °C for 10 h; and (C) after high-energy milling of initial starting powder mixture and firing at 1000 °C, the material was ground and reheated to 1350 °C for 5 h.

To speed up the solid-state reaction the use of high-energy milling before thermal treatment is a common procedure. By high-energy milling, three characteristics of a starting powder mixture, which are important for the reaction kinetics, are influenced: the mixture is thoroughly homogenized, the particle size is reduced, and high-energy structural defects (e.g., dislocations) are introduced into the particle crystal lattice.

For our system the step in magnetic susceptibility below 44 K was significantly reduced when the high-energy milling was applied. A further reduction of the magnetic anomaly and its effective disappearance was achieved after a second step of firing at even higher temperature of 1350 °C. The high-temperature processing assured better incorporation and distribution of Mn ions within the crystal lattice and brought the system further toward the thermodynamic equilibrium. As shown in Figure 4, the magnitude of the magnetic anomaly is

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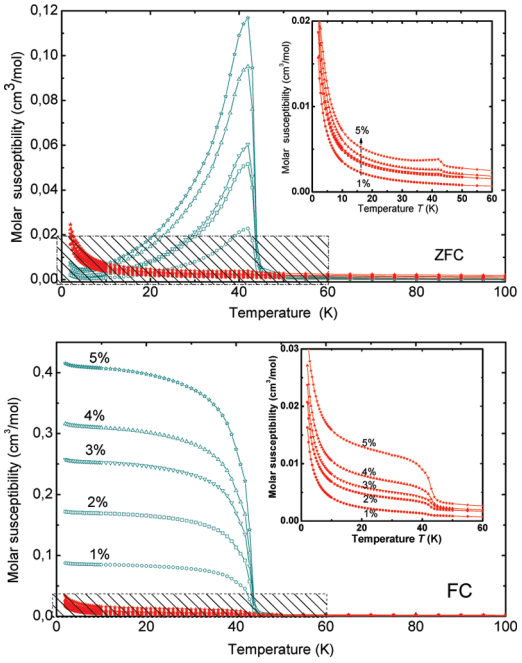

Figure 4. Zero-field cooled (ZFC) and field cooled (FC) molar magnetic susceptibilities measured upon heating in a field of 50 Oe. Mn-doped $KTaO_3$ samples with Mn content from 0 to 5% before (green line) and after (red line) applying the second-step firing at 1350 °C. The inset shows a close-up of the magnetic behavior for samples after firing at 1350 °C. The same area in the main plot is shown hatched.

essentially negligible for all samples fired at 1350 °C as compared to the samples fired at 1000 °C.

For additional confirmation that Mn is indeed incorporated into $KTaO_3$ (despite no magnetic anomaly being detected), we performed dielectric measurement on the samples fired at 1350 °C. The measurements showed the presence of a relaxor-like dielectric anomaly in a temperature range from 50 to 100 K (Figure 5). This is known to appear as a consequence of a coupling of polar nanodomains, which are, within the $KTaO_3$ lattice, generated by the presence of Mn dopant ions. However, in contrast to the notion postulated in ref 9 that "electric frustration goes for spin glass order", we found no evidence of the relaxor-induced spin glass behavior in our well-processed $(K_{1-2x}Mn_x)TaO_3$.

This set of experimental results confirms that the magnetic anomaly occurs because of the incomplete incorporation of Mn into the $KTaO_3$ lattice. During the search for "diluted" ferromagnetism in metal oxide semiconductors, a very similar magnetic anomaly at $T \approx 38-44$ K has been reported for a number of Mn-doped metal oxides including In_2O_3 and ZnO.[2,3] Although early reports have suggested an intrinsic "diluted" magnetism, a more detailed analysis has shown that the magnetic anomaly in these compounds can be attributed to the presence of a secondary phase that is, Mn_3O_4.[6−8] The magnetic ordering temperature of pure Mn_3O_4 is around 43−44 K.[22] This temperature may vary substantially when nonmagnetic metal ions are incorporated into Mn_3O_4 spinel. For example, substitution of Zn

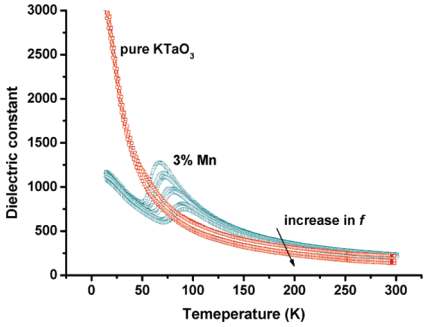

Figure 5. Temperature dependence of the dielectric constant as a function of frequency (from 1 kHz to 1 MHz) for pure $KTaO_3$ and 3% Mn-doped $KTaO_3$ after firing at 1350 °C.

into Mn_3O_4 decreases the magnetic ordering temperature from 43 K for pure Mn_3O_4 to 38 K for 10% Zn incorporated Mn_3O_4.[7]

Also for Mn-doped $KTaO_3$, analyzed within this work and elsewhere,[9] the anomaly occurs at the temperature that is characteristic for Mn_3O_4. During the reaction not all Mn incorporates into the $KTaO_3$ lattice, and the remaining free Mn_3O_4 is responsible for the observed magnetic anomaly. As the electron density and related X-ray scattering coefficients of Mn_3O_4 are much lower than those for $KTaO_3$-based phase, the XRD detection limit of Mn_3O_4 in this system is low. A small amount of Mn_3O_4 cannot be detected by a standard XRD analysis, which can lead to the erroneous conclusion that Mn is fully incorporated.[23]

With more energetic material processing the concentration of residual Mn_3O_4 becomes smaller, which gives smaller magnetic response. When all Mn enters the $KTaO_3$ lattice there is no intrinsic spin ordering or spin glass behavior in such a crystal lattice even at very low temperatures. It becomes evident that there is no intrinsic DMS or magnetoelectric coupling in homogeneous thermodynamically equilibrated Mn-doped $KTaO_3$.

For an accurate and complete description of our system we must note that even for the samples heat treated at 1350 °C a very small, almost negligible, magnetic anomaly was detected at around 44 K. This demonstrates that even after such heat treatment some traces of residual Mn_3O_4 exist in the material.

We have shown that no intrinsic coupling of magnetic moments of dopant Mn ions occurs for thermodynamically equilibrated Mn-doped $KTaO_3$ even at cryogenic temperatures. We also found no evidence of the spin glass behavior in our well-processed $(K_{1-2x}Mn_x)TaO_3$. If the magnetic anomaly is detected it is of an extrinsic nature from Mn clustering inside the $KTaO_3$ lattice or Mn-oxide precipitates. We also showed that incomplete processing can result in an antiferromagnetic response due to a presence of residual Mn_3O_4.

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