Properties of Mn-Implanted BaTiO$_3$, SrTiO$_3$, and KTaO$_3$

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Mn ion implantation into single-crystal BaTiO$_3$(K), SrTiO$_3$, or KTaO$_3$(Ca) was investigated for its effects on the magnetic properties of these materials. Following annealing at 700°C, the Mn implantation was found to induce ferromagnetic behavior for most of the concentration range investigated. For BaTiO$_3$, Mn implantation produced magnetic ordering temperatures near 300 K with coercivities $<70$ Oe. The magnetization/temperature plots showed a non-Brillouin-shaped curve. No secondary phases were detected by high resolution X-ray diffraction. The results are consistent with theoretical predictions for transition metal doping of BaTiO$_3$. The same basic trends were observed for both SrTiO$_3$ and KTaO$_3$, with the exception that at high Mn concentrations (~5 atom %) the SrTiO$_3$ was no longer ferromagnetic.© 2002 The Electrochemical Society. [DOI: 10.1149/1.1531871] All rights reserved.


There has been tremendous interest in thin film oxide perovskite materials since the discovery of a large negative magnetoresistance (MR) at room temperature in doped magnate perovskites. The resistivity of materials is found to be at maximum around the Curie temperature. This effect is commonly referred to as colossal magnetoresistance (CMR). In addition, these materials may have application in magnetic sensing, while other complex oxides are attractive for a broad range of applications including gas sensors, UV emitters and detectors, transparent high temperature electronics, gate dielectrics on semiconductors, and transparent passivation films on solar cells.

There is also strong interest in developing new materials for spintronic devices, in which the spin of the electron rather than its charge would carry the information of interest. Dilute magnetic semiconductors such as GaMnAs, GaMnP, and GaMnN have shown rapid progress in recent years, with the latter two displaying, a ferromagnetism signature above room temperature. In addition, transparent ferromagnetic ZnMnO, ZnCoO, and TiCoO$_2$ have all been reported and doping with other transition metal impurities is predicted to be effective in stabilizing the ferromagnetic state. Very little work has been carried out on oxide perovskite materials, although there is a prediction that BaTiO$_3$ doped with Mn, Cr, or Fe will be promising candidates for ferromagnetism. MR of a number of other ZnO and SnO$_2$ films doped with various impurities have also been reported, while all oxide perovskite oxide p-n junctions with room temperature ferromagnetism have been demonstrated.

In this paper, we report on an investigation of the effects of direct Mn ion implantation into bulk BaTiO$_3$, SrTiO$_3$, and KTaO$_3$ single crystals. In each case, we observe signatures of ferromagnetism near room temperature. These results show the promise of complex oxides for potential spintronic applications.

Bulk, single crystal BaTiO$_3$(K), SrTiO$_3$, or KTaO$_3$(Ca) were implanted at ~350°C with 250 keV Mn$^+$ ions at doses of 3 or $5 \times 10^{16}$ cm$^{-2}$, producing incorporation depths of ~2000 and an average Mn concentration of 3 or 5 atom %. The elevated temperature during implantation is employed to minimize the possibility of amorphization. Postimplant annealing at 700°C for 5 min under flowing N$_2$ was used to partially repair the remaining implant damage. The samples were examined by high-resolution X-ray diffraction (XRD) and superconducting quantum interference device (SQUID) magnetization measurements.

Figure 1 (top) shows a magnetization vs. field (M-H) plot at 10 K from BaTiO$_3$ implanted with 5 atom % Mn, while the difference in magnetization between field-cooled and zero field-cooled conditions (at 1000 Oe) is shown at the bottom of the figure. Qualitatively similar results were obtained for 3 atom % Mn samples, with coercivities of ~600 G at 10 K and ~400 G at 100 K. The magnetization vs. temperature M-T plots do not show a classical Curie-Weiss behavior during the temperature range investigated.
shape, but current theories suggest the shape of these plots is controlled by disorder in the sample, and any shape from concave to linear to convex is possible.\textsuperscript{28} Note that the net magnetization reaches zero at approximately room temperature. XRD showed no evidence of other phases present in the implanted samples.

The \textit{ab initio} total energy calculations for BaTiO\textsubscript{3} doped with all the 3d transition metals from Sc to Cu indicate that Mn, Fe, Cr, and Co are the most promising candidates for achieving ferromagnetism in conducting samples. While these calculations should be used as a guide only due to hybridization effects and the high transition metal concentrations assumed, they are in relatively good agreement with our initial experimental data. The mechanism for the observed ferromagnetism is still not clear and may be due to bound magnetic polarons\textsuperscript{28,29} or the carrier-induced magnetism inherent in the Zener mechanism.\textsuperscript{20}

While SrTiO\textsubscript{3} samples with 5 atom \% Mn showed paramagnetic behavior, at the 3 atom \% Mn concentration clear signatures of ferromagnetism near 300 K were evident in the M-H and M-T plots (Fig. 2). These results would be consistent with the Dietl \textit{et al.}\textsuperscript{20} model in which the net magnetization is given by the difference between the carrier-mediated ferromagnetism and the antiferromagnetic direct interactions between Mn\textsuperscript{2+} ions. In this model, the Curie temperature, $T_C$, can be represented as

$$T_C = \frac{x_{\text{Mn}} V_0 S (S + 1) \beta^2 A_F |\psi|^2}{12 k_B} - T_{AF}$$

where $x_{\text{Mn}} V_0$ is the Mn concentration, $\beta$ is the strength of the interaction between the Mn and the carriers, $\rho$ is proportional to the effective mass of the carriers, and $T_{AF}$ takes into account antiferromagnetic Mn-Mn interactions. Thus, the $T_C$ can decrease at high Mn concentrations due to the increase in the latter contribution to the magnetization.

In the disorder model,\textsuperscript{28,29} holes are allowed only to hop between transition metal acceptor sites, and the interaction between the holes and the magnetic ions is of the antiferromagnetic Heisenberg exchange type. The shape of the M-T plot is then determined by the wide distribution of exchange couplings because of disorder because some Mn atoms do not order until lower temperatures. This unusual magnetization is in good agreement with our experimental data, as shown in Fig. 1 and 2. Another interesting feature of this theory is that with increasing randomness, the $T_C$ increases and the saturation value of the magnetization is decreased.\textsuperscript{28,29} Within the same model, if the carrier concentration is increased, the change of the magnetization becomes more Brillouin-like because the width of the exchange interaction decreases.\textsuperscript{30-33}

Figure 3 shows the M-H (top) and M-T (bottom) plots from the material implanted with 3 atom \% Mn. Quantitatively similar results were obtained for the 5 atom \% condition. The magnetic ordering is present to $\sim 250$ K and once again no additional peaks were observed in the XRD spectra from the samples.

In summary, three different oxide perovskites, BaTiO\textsubscript{3}, SrTiO\textsubscript{3}, and KTaO\textsubscript{3}, show promising magnetic behavior when doped with Mn by direct ion implantation. In each material, the Mn introduction led to magnetic ordering temperatures $> 250$ K. The magnetization has the opposite curvature to the usual Brillouin-like dependence on temperature, as is predicted by a model that takes into account the effects of disorder in dilute magnetic systems.\textsuperscript{28-33} In this model, the ferromagnetism may arise from the interaction between magnetic polarons in the case of either low carrier density or equivalently, strong carrier localization.
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