Ferromagnetism in a MgTiO$_3$-Ti$_2$O$_3$ Solid-Solution

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Magnesium titanate, MgTiO$_3$, is a typical dielectric material with a large optical band gap of 4 eV. MgTiO$_3$ has been widely studied for microwave applications due to its high quality factor ($Q$) value. MgTiO$_3$ possesses the ilmenite structure with the space group $R-3$ in which basal planes, consisting of triangular networks of Mg$^{2+}$ and Ti$^{4+}$ ions, alternate along the hexagonal c axis. The crystal structure of Ti$_2$O$_3$ is the corundum, which is a special case of the ilmenite structure. Since the cation sizes and crystal structures are similar, a solid-solution (Mg$_x$Ti$_{1-x}$)TiO$_3$ can be formed when $x > 0.9$. To address the role of excess titanium, and the corresponding changes in the cation valence state(s), and oxygen vacancies for magnetic properties, polycrystalline MgTiO$_3$ samples were prepared through a solid-state technique from MgO and TiO$_2$ powders sintered in air. One sample was further annealed in a sealed quartz tube with a titanium foil to reduce the oxygen content. Also a solid-solution of MgTiO$_3$ and Ti$_2$O$_3$ in the molar ratio 9:1 was prepared. This sample was sintered in a sealed quartz tube. The sample homogeneity was confirmed by scanning-electron microscopy and energy-dispersive-spectroscopy-of-x-rays experiments. The x-ray photoelectron spectroscopy (XPS, detection limit $10^{-4}$) and Time-of-Flight-Secondary-Ion-Mass-Spectroscopy (ToF-SIMS, detection limit $10^{-6}$) studies showed that no magnetic impurities were present.

Magnetization hysteresis loops and magnetic susceptibility were measured from a MgTiO$_3$-Ti$_2$O$_3$ solid-solution and oxygen reduced MgTiO$_{3-\delta}$ samples. The hysteresis loops revealed that the ferromagnetic transition occurs at or below 260 K in both samples. The magnetization did not reach saturation up to 70 kOe at 5 K. In contrast, stoichiometric MgTiO$_3$, consisting of closed-shell ions, does not exhibit magnetic ordering. Combined magnetic susceptibility measurements, x-ray diffraction, XPS, and spin-polarized density-functional theory computations show that the ferromagnetism is due to the conduction electrons, which are responsible for the semimetallic nature of the MgTiO$_{3}$-Ti$_2$O$_3$ solid-solution. Excess Ti at the Mg-O cation layer results in a partially occupied band at the conduction band edge. This in turn shows that the magnetic properties can be controlled by a transition metal element substitution in a cation layer, which is a technological advantage especially for thin film applications.