Electronic structure and magnetic properties of TiO$_2$-MnTiO$_3$ eutectics

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Abstract. MnTiO$_3$ single crystals and a self-organized TiO$_2$-MnTiO$_3$ eutectic grown by the micro-pulling down method from a TiO$_2$-MnO system were examined by SQUID magnetometry and XPS photoelectron spectroscopy. The measurements on the MnTiO$_3$ single crystals and eutectic show that manganese is in one Mn$^{2+}$ ionic state with an effective magnetic moment of about 5.8 $\mu_B$. Ferrimagnetic-like behaviour was observed due to nonstoichiometry. For the single crystals, deficiency of Ti and enhancement of Mn were found. For the TiO$_2$-MnTiO$_3$ eutectic the higher amount of titanium and oxygen is explained by the presence of the TiO$_2$ phase.

1. Introduction

The self-organized micro- and nanostructured eutectic materials obtained by the directional solidification could be used for various types of light manipulation. Oxide-oxide eutectics have been identified as materials which may act as photonic crystals. The next potential application is in the field of metamaterials [1]. Recently, the TiO$_2$ – MnTiO$_3$ eutectics were examined [2]. The microstructure consists of 3D-oval TiO$_2$ inclusions/particles interconnected with each other by thin TiO$_2$ layers/plates and this interconnected structure is embedded in the MnTiO$_3$ matrix. It was expected that MnTiO$_3$ forms an antiferromagnetic structure with the Mn$^{2+}$ while TiO$_2$ in form of rutile is a semiconductor. Such a combination might result in the possibility to create a structure with a negative refractive index. This kind of structure could be used as the alternative structure for the split ring resonators (SRRs) [2]. The aim of this work was the determination of the chemical composition, electronic structure and magnetic properties of TiO$_2$-MnTiO$_3$ eutectic in comparison with the same properties obtained for MnTiO$_3$ single crystals.

2. Experimental

The TiO$_2$-MnTiO$_3$ eutectics and MnTiO$_3$ crystals have been grown by the micro-pulling down method (m-PD). The m-PD method has been invented in Japan, originally for growth of single crystal fibres, but it is perfectly well suited for directional growth of oxide-oxide eutectics [3]. High purity oxide powders (99.995%), TiO$_2$ and MnO were used as starting materials. The oxides were mixed with ethanol in alumina mortar and then dried. The crystals were grown with 5 mm/min and 15 mm/min pulling rate under a nitrogen atmosphere. The crystals grown were seeded with a Y$_3$Al$_2$O$_12$
single crystal. The single crystals were additionally annealed in oxygen at 900 °C. The details of the thermal system we used for micro-pulling down, as well as the growth conditions, are described elsewhere [1]. As investigated by X-ray powder diffraction, two phases have been formed: MnTiO₃ and TiO₂ [2].

Magnetic measurements were conducted using a Quantum Design MPMS-XL-7AC SQUID magnetometer. Magnetization of the samples was measured in the temperature range 1.9 - 400 K.

The XPS spectra were obtained using a PHI 5700/660 Physical Electronics Photoelectron Spectrometer with monochromatized Al Kα X-ray radiation (1486.6 eV). The photoelectron emission from a surface area of 800 μm x 2000 μm was recorded. The binding energy was determined with reference to the C 1s component set at 284.6 eV. The Gaussian-Lorentzian functions were used to fit the XPS core level spectra.

3. Results and discussion

The magnetic susceptibility temperature dependence in the temperature range 1.9-400 K of the as grown TiO₂-MnTiO₃ eutectic and as grown, and annealed MnTiO₃ single crystals was measured (figure 1). Around 100 K a broad peak for each sample was observed. Such peak was attributed to the antiferromagnetic ordering, suggesting that two-dimensional antiferromagnetic order exists above a Néel temperature [4]. The Néel temperature was estimated as Tₙₑₑ = 65 K for the as grown crystal, Tₙₑₑ = 70 K for annealed crystal and as grown eutectic using derivatives of the susceptibility. Below ordering temperature the ferromagnetic contribution for all investigated samples was observed. The strongest is for the eutectics. The reciprocal susceptibility (figure 1) was fitted using the Néel formula:

\[ \chi^{-1} = \frac{T}{C + \chi_0^{-1}} - \sigma(T - \theta) \]  

(1)

Using this equation, the analysis data gives σ, \( \chi_0^{-1} \) – complex functions of parameters of exchange interactions, C - constant, the Curie-Weiss temperature \( \theta \) which are collected in Table 1. The effective magnetic moments for all measured samples indicate manganese as Mn²⁺ ion.

Table 1. Fitting parameters and effective magnetic moment \( \mu_{\text{eff}} \) for MnTiO₃ single crystals and TiO₂-MnTiO₃ eutectic.

| Sample                              | \( \sigma \) | \( \chi_0^{-1} \) | C [emuK/mole] | \( \theta \) [K] | \( \mu_{\text{eff}} \) [μB] |
|-------------------------------------|--------------|-------------------|---------------|-----------------|-----------------|
| MnTiO₃ single crystal, as grown     | -903.9       | 51.6              | 4.17          | 23.5            | 5.8             |
| MnTiO₃ single crystal, annealed     | -1852.0      | 41.3              | 4.07          | 5.6             | 5.7             |
| MnTiO₃-TiO₂ eutectic, as grown     | -1279.7      | 46.3              | 4.3           | 21.3            | 5.9             |

![Figure 1](image-url)  

Figure 1. Magnetic susceptibility vs temperature.

Stickler et al [5] published the magnetic susceptibility results for MnTiO₃ but without ferromagnetic contribution at low temperatures. Using the Curie – Weiss formula they obtained the effective moment
value in agreement with our results. For the crystals grown by m-PD method the Curie – Weiss fit gives unreasonable parameters. H. Kageyama et al [6] observed ferrimagnetic-like response in canted antiferromagnets, where a weak ferromagnetic moment is due to the tilting of sublattice magnetizations. Such situation may take place for the investigated samples due to their nonstoichiometry as was found from the XPS measurements.

The XPS spectra of the MnTiO₃ single crystal and eutectic in a wide energy range are shown in figure 2. Any contamination, besides carbon, was not found in the spectra. Using the Multipak programme, the chemical compositions of the fractured under UHV surface were obtained (table 2). The chemical composition of the single crystal indicate a deficiency of titanium and an enhancement of manganese in relation to the nominal value. For the eutectic the amount of titanium and oxygen is higher due to TiO₂ phase.

| Sample                                    | Atomic concentration [at.%] |
|-------------------------------------------|-----------------------------|
| MnTiO₃ single crystal, as grown            | 23.2 16.7 60.1              |
| MnTiO₃ single crystal, annealed            | 22.8 17.1 60.1              |
| MnTiO₂-TiO₂ eutectic, as grown            | 19.7 18.5 61.8              |

Figure 2. XPS spectra in the wide energy range of the MnTiO₃ crystals and TiO₂-MnTiO₃ eutectic.

Figure 3. Mn 2p lines of the MnTiO₃ crystals and TiO₂-MnTiO₃ eutectic.

Figure 4. Ti 2p lines of the MnTiO₃ crystals and TiO₂-MnTiO₃ eutectic.
corresponding to their angular momentum of electrons. The Mn 2p lines are split due to existence of samples are very similar and narrow about 1 eV. The Ti 2p and Mn 2p spectra consist of two peaks. The core level lines and valence bands for all measured samples are very similar and narrow about 1 eV. The Mn 2p lines are split due to existence of the large magnetic moment [7]. This splitting is about 1.2 eV. A position of the Mn 2p at 640.3 eV contributes at about 3 eV. The satellite O 1s lines at a higher binding energy may be related to the oxygen vacancies, which are less electronegative or some oxygen contamination connected with the other phases.

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