

Synthesis, structure and physical properties of spinel solid solutions $\text{Mg}_2\text{TiO}_4\text{--MgTi}_2\text{O}_4$

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Abstract

We investigated the preparation condition for stoichiometric MgTi_2O_4 and the electromagnetic properties of the spinel solid solution $\text{Mg}_{2-x}\text{Ti}_{1+x}\text{O}_4$ ($0 \leq x \leq 1$). Only a highly reductive sintering atmosphere gives a possibility for the preparation of stoichiometric MgTi_2O_4 , based on Ti^{3+} . MgTi_2O_4 thus obtained shows a metal to spin singlet insulator transition accompanied by the structural change from cubic to tetragonal. Introduction of Ti^{3+} (d^1 , $S = 1/2$) to the non-magnetic insulator $\text{Mg}_2\text{Ti}^{4+}\text{O}_4$ acts partly as doping of carrier dopants and partly as a source of localized electrons. Increasing content of Ti^{3+} leads to their delocalization, resulting in the metallic MgTi_2O_4 at $x = 1.0$. The Peierls-like transition observed in the stoichiometric MgTi_2O_4 rapidly smears out with the content of Ti^{3+} ion decrease, suggesting an important role of orbital degree of freedom as an effective mechanism for the transition, which seems to be significantly influenced by the randomness associated with the appearance of Ti^{4+} ions.

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1. Introduction

The discovery of high temperature superconductivity in layered cuprates renewed the study on transition metal oxides. It has been argued that the high temperature superconductivity is closely related to unusual properties of low dimensional quantum spin systems, such as the resonating valence bond (RVB) state. Therefore, for the last several decades, $S = 1/2$ quantum magnets involving the transition metal ions with $3d^1$ or $3d^9$ configurations have been attracting strong attention. In the history of these investigations, many interesting spin-gap compounds have been discovered, for example SrCu_2O_3 [1], CaV_4O_9 [2], CaV_2O_5 [3], NaV_2O_5 [4] and others. Recently, geometrically frustrated spin systems occurred a fascinating subject to study the quantum spin liquid state. Recent theoretical progress on pyrochlore spin systems reveals that the spin (1/2) anti-ferromagnetic Heisenberg system has a spin liquid ground state [5–7]. In spinel oxides AB_2O_4 , its sublattice of B

constitutes the three dimensional network formed of corner sharing tetrahedral, so-called pyrochlore lattice, as shown in Fig. 1.

Transition metal spinel oxides have provided various properties such as superconductivity found in LiTi_2O_4 [8], heavy fermion behavior in LiV_2O_4 [9–11], charge order in AlV_2O_4 [12] and unusual magnetic transition in ZnV_2O_4 [13] and ZnCr_2O_4 [14]. Recently, LiMn_2O_4 has been used as promising cathode for batteries. Among transition metal spinel oxides, it has been well known that MgTi_2O_4 is a candidate of spin (1/2) compound with the pyrochlore lattice, where novel quantum phenomena have been expected [5–7].

Our recent investigation of the ternary MgO--TiO--TiO_2 phase diagram has lead to a successful preparation of powder sample of MgTi_2O_4 . As shown in Fig. 2, a novel transition from metal to spin-singlet insulator in MgTi_2O_4 has been found [15]. This transition is accompanied by the structural change from cubic to tetragonal. A significant role of the orbital degree of freedom for such Peierls-like transition in three-dimensional systems is proposed therein. In this paper, we report the preparation conditions of MgTi_2O_4 and the magnetic susceptibility and electrical resistivity of the spinel solid solution $\text{Mg}_2\text{TiO}_4\text{--MgTi}_2\text{O}_4$.

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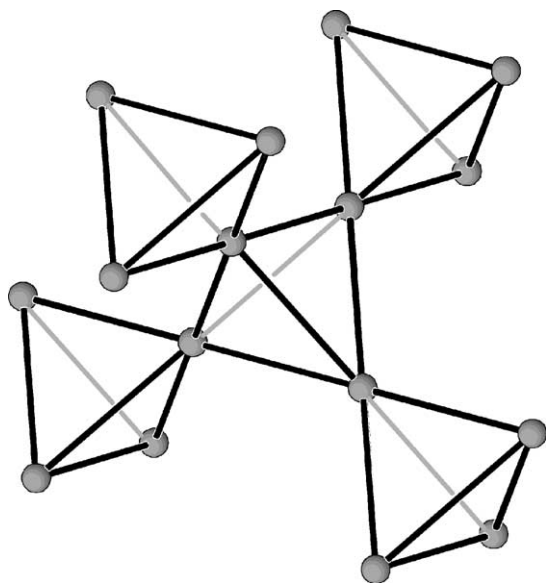


Fig. 1. A three-dimensional network of corner-sharing tetrahedra formed by B-cations in spinel oxide AB_2O_4 (pyrochlore lattice).

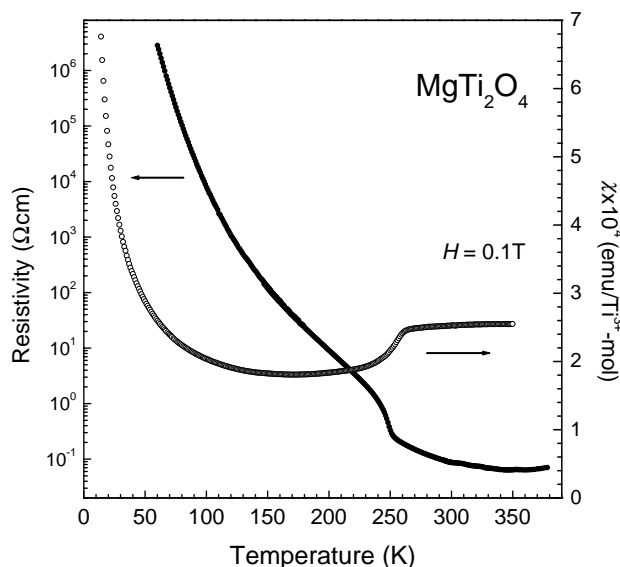


Fig. 2. Temperature dependences of magnetic susceptibility and resistivity for $MgTi_2O_4$ [15].

2. Experimental

Powder samples with $x = 0, 0.125, 0.25, 0.5, 0.75$ and 1.0 in $Mg_{2-x}Ti_{1+x}O_4$ were prepared by a solid state reaction of mixture with an appropriate molar ratio of MgO, titanium metal powder and TiO_2 . The weighted mixture was pressed into a pellet and heated at 1273 K in an evacuated silica tube for several days. Sample characterization and structural analysis were performed by powder X-ray diffraction using a Mac Science MXP21 with a rotating anode generator and a monochromator of single-crystalline graphite for Cu

$K\alpha$ radiation. Magnetic susceptibility was measured using a quantum design SQUID magnetometer in the temperature range from 5 to 330 K . The electrical resistivity measurements were made by ordinary four-probe method using ceramic samples.

3. Results and discussion

The system $Mg_{2-x}Ti_{1+x}O_4$ forms a solid solution with the cubic spinel structure in the whole composition range ($0 \leq x \leq 1$) in the present work, which was in agreement with the previous report [16]. The lattice constant at room temperature increases with increasing x in $Mg_{2-x}Ti_{1+x}O_4$, roughly obeying the Vegard's law as shown in Fig. 3. The product resulting of $x = 1.0$ ($MgTi_2O_4$) thus prepared occurred multiphase. Since it included a considerable amount of the corundum phase (apparently Ti_2O_3), we first thought the reaction was incomplete. The product was then reground, palletized and heated in an evacuated silica tube, again. However, after the second heating the corundum phase unexpectedly increased in quantity. From the consideration of the phase diagram, MgO – TiO – TiO_2 (see Fig. 4) [16,17], we come to a conclusion that the corundum phase should not be Ti_2O_3 but its solid solution with $MgTiO_3$, existing along the line $MgTiO_3$ – Ti_2O_3 . Lattice parameters of this corundum phase were slightly different from those of Ti_2O_3 . Presence of the corundum type solid solution in our sample as the minor phase indicates that the major phase has to be the spinel solid solution $Mg_{2-x}Ti_{1+x}O_4$. Growing quantity of the secondary phase, however, means the oxidization of Ti^{3+} to Ti^{4+} . The experiment has revealed that $MgTi_2O_4$ is very easily oxidizable at high temperatures even though it is under the evacuated atmosphere. Therefore, we tried to prepare the stoichiometric compound under the reductive starting composition $MgTi_2O_{4-\delta}$ ($\delta = 0.1$ – 0.2). As a result, the

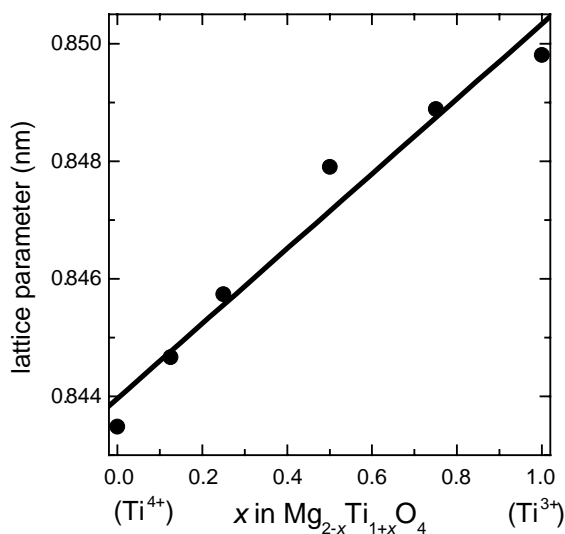


Fig. 3. Phase diagram of ternary system MgO – TiO – TiO_2 [16,17].

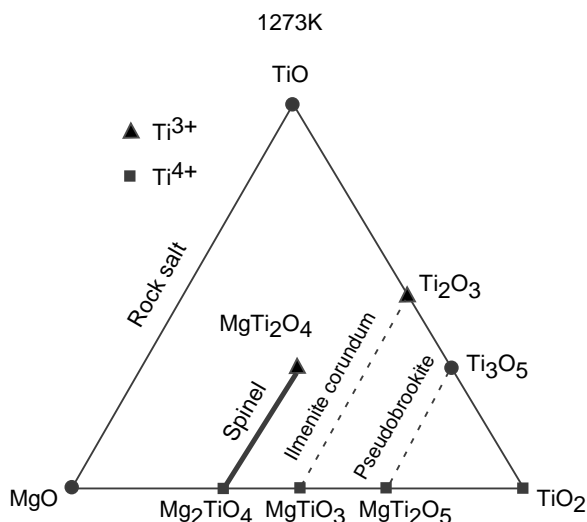


Fig. 4. Compositional dependence of the lattice constant in $\text{Mg}_{1+x}\text{Ti}_{2-x}\text{O}_4$ at room temperature.

corundum phase was completely eliminated, although the obtained sample included a small amount of an unknown impurity phase. Nevertheless, we conclude from the structure and physical property measurements that thus obtained sample is stoichiometric.

Fig. 5 shows the magnetic susceptibility of the powdered $\text{Mg}_{2-x}\text{Ti}_{1+x}\text{O}_4$. Only the end member of MgTi_2O_4 shows the transition [15] accompanied by effective reduction of magnetic susceptibility. The transition is very sensitive to Ti^{4+} ion content and it smears out with decreasing x . An overlooking of the transition in the previous study [16] may be due to the deviation from stoichiometry in their sample. The nonmagnetic compound Mg_2TiO_4 is diamagnetic [16]. With increasing x in $\text{Mg}_{2-x}\text{Ti}_{1+x}\text{O}_4$, the magnetic Ti^{3+} (d^1 ,

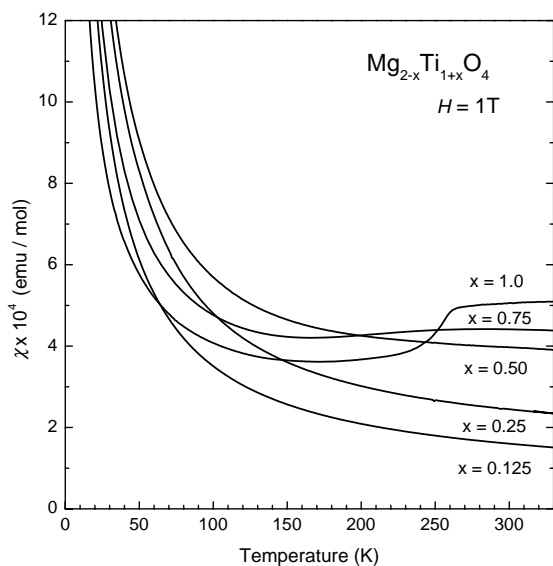


Fig. 5. Temperature dependence of magnetic susceptibility for $\text{Mg}_{1+x}\text{Ti}_{2-x}\text{O}_4$ with various x .

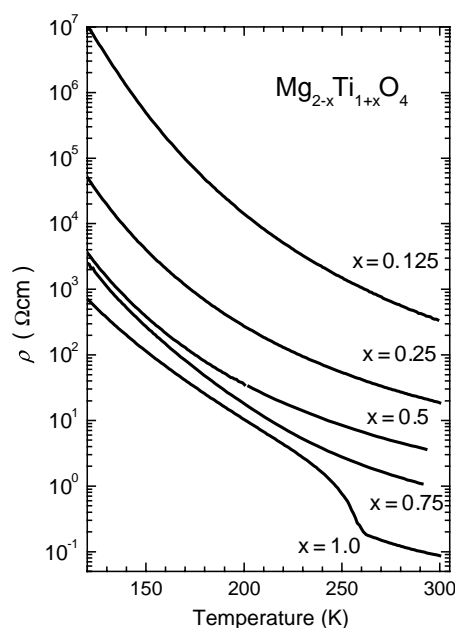


Fig. 6. Logarithm of electrical resistivity vs. temperature plots for $\text{Mg}_{1+x}\text{Ti}_{2-x}\text{O}_4$ with various x .

$S = 1/2$) ions are introduced into the pyrochlore lattice formed by non-magnetic Mg^{2+} and Ti^{4+} ions. A Curie-like behavior of magnetic susceptibility is seen in sample of low x values. However, it is impossible to explain the temperature dependence of magnetic susceptibility by fixed parameters in the whole temperature range measured even for sample of $x = 0.125$. The magnetic susceptibility for this sample obeys well the Curie law but only at low temperature region and below 20 K the fitting gives the Curie constant corresponding to 40% of the ideal value for isolated Ti^{3+} (d^1 , $S = 1/2$). Such non-Curie-like behavior in the whole temperature range is enhancing with increasing x . The Curie constant obtained for $x = 1.0$ sample corresponds to about 2% of isolated Ti^{3+} (d^1 , $S = 1/2$), which is considered to be a contribution coming from impurities and/or defects. These experimental results suggest a scenario in which the induced Ti^{3+} ions work as a source of localized spins and partly as carrier dopants. A proportion of delocalized electrons increases with increasing x . This is supported by the fact that the temperature independent magnetic susceptibility increases with increasing x . At $x = 1.0$, all electrons are delocalized, resulting in metallic behavior and the temperature independent magnetic susceptibility. We previously proposed an important role of orbital degree of freedom for the Peierls-like transition in MgTi_2O_4 [15]. In the solid solution of $\text{Mg}_{2-x}\text{Ti}_{1+x}\text{O}_4$ type, the pyrochlore lattice is disturbed by both Mg^{2+} and Ti^{4+} without orbital degree of freedom and consequently the transition rapidly smears out with increasing content of Ti^{4+} .

Such trend in $\text{Mg}_{2-x}\text{Ti}_{1+x}\text{O}_4$ can be seen in the resistivity. Fig. 6 shows the resistivity of $\text{Mg}_{2-x}\text{Ti}_{1+x}\text{O}_4$ as a linear function of temperature. The resistivity of Mg_2TiO_4 terminal

occurred too high for our apparatus to measure. With increasing x , however, the resistivity decreases suggesting an increase of carriers. The temperature dependence of resistivity is semiconductive in all samples except for the high temperature phase of MgTi_2O_4 . The metal–insulator transition observed in MgTi_2O_4 rapidly disappears with the Ti^{4+} content, agreeing with the results of magnetic susceptibility measurements.

In summary, we found the synthesis condition to prepare the stoichiometric MgTi_2O_4 . We also prepared the spinel solid solution $\text{Mg}_{2-x}\text{Ti}_{1+x}\text{O}_4$ ($0 \leq x \leq 1$) and investigated its magnetic and electric properties. The results indicate that starting from the insulator Mg_2TiO_4 , the induced Ti^{3+} with x partly works as carrier dopants and finally lead to metallic MgTi_2O_4 at $x = 1.0$. The Peierls-like transition observed in the stoichiometric MgTi_2O_4 rapidly smears out with the Ti^{4+} content, suggesting an important role of orbital degree of freedom as an effective mechanism for the transition, which could be significantly influenced by the randomness associated with the appearance of Ti^{4+} ions. In order to understand the essence of the transition, it is necessary to investigate the structure and electromagnetic properties in detail using single crystals. Crystal growth is now in progress.

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