Available online at www.sciencedirect.com
ScienceDirect
Journal of Magnetism and Magnetic Materials 310 (2007) 888–889
Journal of magnetism and magnetic materials
www.elsevier.com/locate/jmmm

Ti-doping effect on the MI transition of hollandite vanadate, $K_2V_8O_{16}$

Masahiko Isobe, Shigenori Koishi, Yutaka Ueda*

Materials Design and Characterization Laboratory, Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan

Abstract

Ti-doping effect on the metal-insulator transition of hollandite vanadate, $K_2V_8O_{16}$ has been investigated. The transition is accompanied by the charge ordering and the structural change from tetragonal to monoclinic structures with the increase of volume in the low-temperature monoclinic insulator phase. A slight amount of Ti-substitution for V atoms raises the transition temperature up to 270 K at $x = 0.5$ in $K_2V_{8-x}Ti_xO_{16}$ from 170 K at $x = 0$. This significant rise of transition temperature can be understood as a negative chemical pressure effect caused by the Ti-substitution. On the other hand, the disorder effect from the Ti-substitution makes the transition broad and finally the transition smears out around $x = 1.0$.

PACS: 72.80.Ga; 72.60.+g; 75.30.Kz

Keywords: Hollandite vanadium oxide; Metal-insulator transition; Substitution effect; Magnetic susceptibility

Vanadium oxides exhibit a rich variety of electromagnetic properties. The most characteristic property among them is metal-insulator (MI) transition as a function of temperature, as typically observed in binary vanadium oxides [1]. The MI transitions in mixed valent vanadium oxides such as V_4O_7 are accompanied by the charge separation and charge order, and spin singlet V^{4+}–V^{4+} pairs are formed in the low-temperature insulator phases, resulting in the large reduction of magnetic susceptibility at the MI transitions [2]. In our current study on vanadium oxides, an MI transition at 170 K was recently found in a hollandite vanadium oxide $K_2V_8O_{16}$ [3]. "Hollandite" is one of manganese minerals. Hollandite-type compounds have the general chemical formula $A_xM_8O_{16}$ ($x \leqslant 2$). The hollandite structure consists of the tubular M_8O_{16}-network and A-cations at the tunnel sites of the M_8O_{16}-framework, as shown in the inset of Fig. 1. The M_8O_{16}-framework is constructed from the double-chains running along the c-axis in the tetragonal structure and each double-chain is formed by sharing the edges of MO_6 octahedra. The MI transition of $K_2V_8O_{16}$ is accompanied by two step jumps about three orders in the resistivity along the c-axis and the reduction of magnetic susceptibility down to a small value (see Fig. 2), suggesting the formation of V^{4+}–V^{4+} singlet pairs and V^{3+}–V^{3+} pairs in the low-temperature insulator phase [3]. The transition is of first order accompanied by the structural change from a tetragonal to a monoclinic structure, and the low-temperature phase has a superlattice of $\sqrt{2}a \times \sqrt{2}a \times 2c$, where a and c denote the primitive cell parameters for the simple tetragonal hollandite structure, suggesting a charge ordering of V^{4+} and V^{3+} [3]. From these results we proposed a possible charge order model, where two kinds of double-chain formed by V^{3+} and V^{4+} chains and by single V^{4+} chains, respectively, order in a manner that gives a superlattice of $\sqrt{2} \times \sqrt{2}$ in the a–b plane, and the V^{4+}–V^{4+} and V^{3+}–V^{3+} pairs are formed in each chain along the c-axis, resulting in a duplication of the c-axis [3]. In order to elucidate the origin of the transition, we have investigated the substitution effect of Ti for V sites. We found the significant enhancement of transition temperature by the substitution. This means the transition is not of a simple charge order transition in which a significant damage on the transition is expected by the introduction of disorder. In this short paper, we report the structural and magnetic properties of $K_2V_{8-x}Ti_xO_{16}$ and discuss the Ti-substitution effect on the transition.

Powdered samples were prepared by a solid-state reaction of KVO_3, V_2O_3, V_2O_5 and TiO_2 under high

---

*Corresponding author. Tel./fax: +81 4 7136 3435.
E-mail address: yueda@issp.u-tokyo.ac.jp (Y. Ueda).

0304-8853/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jmmm.2006.10.1087

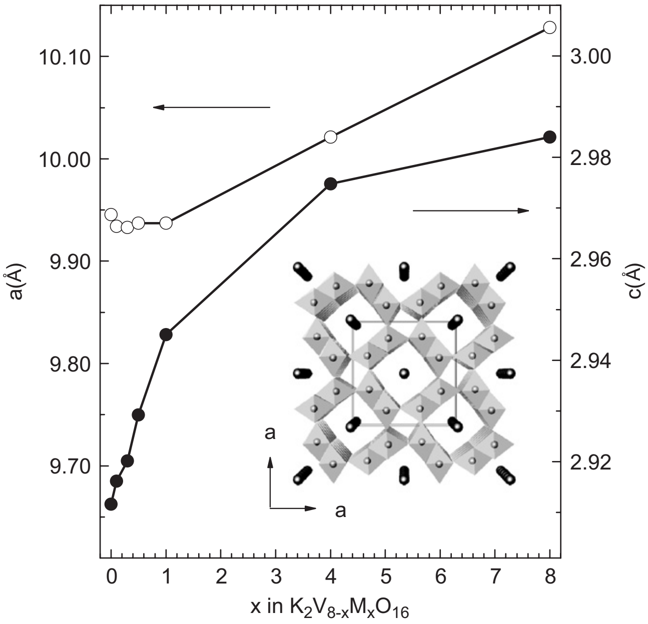

Fig. 1. Composition (x) dependence of lattice parameters in $K_2V_{8-x}Ti_xO_{16}$. The inset shows a schematic structure of $K_2V_8O_{16}$ viewed from the c-axis of the tetragonal structure.

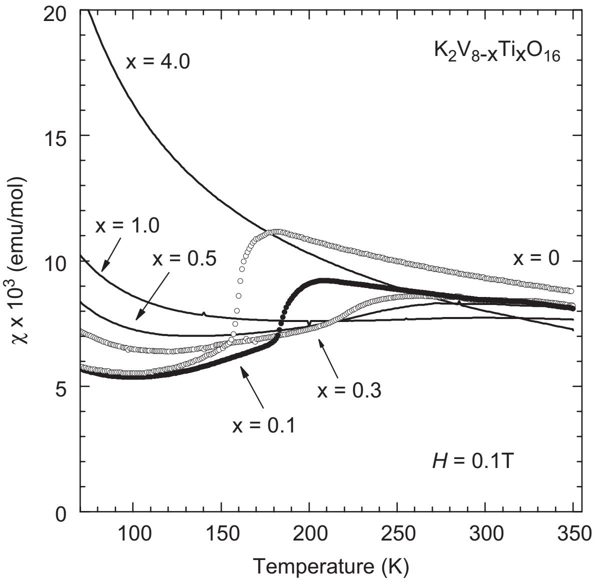

Fig. 2. Temperature dependence of magnetic susceptibility for various x in $K_2V_{8-x}Ti_xO_{16}$.

pressure of 4 GPa at 1473 K for 1 h. Starting reagents were ground thoroughly and the mixture was wraped by platinum foil and then put into a pressure cell. KVO_3 was obtained by a reaction of K_2CO_3 and V_2O_5. V_2O_3 was prepared by the reduction of V_2O_5 under flowing H_2 gas at 1173 K. A cubic type apparatus was used for high pressure synthesis. The sample identification and the determination of lattice parameters were made by powder X-ray diffraction. Magnetic susceptibility of powdered sample was measured by using a SQUID magnetometer.

All samples of $K_2V_{8-x}Ti_xO_{16}$ ($0 \leqslant x \leqslant 8$) are obtained as a single phase with a simple tetragonal hollandite structure at room temperature. This means Ti forms an entire solid solution of $K_2V_{8-x}Ti_xO_{16}$. Fig. 1 shows the lattice parameters as a function of x in $K_2V_{8-x}Ti_xO_{16}$ at room temperature. The lattice parameters of both a and c increase with x, namely the volume increases with x. Fig. 2 shows temperature dependence of magnetic susceptibility (χ) for $K_2V_{8-x}Ti_xO_{16}$. The most remarkable point is a significant rise of transition temperature by a slight substitution of Ti. As mentioned above, the MI transition of $K_2V_8O_{16}$ is characterized by the reduction of magnetic susceptibility. The onset temperature of the reduction of magnetic susceptibility goes upto 270 K at $x = 0.5$ from 170 K at $x = 0$. Simultaneously, the transition becomes broad and smears out around $x = 1.0$. On the other hand, the magnetic susceptibility of low-temperature phase increases with x and then above $x = 1$, the magnetic susceptibility continuously changes as a function of temperature. There is no anomaly suggesting any transition.

In general, phase transitions accompanied by some kinds of order suffer a significant damage by the introduction of disorder and the transition temperature could be lowered. $K_2V_8O_{16}$ is a mixed valent compound with $V^{3+}/V^{4+} = \frac{1}{3}$. Since a stable valence state of Ti is Ti^{4+} in the coexistence with V^{3+}/V^{4+}, the substitution of Ti for V must give a significant disorder in the charge ordering at the transition. Therefore, the observed enhancement of transition temperature is not understood in terms of such general disorder effect. The transition of $K_2V_8O_{16}$ is accompanied by a volume increase about 0.14% in the low-temperature phase. On the other hand, the substitution of Ti for V also increases the volume. This means the Ti-substitution gives a negative pressure to the system as a chemical pressure, and as a result the transition temperature might be raised by a slight substitution of Ti. However, the further Ti-substitution leads to a significant disorder, and finally the transition smears out. The (chemical) pressure effect on the transition is dominant at the initial stage of the Ti-substitution, while the disorder effect becomes dominant with the progress of the Ti-substitution.

This study has been supported by a Grant-in-Aid for Scientific Research (No. 18104008) from the Japan Society for the Promotion of Science.

References

[1] Y. Ueda, J. Phys. Soc. Japan 69 (Suppl. B) (2000) 149.

[2] M. Marezio, D.B. McWhan, P.D. Dernier, J.P. Remeika, Phys. Rev. Lett. 28 (1972) 1390;
Y. Ueda, Y. Kitaoka, H. Yasuoka, K. Kosuge, S. Kachi, J. Phys. Soc. Japan 47 (1979) 333.

[3] M. Isobe, S. Koishi, N. Kouno, J. Yamaura, T. Yamauchi, H. Ueda, H. Gotou, T. Yagi, Y. Ueda, J. Phys. Soc. Japan 75 (2006) 073801.