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Science and Technology of Advanced Materials 7 (2006) 17–21

SCIENCE AND TECHNOLOGY OF ADVANCED MATERIALS

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Crystal symmetry and superlattice reflections in spin-Peierls system TiOBr

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Received 15 September 2005; received in revised form 18 October 2005; accepted 9 November 2005

Abstract

We have demonstrated the direct observation of the crystal symmetry by electron and synchrotron X-ray diffraction analyses. Although the crystal structure at room temperature can be explained by orthorhombic *Pmmn* symmetry in our powder X-ray diffraction analysis, we detected weak reflections which should be the forbidden reflections of the *Pmmn* symmetry by electron and synchrotron X-ray diffraction analyses using single-crystalline TiOBr samples. We concluded that the crystal symmetry of TiOBr is different from the orthorhombic *Pmmn* symmetry. In this report, we discuss the crystal symmetry on the basis of the subgroup of orthorhombic *Pmmn* at room temperature and low temperature below $T_{c1}(=27\ \mathrm{K})$.

Keywords: Spin-Peierls; Crystal symmetry; X-ray diffraction; Electron diffraction; TiOBr

1. Introduction

Spin-Peierls transition is associated with an intrinsic lattice instability in a system of quantum mechanical antiferromagnetic chains, where $S=1/2$ spins interact with each other via a Heisenberg exchange interaction and are coupled to the lattice. From the experimental point of view, all the spin-Peierls compounds discovered so far have been organic and difficult to substitute the other atoms. However, in 1993 Hase et al. discovered the first inorganic spin-Peierls material $CuGeO_3$ [1]. The discovery of $CuGeO_3$ has not only deepened our understanding of spin-Peierls system but also resulted in new phenomena, such as impurity effects [2]. Discovering a new inorganic spin-Peierls material is, therefore, considered to be highly valuable.

Recently, TiOX (X=Cl and Br) has been suggested to be a quasi-one-dimensional (1D) $S=1/2$ spin system due to an one-dimensional overlapping of the wave function and a spin-Peierls compound [3]. The temperature dependence of the susceptibility of TiOX showed two successive phase transitions with a sudden drop to zero at T_{c1} and started to gradually decrease at T_{c2} ($T_{c1}=67$ K and $T_{c2}=95$ K for X=Cl [3], and $T_{c1}=27$ K and $T_{c2}=47$ K for X=Br [4]). Subsequently, heat capacity measurement confirmed these successive phase transitions, i.e. T_{c1} is the first-order, and T_{c2} is the second-order phase transition temperatures [5]. According to the nuclear spin resonance (NMR) analysis [6], TiOCl exhibited a pre-existing pseudo-spin gap above T_{c2} and the unconventional intermediate state accompanying the decrease of $1/T_1$ between T_{c2} and T_{c1}, and a first-order phase transition into a singlet ground state with an unusual large energy gap.

TiOX has a FeOCl-type crystal structure [4,7], where the TiO_4X_2 bilayers separate from each other along the *c*-axis, as schematically shown in Fig. 1. Direct exchange interactions are produced in the chains along the *b*-axis. Seidel et al. have suggested three types of chains; the strong one-dimensionality along the *b*-axis have been confirmed by electron spin resonance (ESR) analysis [8], which was supported by the temperature dependence of optical reflectivity [9] and angle-resolved photoelectron spectroscopy (ARPES) [10].

Recently, two successive lattice distortions related to the spin-Peierls transition were observed below T_{c1} [4,11,12] and the incommensurate modulation within $T_{c1}<T<T_{c2}$ (intermediate temperature) [13,14]. Superlattice reflections were

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doi:10.1016/j.stam.2005.11.002

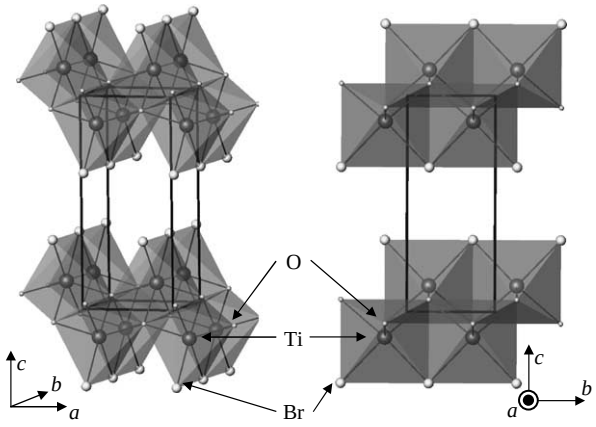

Fig. 1. Schematic representation of crystal structure of orthorhombic TiOBr at room temperature. Ti^{3+} ions align along the *b*-axis.

observed at (h, $k+1/2$, 0) below T_{c1} and at ($h\pm\delta_h$, $k\pm\delta_k$, l) between T_{c1} and T_{c2}. Strong diffuse scattering was observed along the *h*- and *l*-directions above T_{c2}, indicating that the structural correlation along the chains develops far above T_{c2}. This structural short-range correlation above T_{c2} can explain the well-fitted Bonner–Fisher curve to the temperature dependence of susceptibility of TiOBr [3,4,15]. T_{c1} is a first-order incommensurate to commensurate phase transition temperature with the spin-Peierls lattice distortion, and T_{c2}, a second-order phase transition temperature which is related to the spin-Peierls lattice distortion with an incommensurate structure [16]. The study of both superstructures, the commensurate (below T_{c1}) and incommensurate (intermediate) phases, is the best way of solving this problem.

Two-fold superlattice reflections indicate the dimer formation of Ti–Ti on the chains along the *b*-axis below T_{c1}, where a dimerized superstructure was reported in TiOX [4,11,12]. Palatinus et al. and Shaz et al. considered that superstructure exhibits a monoclinic symmetry and the space group $P2_1/m$ (*a*-axis unique) with a doubled lattice constant *b* observed below T_{c1} [11,12]. However, they also pointed out the possibility that this superstructure can be explained by an orthorhombic symmetry. In conclusion, they could not experimentally determine the final crystal symmetry of the lowest temperature phase, because they did not have direct information necessary for resolving the symmetry due to the limited range of setting angles of the crystal.

In our present paper, we report on electron diffraction patterns at the *hk*0 reciprocal lattice plane under various temperatures in TiOBr [13,16]. We conclude that the crystal symmetry of TiOBr at room temperature is different from the orthorhombic *Pmmn* symmetry.

2. Experimental details

Polycrystalline and single-crystalline samples of TiOBr were prepared by a chemical vapor transport technique [4,15]. Rammed mixtures of Ti, TiO_2 and $TiBr_4$ were vacuum-encapsulated in a quartz ampoule. The mixtures were set on one side (hot side) of the ampoule, which was heated up to 680 °C with a gradient of 100 °C within 20 cm. It took 2 days for the samples to cool down to room temperature. Although single crystals were obtained on both sides, polycrystals and high-quality single crystals were obtained on the hot side. The crystals are dark brown and have rectangular shape with a typical surface area of 2×8 mm^2 at the *ab*-plane.

Thin specimens for electron diffraction were prepared by crushing or thinning the samples by Ar^+ ion sputtering. Some samples were ground using CCl_4 and dispersed on Cu grids coated with carbon support films. These specimens were analyzed using a Hitachi HF-3000 high-voltage transmission electron microscopy (TEM) operating at 300 kV. For precise crystal structure determination, a synchrotron radiation (SR) powder X-ray diffraction experiment was carried out using a large Debye–Scherrer camera installed at BL02B2, SPring-8. The obtained powder data were analyzed by the Rietveld method. For precise crystal symmetry determination, SR X-ray diffraction experiments were carried out using the four-circle diffractometer at BL46XU, SPring-8. A single crystal with dimensions of $1.5\times6\times0.03$ mm^3 was glued on a BN plate, which was mounted on a refrigerator with the *hk*0 reciprocal plane parallel to the χ-axis.

3. Experimental results

Fig. 2 shows the SR powder X-ray diffraction pattern of TiOBr with a wavelength of 0.0922 nm at room temperature. The crystal structure of TiOBr was determined by the Rietveld analysis of the SR powder X-ray diffraction pattern. The main reflections can be explained with orthorhombic *Pmmn* symmetry. A small amount of Ti_2O_3 impurities was found, which might be formed by the reaction of TiOBr with moisture. In our powder X-ray diffraction experiments at room temperature, these data could roughly explain the orthorhombic structure model with the space group *Pmmn*. Table 1 shows the atomic parameters of TiOBr at room temperature, assuming the *Pmmn* space group.

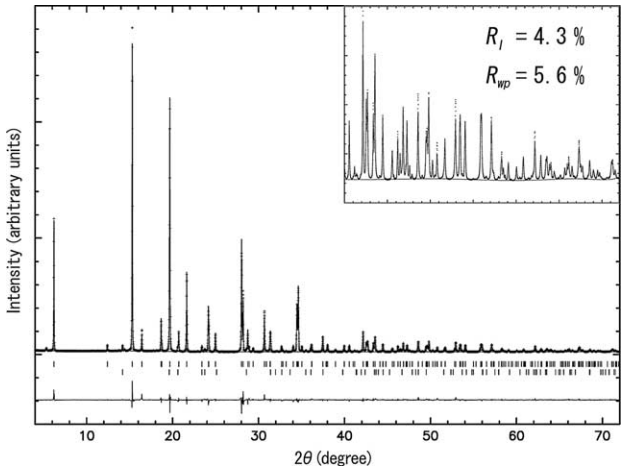

Fig. 2. SR powder X-ray diffraction pattern of TiOBr with wavelength of 0.0922 nm at room temperature. The solid line indicates the calculated profile, for which the orthorhombic *Pmmn* model is fitted. Vertical marks show the positions of allowed reflections for the main phase and impurity Ti_2O_3.