Journal of Magnetism and Magnetic Materials 370 (2014) 13–17

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Magnetic and thermal property studies of $RCrTeO_6$ (R=trivalent lanthanides) with layered honeycomb sublattices

G. Narsinga Rao [a], R. Sankar [a], I. Panneer Muthuselvam [a], F.C. Chou [a,b,c,*]

[a] Center for Condensed Matter Sciences, National Taiwan University, Taipei 10617, Taiwan
[b] National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan
[c] Taiwan Consortium of Emergent Crystalline Materials, National Science Council, Taipei 10622, Taiwan

ARTICLE INFO

Article history:
Received 8 March 2014
Received in revised form
19 May 2014
Available online 2 July 2014

Keywords:
Antiferromagnetic ordering
Super–super exchange interaction
Honeycomb lattice
Heat capacity

ABSTRACT

We have investigated the magnetic ordering of the $RCrTeO_6$ (R=Y, La, Tb and Er) samples comprising Cr^{3+} ($S=3/2$). The X-ray diffraction structure analysis revealed that all samples are a hexagonal structure with the space group P $\bar{3}$. The magnetic susceptibility $\chi(T)$ and heat capacity $C_P(T)$ measurement results reveal that both short range and long range antiferromagnetic (AFM) orderings exist in non-magnetic rare earth R=Y and La compounds. For isostructural compounds of R=Tb and Er, $C_P(T)$ curves show long range ordering at the same temperature as non-magnetic R=Y, which indicates that the super-super exchange of Cr spins dominates. For R elements of Tb and Er with large spins sitting between honeycomb sublattices composed of CrO_6–TeO_6 octahedra, the two sublattices of R and Cr appear to be independently magnetic.

1. Introduction

Geometrically frustrated magnetic systems exhibit a variety of ground states depending on the spin size and the spin configuration [1,2]. The spin interactions of these systems cannot be simultaneously satisfied because of the connectivity of lattice. This opens up the possibility to have an unconventional magnetic order or even novel spin-liquid state without any long range spin order at low temperatures [1]. The honeycomb lattice Heisenberg antiferromagnetic (AFM) compounds have attracted much attention due to the existence of diverse novel magnetic ground states [3,4]. For example, Venderbos et al. found that the interplay between the superexchange interaction of localized spins and the double exchange interactions of itinerant spins on the non-frustrated honeycomb lattice leads to an unexpectedly rich phase diagram with exotic magnetic phases [5]. Recent experimental results of the honeycomb lattice compound $Bi_3Mn_4O_{12}(NO_3)$ showed a spin-liquid behavior down to low temperature 0.4 K, which has been ascribed to the frustration effect due to the competition between AFM nearest and next nearest neighbor interactions [6–8]. The spin-1/2 honeycomb lattice $InCu_{2/3}V_{1/3}O_3$ exhibits an AFM transition at 38 K with an estimated nearest neighbor exchange coupling constant $\sim$280 K [9]. On the other hand, $Na_3M_2SbO_6$ (M=Cu, Ni, and Co) compounds show different magnetic behaviors from spin gap (M=Cu) to AFM order (M=Ni and Co) [10,11]. For such a variety of magnetic ground state structures, honeycomb lattice with various types of spin systems offers new and interesting possibilities of low temperature properties.

The $PbSb_2O_6$ structure is one of the typical mixed oxides with a honeycomb structure [12,13]. The mixed oxides of $RCrTeO_6$, where R=trivalent lanthanides, have been proposed to be a superstructure of $PbSb_2O_6$ [14,15]. The unit cell of $RCrTeO_6$ comprises two formula units and adopts the hexagonal structure with the space group P $\bar{3}$. All Cr and Te cations in $RCrTeO_6$ have octahedral coordination with oxygen atoms. In this superstructure, the honeycomb layers are formed by edge-shared TeO_6 and CrO_6 octahedra as a sheet and stacked along the *c*-axis as shown in Fig. 1(a). The rare earth elements can be viewed to be sandwiched between $(Cr/Te)O_6$ honeycomb layers. The $(Cr/Te)O_6$ honeycomb lattice is depicted in Fig. 1(b). Except the structural studies, no other information related to the physical properties of this interesting class of materials are available in the literature. Here we present spin susceptibility and heat capacity measurement results on $RCrTeO_6$ (R=Y, La, Tb and Er) compounds and compare the impact of trivalent rare-earth elements which are sandwiched between $(Cr/Te)O_6$ honeycomb layers.

2. Experimental details

Polycrystalline samples of $RCrTeO_6$ (R=trivalent lanthanides) were prepared by the solid state reaction method. R_2O_3 were heat treated at 900 °C for 12 h before mixing to remove the hydroxide

* Corresponding author at: Center for Condensed Matter Sciences, National Taiwan University, Taipei 10617, Taiwan.
E-mail address: fcchou@ntu.edu.tw (F.C. Chou).

http://dx.doi.org/10.1016/j.jmmm.2014.06.057
0304-8853/

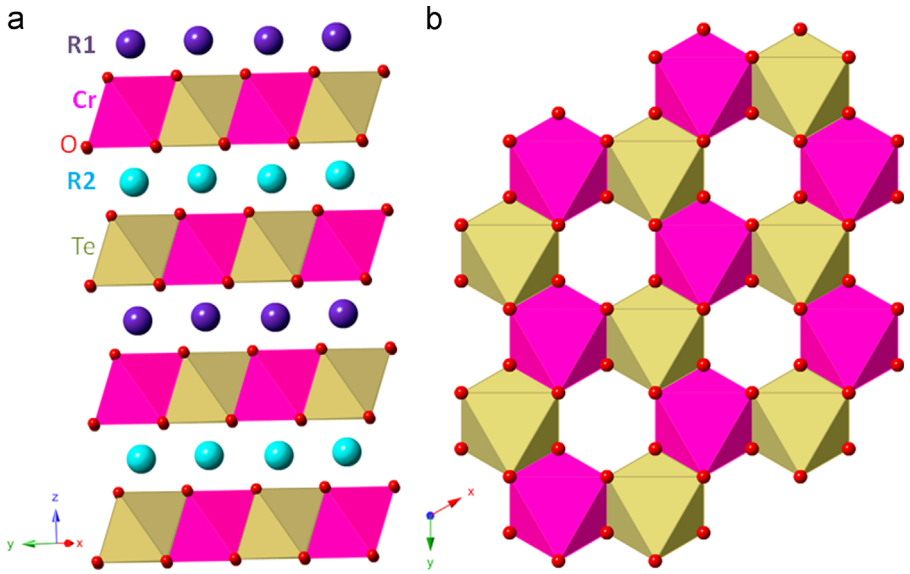

Fig. 1. (a) Crystal structure of $RCrTeO_6$ showing stacking of a alternative layers of rare earth (R_1O_6 and R_2O_6) and $(Cr,Te)O_6$ octahedra (pink and yellow color). The small red colored sphere are oxygen atoms. (b) The honeycomb sheet topology of $(Cr/Te)O_6$ in *ab*-plane. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

impurity. Stoichiometric proportions of high purity R_2O_3, Cr_2O_3, and TeO_2 powders were mixed and heated at 600 °C for 12 h to ensure that all the tellurium was oxidized to the hexavalent state. The pre-heated powders were well ground and calcined at 700 °C for 12 h with a heating rate of 2 °C/min and cooled down to room temperature at the same rate. The calcined powders were pressed into pellets and sintered at 850 °C for 12 h. The preparation conditions are the same for all the samples. The structure and the phase purity of the samples were checked by powder X-ray diffraction (XRD) using the Cu–K_α radiation at room temperature. The field cooled (FC) and the zero field cooled (ZFC) magnetization were measured in a commercial Vibrating Sample Magnetometer (VSM, Quantum Design, USA) from 1.8 K to 300 K in the presence of different applied magnetic fields. The temperature dependence of average spin susceptibilities $\chi(T)$ is defined with $M(T)/H$ based on the linear $M(H)$ isotherms. The isothermal magnetization (M) data were also recorded at selected temperatures. The heat-capacity (C_P) measurements were carried out by a relaxation method using commercial Physical Properties Measurement System (PPMS, Quantum Design, USA).

3. Result and discussion

The powder XRD pattern of the polycrystalline $RCrTeO_6$ (R=trivalent lanthanides) samples is shown in Fig. 2. The XRD patterns can be indexed to the hexagonal structure with the space group P $\overline{3}$ without any observable trace of impurity phase. The structural parameters were refined by the Rietveld technique with good quality refinement parameters (R_{wp}=8.75% and R_p=6.61%). The obtained values of the lattice parameters are depicted in Fig. 3 as a function of R^{3+} ionic radius. Both the a and c parameters increase with the R^{3+} ionic radius as expected. These parameters are in good agreement with those previously reported data [14]. The distances between chromium are larger along the c direction than in the *ab*-plane (Fig. 1(a)). In addition, partially substituted La/Y by Er samples also show the same hexagonal structure. The refined lattice parameters are decreased significantly with increasing Er content in the case of R=La, whereas in R=Y a small decreasing is observed (Fig. 3). The decrease in the lattice parameters is consistent with the smaller ionic radius of Er^{3+} (1.144 Å)

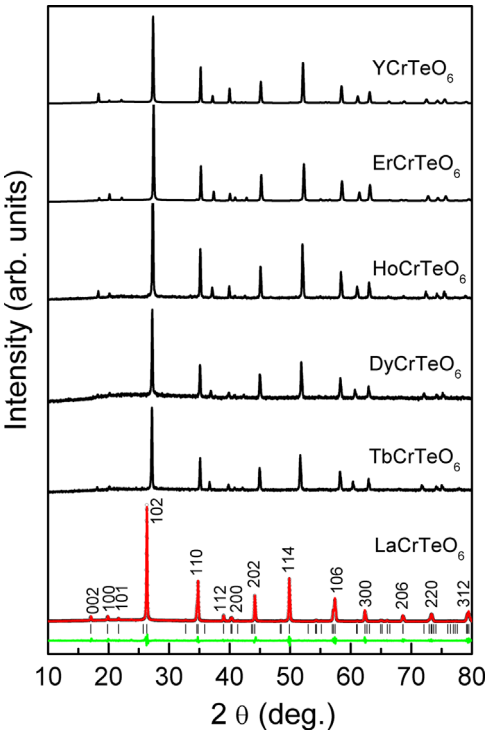

Fig. 2. Room temperature powder XRD pattern for $RCrTeO_6$ (R=trivalent lanthanides). The symbols are experimental points, solid curve is the best fit from the Rietveld refinement. The vertical bars indicate the position of Bragg peaks and the bottom curve shows the difference between the observed and calculated intensities.

comparing to that of the ionic radius of La^{3+} (1.300 Å) or Y^{3+} (1.159 Å) [16].

The temperature dependence of magnetic susceptibility $\chi(T)$ and $1/\chi(T)$ measured in an applied magnetic field of 10 kOe for $RCrTeO_6$ (R=La and Y) is shown in Fig. 4(a) and (b). No divergence between the zero field cooled (ZFC) and field cooled (FC) $\chi(T)$ curves has been found for both compounds through out the whole experimental temperature range. At low temperature, the $\chi(T)$ curves for R=La and Y exhibit a rounded maximum at 10.2 K and