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Phase transition induced by pressure in $TbCrO_4$ oxide: Relationship structure–properties

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ABSTRACT

Terbium chromate $TbCrO_4$, which has been described as belonging to the zircon-type structure showing tetragonal symmetry, space group $I4_1/amd$, has been prepared as a dimorphic compound. When the zircon-type $TbCrO_4$ polymorph is treated at 40 kbar and 833 K takes place a phase transition to the tetragonal scheelite-type $TbCrO_4$ polymorph, space group $I4_1/a$, with lattice parameters $a = 5.0315(10)$ Å and $c = 11.3740(2)$ Å. Magnetic susceptibility measurements reveal dramatic changes concerning the magnetic behavior of these two polymorphs. In this sense, the zircon-type $TbCrO_4$ polymorph behaves as ferromagnetic with a Curie temperature of 22 K, while the scheelite-type $TbCrO_4$ polymorph is antiferromagnetic with $T_N = 29$ K. M vs. H plots at different temperatures show the presence of a metamagnetic transition for the scheelite-type $TbCrO_4$ polymorph with a critical field of 2.6 T. The change of the sign of the magnetic interaction has been explained taking into account the differences found in the distances and bond angles of the superexchange Tb–O–Cr pathway through these interactions take place in both zircon and scheelite polymorphs.

1. Introduction

$RCrO_4$ oxides (R = rare earth) form a family of compounds with very interesting magnetic properties [1] and structural behavior [2]. The first member $LaCrO_4$ crystallizes with monazite-type structure, space group $P2_1/n$ [3]. In the case of the remaining rare earths show the zircon-type structure with tetragonal symmetry, space group $I4_1/amd$ [4]. Recently we have found that $PrCrO_4$ is a dimorphic oxide showing the mentioned zircon or monazite-type structure depending on the synthesis conditions [5].

Although phase transitions induced by pressure from zircon- to scheelite-type structure have been studied in some detail for the vanadate and arsenate families RXO_4 (X = V and As) [6,7], however only few studies have been recently reported for the analogous $HoCrO_4$ [8] and $YCrO_4$ [9] oxides. This could be due to the difficulty to prepare these oxides as pure phases because of the trouble to achieve the stabilization of the unusual 5+ oxidation state of chromium present in these phases. In fact, these high pressure scheelite phases show minor impurities of the perovskite-type $RCrO_3$ oxides [8,9]. Accompanying this structural phase transition from zircon to scheelite the magnetic properties change dramatically. The coexistence of two paramagnetic cations, namely Cr^{5+} and R^{3+}, in these oxides constitutes a very interesting scenario to study 3d–4f magnetic interactions and the predominant role that the rare earth anisotropy plays in the resulting magnetic properties of these two forms of the $RCrO_4$ oxides. In this sense, the most of the zircon-type $RCrO_4$ oxides being ferromagnetic [10] become antiferromagnetic for the corresponding known scheelite polymorph [8,9].

The aims of this work are the determination of the specific synthesis conditions such as pressure and temperature necessary to prepare the scheelite-type $TbCrO_4$ polymorph and the subsequent structural characterization using X-ray diffraction. Magnetic properties have been also studied from magnetic susceptibility and magnetization measurements at different temperatures and magnetic field strengths.

2. Experimental details

The zircon-type $TbCrO_4$ polymorph was prepared by using a precursor method based on the decomposition of stoichiometric amounts of $Tb(NO_3)_3$ $6H_2O$ and $Cr(NO_3)_3$ $9H_2O$ according to the experimental procedure described elsewhere [2]. Then this zircon $TbCrO_4$ oxide was placed within a platinum capsule and treated in a Belt-type apparatus at different high pressures, temperatures and reaction times. In order to eliminate the perovskite $TbCrO_3$ impurity different synthesis conditions were explored and 40 kbar and 833 K for 30 min were inferred as the optimized synthesis conditions.

X-ray powder diffraction data were collected on a Philips Panalytical X'Pert MPD diffractometer using the monochromatic Cu Kα_1 radiation ($\lambda = 1.54056$ Å). X-ray

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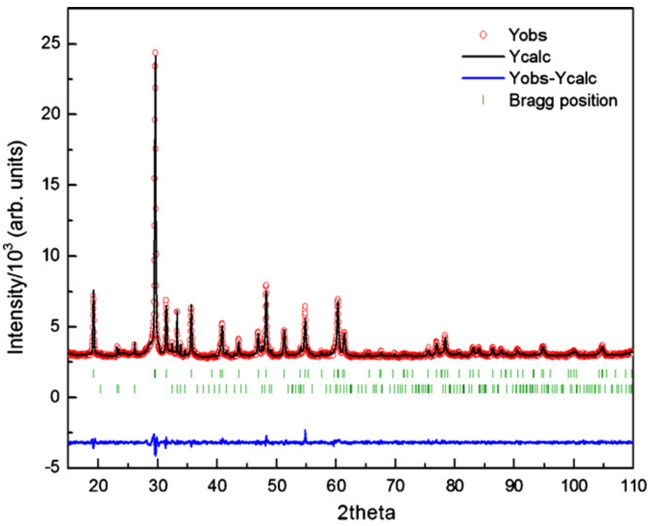

Fig. 1. Refined X-ray powder diffraction data for the scheelite-type $TbCrO_4$ oxide. Vertical marks indicate the position of the allowed reflections for the scheelite-type – 91.4(7)% – (upper) and for the perovskite-type – 8.6(3)% – oxides (lower).

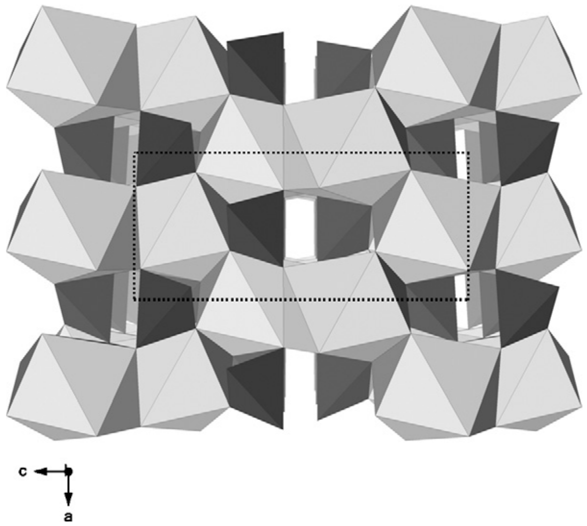

Fig. 2. Perspective view of the *ac*-plane of the scheelite-type structure showing the arrangement of $[TbO_8]$ bisdisphenoids polyhedra (light grey) and $[CrO_4]$ tetrahedra (dark grey).

diffraction data using for the Rietveld refinement were collected between 5 and 110 (2θ) with a step width 0.033° over a total exposure time period of 9 h. The X-ray diffraction data were refined with the Rietveld method using the FullProf program package [11].

Magnetic susceptibility measurements were made at different magnetic field strengths over the temperature range of 2–300 K using a SQUID Quantum Design XL-MPMS magnetometer. The variation of the magnetization as a function of the magnetic field was measured up to 5 T at different temperatures.

3. Results and discussion

3.1. Structural characterization

The Rietveld refinement of the X-ray diffraction data given in Fig. 1 for $TbCrO_4$ indicates that crystallizes with the scheelite-type structure showing tetragonal symmetry, space group $I4_1/a$, which has been obtained under high pressure and temperature from the zircon-type $TbCrO_4$ oxide. The metallic atoms Tb and Cr were located on 4b (0, 1/4, 5/8) and 4a (0, 1/4, 1/8) atomic positions, respectively, while the oxygen was located on 16f (x,y,z) position. Minor impurities of $TbCrO_3$ (8.6(3)%) are included in the refinement because appear during the high-pressure synthesis procedure as consequence of the mentioned previously high instability of Cr^{5+}. However, this impurity will not influence the magnetic properties of the scheelite phase as it will be discussed later.

The corresponding structural parameters for zircon and scheelite forms of $TbCrO_4$ are included in Table 1. According to these crystallographic data the crystal structure of the scheelite-type $TbCrO_4$ is shown in Fig. 2. As in the case of the zircon-type structure each Tb/Cr ion is also coordinated by eight and four oxygen atoms forming bisdisphenoids and tetrahedra polyhedra in this scheelite structure. This structure given in Fig. 2 can be described as formed by chains of alternate $[RO_8]$ bisdisphenoids and $[CrO_4]$ tetrahedra units along the a-axis of the structure, which are sharing corners. The $[RO_8]$ polyhedra of two consecutive chains are sharing edges along the c-axis giving rise to dimmers of $[R_2O_{14}]$ composition. As in the case of the zircon-type polymorph, the $[CrO_4]$ tetrahedra are well isolated one from another.

Moreover, the point symmetry of terbium atoms D_{2d} in the zircon-type polymorph changes to S_4 for scheelite type structure. The increasing density about 10% that takes place in this structural transition has been explained by Kusaba et al. [12] for $ZrSiO_4$ and more recently by Wang et al. [13] by means a two-step mechanism where a simple shearing coupled with a small displacements of atoms were involved giving as result a more efficient packing in

Table 1
Rietveld refined lattice parameters, atomic positions and reliability factors for the polymorph of the $TbCrO_4$ oxide.

$TbCrO_4$				Zircon-type			Scheelite-type
Space group				I 4_1/amd			I 4_1/a
Cell parameters	a (Å)			7.1650 (17)			5.0316 (10)
	c (Å)			6.2282 (15)			11.3740 (2)
Rietveld R-factors	R_p			0.0204			0.0156
	R_{wp}			0.0287			0.0214
	χ^2			1.90			1.55
Bragg R-factors	R_B			0.0320			0.0236
	R_f			0.0258			0.0160
Atoms, wyckoff positions, occupations, x/a, y/b, z/c	R	4a	1	0, 3/4, 1/8	4b	1	0, 1/4, 5/8
	Cr	4b	1	0, 1/4, 3/8	4a	1	0, 1/4, 1/8
	O	16h	1	0.0	16f	1	0.2456 (11)
				0.4399 (8)			0.6104 (16)
				0.2058 (9)			0.5501 (6)
Overall tem. factor				0.10 (4)			0.10 (3)

Table 2
Main interatomic distances, bond angles and volume for the zircon and scheelite polymorphs of the $TbCrO_4$ oxide.

$TbCrO_4$	V (Å^3)	d(Cr–O) (Å)	O–Cr–O (°)	d(Tb–O) (Å)	O–Tb–O (°)		Cr–O–Tb (°)
Zircon-type	322.813 (13)	1.727 (4) × 4	112.3 (2) × 2 103.9 (2) × 4	2.279 (6) × 4 2.481 (5) × 4	154.24 (16) × 2 134.46 (15) × 4	92.85 (16) × 4 66.38 (15) × 2	154.8 (3) × 1 94.84 (20) × 1
Scheelite-type	287.965 (10)	1.690 (7) × 4	119.5 (7) × 2 104.7 (7) × 4	2.354 (6) × 4 2.447 (7) × 4	137.6 (5) × 2 131.5 (5) × 4	97.5 (4) × 4 70.2 (2) × 2	122.4 (3) × 1 132.3 (3) × 1

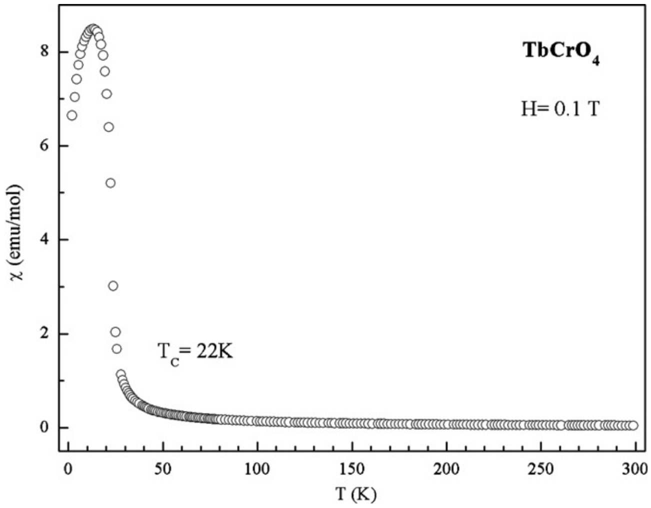

Fig. 3. Thermal variation of the magnetic susceptibility for the zircon-type $TbCrO_4$ polymorph.

the scheelite form due to the cooperative rotation of the tetrahedral polyhedra. Furthermore, structural refinements show that the Cr–O and Tb–O distances do not change very much in both polymorphs, but there are remarkable changes in O–Cr–O and Cr–O–Tb bond angles between the zircon and scheelite polymorphs that are the responsible of the mentioned increase in the density in the zircon–scheelite transition (see Table 2).

3.2. Magnetic properties

Figs. 3 and 4 show the thermal variation of the magnetic susceptibility for the zircon- and scheelite-type $TbCrO_4$ polymorphs, respectively. In both cases the magnetic susceptibility follows a Curie–Weiss behavior of the type $\chi = C/T-\theta$ between 50 and 300 K, where C is the Curie constant and θ denotes the Weiss constant ($\theta_{Zircon} = 7.31$ K; $\theta_{Scheelite} = -1.94$ K). The obtained effective magnetic moment for both compounds is 9.6 μ_B, after discounting the value expected for Cr^{5+} which is 1.63 μ_B, which agrees well with the calculated for the $^7F_6$ ground state associated to the free ion Tb^{3+}. However, at low temperature dramatic changes have been observed in the magnetic behavior. In this sense, in the case of the zircon-type $TbCrO_4$ polymorph (Fig. 3), a sudden jump is observed in the susceptibility at 22 K which is indicative of the onset of ferromagnetic interactions. This behavior has been confirmed from our recent neutron diffraction results where the terbium and chromium sublattices are ferromagnetic aligned along the *c*-axis of the zircon-type structure [10]. By contrast, in the case of the scheelite polymorph the observed net maximum at 29 K in the magnetic susceptibility (Fig. 4), indicates the presence of antiferromagnetic interactions. The small increasing found in the susceptibility below 10 K are due to presence of a small amount of $TbCrO_3$, around 8%, also detected from X-ray diffraction and included in the Rietveld refinement as it can be observed in Fig. 1 [14].

Magnetization measurements performed at different temperatures for the scheelite-type $TbCrO_4$ polymorph are shown in Fig. 5. It can be observed that the isotherm obtained at 40 K exhibits a lineal behavior as it was expected above the ordering temperature. However, the corresponding M vs. H plots obtained below the ordering temperature shows a S-shape feature characteristic for an antiferromagnetic material showing a metamagnetic transition. The critical field of such a metamagnetic transition is 2.6 T.

Recent results obtained from neutron diffraction experiments confirm this antiferromagnetic behavior, and the Néel temperature determined from the thermal evolution of the integrated intensities of the (0 1 1) and (1 1 0) reflections is almost coincident with the estimated one from the magnetic susceptibility measurements (see

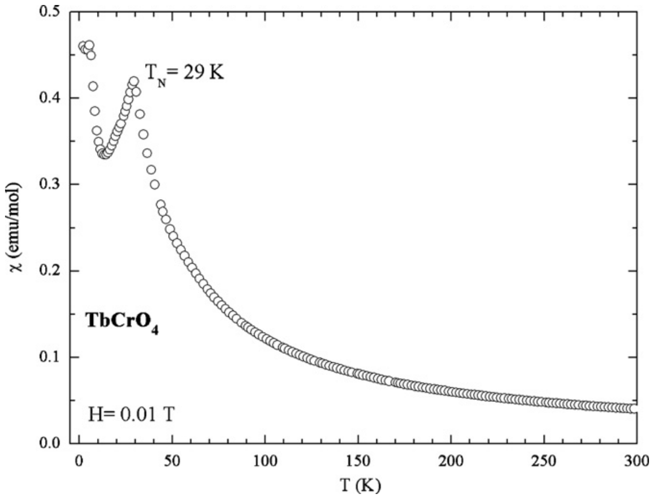

Fig. 4. Magnetic susceptibility as a function of the temperature for the scheelite-type $TbCrO_4$ polymorph.

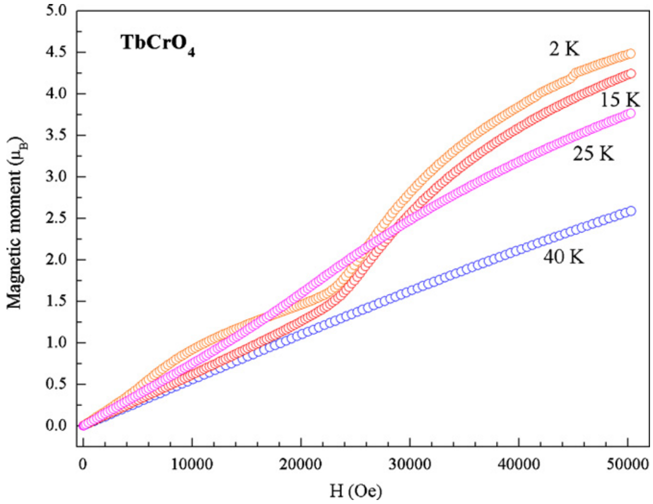

Fig. 5. Magnetization versus magnetic field plots at different temperatures for scheelite-type $TbCrO_4$ polymorph.

Fig. 5). We are currently analyzing these data in order to determine the magnetic structure that presents this new scheelite polymorph of $TbCrO_4$ oxide [15].

The analysis of the structure of both polymorphs will be very important to explain the different magnetic behavior that they present. As it was reported in a previous paper [8] the main operative pathway through these interactions take place is of superexchange-type Tb^{3+}–O–Cr^{5+} in which the $[CrO_4]$ and $[TbO_8]$ polyhedra are involved. It can be observed that both Cr–O and Tb–O distances do not change very much from zircon to scheelite polymorph by contrast important changes are observed in the Cr–O–Tb angles which could be considered as the main parameter to justify the change of the sign of the magnetic interaction in going from zircon to scheelite (see Table 2).

4. Conclusions

The scheelite-type $TbCrO_4$ has been obtained from the zircon polymorph at 40 kbar and 833 K. This new polymorph shows antiferromagnetic behavior ($T_N = 29$ K) while the zircon form is ferromagnetic ($T_C = 22$ K). The change of the sign of magnetic interactions has been explained taking into account the changes in the bond angles and distances through the superexchange Tb^{3+}–O–Cr^{5+} pathways going from zircon to scheelite.

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