



STRUCTURAL PHASE TRANSITIONS ZIRCON TO SCHEELITE TYPE INDUCED BY PRESSURE IN THE RCrO_4 OXIDES (R=RARE EARTH)

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Abstract

Novel scheelite RCrO_4 oxides have been obtained at high pressure and temperature, i.e. 4-5 GPa and 783-873K, from the ambient zircon RCrO_4 stable phases. They crystallize with tetragonal symmetry, space group $I4_1/a$, and a reconstructive model has been proposed to explain this zircon to scheelite first order transition. Magnetic properties change drastically as consequence of the mentioned phase transitions. In this sense, the most of the zircon RCrO_4 oxides are ferromagnetic, while the RCrO_4 scheelite polymorphs behave as antiferromagnetic. Magnetization versus magnetic field measurements at different temperatures reveal the onset of metamagnetic transitions for the scheelite polymorphs, where the critical field depends on the rare earth ion. The change of the sign

in the magnetic interactions from ferro to antiferromagnetism has been explained taking into account the differences found in the bond angles and distances involved in the superexchange R-O-Cr pathway through which the magnetic interactions take place.

Keywords: high pressure synthesis, phase transitions, antiferromagnetism, metamagnetism, magnetic superexchange.

Resumen

El tratamiento a altas presiones y temperaturas, 4-5GPa y 783-873 K, de los óxidos RCrO_4 que cristalizan con el tipo estructural zircón, grupo espacial $I4_1/amd$ (No.141), da lugar a la familia de óxidos RCrO_4 con la estructura tipo scheelita, grupo espacial $I4_1/a$ (No.88). Esta transición de fase zircón-scheelita inducida por presión es de primer orden y tiene lugar mediante un mecanismo reconstructivo. Las fases scheelitas se han podido congelar en condiciones normales y el estudio de las propiedades magnéticas muestra cambios sustanciales en las mismas al ser comparadas con los polimorfos tipo zircón. En este sentido cabe mencionar que la mayoría de los óxidos tipo zircón son ferromagnéticos, mientras que los correspondientes polimorfos scheelita se comportan como antiferromagnéticos. Este cambio de signo en las interacciones magnéticas se ha explicado teniendo en cuenta los cambios observados en las distancias y ángulos de enlace en el camino de la interacción de superintercambio R-O-Cr que tiene lugar al pasar de las fase zircón a las scheelitas obtenidas a altas presiones y temperaturas. Además, las fases scheelitas presentan metamagnetismo con valores de campos críticos que dependen de la naturaleza de la tierra rara R^{3+} .

Palabras clave: síntesis a alta presión, transiciones de fase, ferromagnetismo, antiferromagnetismo, metamagnetismo, superintercambio magnético.

Introduction

RCrO_4 oxides (R: rare earth) are included within the family of RXO_4 compounds where X: P, As, and V [1,2]. They crystallize in two different structural types depending on the size of both X and R elements [3]. In the case of the RCrO_4 oxides only LaCrO_4 crystallizes with the monazite-type structure, showing monoclinic symmetry and space group $P2_1/n$ (No. 14) [4,5]. Manca and Baran [6] have reported that the PrCrO_4 oxide is a dimorphic compound and the standard conditions of synthesis yield a mixture of both monazite and zircon forms. Recently, our research group has successfully prepared zircon- PrCrO_4 as a pure phase [7]. The remaining RCrO_4 oxides crystallize with the zircon-type structure, showing tetragonal symmetry and space group $I4_1/amd$ (No. 141) [8,9]. Figure 1 shows a perspective view of this zircon-type structure, which can be described as formed by zig-zag chains of edge sharing (RO_8) bisdisphenoids, which run parallel to the a -axis of the structure and are connected to each other by (CrO_4) tetrahedral units.

Zircon-type compounds of general formula RXO_4 have been extensively studied concerning the structural, optical and magnetic properties [8-11]. It has been also reported that under pressure and high temperature these zircon-type phases transform into scheelite-type, showing tetragonal symmetry and space group $I4_1/a$ (No. 88). In this sense, Stubican and Roy [12] reported a series of pressure-temperature diagrams for different rare-earth vanadates and arsenates giving a detailed study of the appropriate conditions to produce zircon-to-scheelite phase transitions. Very recently, the structural response of two rare-earth orthophosphates, namely YbPO_4 and LuPO_4 , has been reported [13] using in situ synchrotron X-ray diffraction, showing that the pressure induced zircon to scheelite transition is reversible and the scheelite high-pressure phase cannot be quenched at ambient conditions. This behaviour is different from that of both ZrSiO_4 and YVO_4 , where the scheelite high-pressure phases can be quenched to ambient conditions [14]. In the case of the RCrO_4 oxides, only few studies has been done concerning these structural phase transitions [15-18], mainly due to the high instability of Cr^{5+} [19,20] and its tendency to be reduced to the most stable RCrO_3

perovskites. The difficulty to prepare these RCrO_4 phases appears to be one of the reasons that justify the scarce information reported until now on these pressure induced phase transitions. However, it has been recently reported that the scheelite polymorph can be quenched at ambient conditions for some members of this RCrO_4 family, namely Y, Ho and Tb derivatives [15-18]. This feature permits us to undertake the study of the structural and magnetic properties of these new scheelite phases at ambient pressure. In this sense, we have recently reported that most of the zircon- RCrO_4 oxides behave as ferromagnetic [21], while their high-pressure scheelite polymorphs are antiferromagnets [16-18].

This paper is devoted to the study of the pressure induced zircon-to-scheelite phase transitions in the family of the RCrO_4 oxides, the thermal stability of new scheelite RCrO_4 -phases and their magnetic properties. Structure-properties relationships are disclosed in order to explain the switching of the sign of the magnetic interaction from the characteristic ferromagnetism of the zircon- RCrO_4 compounds to antiferromagnetism of scheelite- RCrO_4 derivatives.

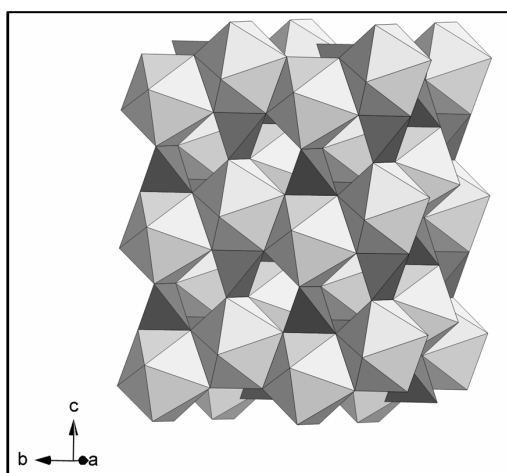
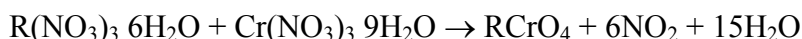


Figure 1. Perspective view of the ac -plane of the zircon-type structure, showing the arrangement of $[\text{RO}_8]$ bisdisphenoids polyhedra (light grey) and $[\text{CrO}_4]$ tetrahedra (dark grey).

Experimental

The powdered zircon-type RCrO_4 samples were prepared by the nitrate precursors method by heating the stoichiometric amounts of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{R}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ according to the overall reaction



An oxygen flow is required to stabilize the unusual Cr^{5+} oxidation state and the following thermal reacting sequence was used: 30 min. at 433 K, 30 min. at 473 K and overnight at 753 K. The obtained compounds were dark green-colored and X-ray diffraction patterns confirm their zircon-type structure and purity.

The scheelite-type RCrO_4 oxides were synthesized from zircon-type RCrO_4 . These powdered zircon phases were packaged in a gold container and then inserted into a pyrophyllite assembly. A belt type press was used to carry out the experiments, where the maximum pressure is 8 GPa and temperature up to 1273 K. The selected conditions to obtain pure samples were in the 4-5 GPa and 783-873 K ranges, depending on the rare-earth element. The conditions used in a typical high pressure synthesis, as for example in the case of scheelite- TbCrO_4 , are as follows: the pressure is increased up to 4 GPa and the sample is heated up to 833 K in 15 min., then the sample is

maintained under these conditions for 30 min., followed by quenching to room temperature and, finally, the pressure is slowly reduced to ambient condition in 2 hours.

Powder X-ray diffraction measurements were performed on both zircon and scheelite polymorphs using a Philips Analytical X'Pert MPD diffractometer (Cu $K\alpha_1$, $\lambda = 1.54056$ Å). Diffraction data were collected in the 2θ angle range from 5 to 110° with a step of 0.017° . X-ray diffraction data were analyzed with the Rietveld method using the Fullprof program package [22].

Thermal stability of the scheelite- RCrO_4 samples was studied on a thermobalance Perking Elmer Pyris 1, under oxygen flow of 9 mL/min. The measurements were carried out over 300-1375 K temperature range with a heating rate of 10 K/min.

Magnetization and magnetic susceptibility measurements were done by using a Quantum Design XL-MPMS SQUID magnetometer after zero field cooling. Thermal dependence of the magnetic susceptibility was measured on heating the sample from 2 to 300 K in an applied magnetic field of 0.1 T. The magnetization curves were measured at different selected temperatures in applied fields of up to 5 T.

The specific heat of the scheelite RCrO_4 samples was measured in a Quantum Design PPMS equipment. Measurements, based on the thermal relaxation method [23], were done in the 2-300 K range, at an applied magnetic field from 0 up to 9 T. A small portion of samples (≈ 4 mg) was fixed to the sapphire platform of the sample-holder by a small amount of Apiezon grease. Previously, the specific heat of this set-up, i.e. the sample holder and the grease, was measured separately in the same conditions, and subtracted from the experimental values in order to obtain the specific heat of scheelite RCrO_4 .

Results and discussion

Structural and thermal analysis

X-ray diffraction data reveal that all the obtained samples at ambient pressure, following the method described in the previous section, are isostructural showing the zircon-type structure, see Tables 1 and 2 where the data correspond to HoCrO_4 and TbCrO_4 as representative examples. Figure 2 shows the Rietveld analysis of the X-ray diffraction data for TbCrO_4 zircon polymorph treated at high pressure where all Bragg reflections can be indexed in the $I4_1/a$ space group, characteristic of the tetragonal scheelite-type structure. The small amount of impurity corresponds to the TbCrO_3 distorted perovskite as a consequence of the high instability of Cr^{5+} and its tendency to be reduced to the most stable Cr^{3+} oxidation state. In the $I4_1/a$ space group of the scheelite-type structure the R^{3+} ions are located in the $4b$ sites (0, 1/4, 5/8), Cr^{5+} in $4a$ sites (0, 1/4, 1/8) and the oxygen atoms are occupying the general position $16f(x, y, z)$. The rare-earth ions are centered in distorted bisdisphenoids in an eight-coordination, while the coordination of chromium is tetrahedral. The crystal structure of the scheelite-type forms, given in Figure 3, can be described as formed by chains of alternate corner-sharing (CrO_4) and (RO_8) units are sharing corners along the a -axis of the structure, while along the c -axis the (RO_8) polyhedra of the two mentioned chains are sharing edges giving rise to (Tb_2O_{14}) dimeric units. The size of the (RO_8) bisdisphenoid polyhedra diminishes progressively along with the size of R^{3+} in going from Tb to Yb. However, the size of the (CrO_4) tetrahedra remains almost constant for the scheelite RCrO_4 solid studied in the present work. According to the above discussion, it can be observed in Figure 4 that the a and c lattice parameters for the different RCrO_4 oxides decrease linearly with the reduction of the rare earth ionic radius in going from Tb to Yb due to the well-known lanthanide contraction.

Some crystallographic relationships have been established between the zircon and scheelite structural types. In this sense, Kusaba et al. [24] reported that the [110] direction in zircon-type structure becomes [100] direction in scheelite-type structure, and experimentally this assumption has been fully confirmed from an electron diffraction study [25]. They explain this zircon to

scheelite phase transition as a displacive-type, where a simple shearing mechanism and small rotations of (CrO_4) tetrahedra give rise to a more effective packing in the scheelite-type structure, which justifies the increasing in density of 10%. Nyman et al [26] described the scheelite-type structure as a simultaneous twinning of the zircon-type along the [200], [020] and [002] directions. However, recent ab-initio calculations and Raman studies [27] show that zircon-to-scheelite phase transition is a first order and reconstructive one. This mechanism explains why the scheelite-phase is metastable at ambient pressure and do not goes back to the zircon phase on release of pressure [28,29]. This model agrees with our previous results obtained from Rietveld refinements of the high resolution neutron diffraction data on TbCrO_4 , which show that the Cr-O and Tb-O distances do not change significantly, but a remarkable change has been observed in bond angles [30]. Same structural features have been obtained from X-ray Rietveld refinement as it can be observed in Table 1 and 2.

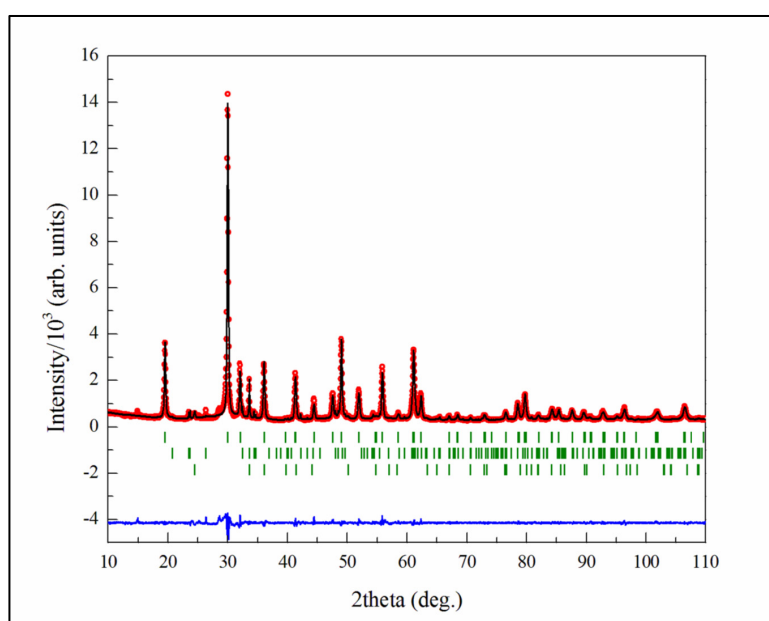


Figure 2. Observed (circles), calculated (upper full line) and difference (lower full line) X-ray powder diffraction profiles for scheelite-type TbCrO_4 . Vertical marks denote the position of allowed Bragg reflections for the scheelite-type oxide (first row), TbCrO_3 (second row, 6 wt. %) and Cr_2O_3 (third row, 2 wt. %).

The thermal stability of these RCrO_4 scheelite phases has been studied under oxygen flow atmosphere. In the case of YbCrO_4 , see Figure 5, the TGA diagram shows two well defined steps centered at 800 and 975 K respectively. In the first step which starts at 750 K the sample losses 1.32 % of its weight and the final product at 900 K has been identified by X-ray diffraction as zircon YbCrO_4 together with a small amount of YbCrO_3 as consequence of the incipient decomposition of YbCrO_4 . Therefore, about 23 % of the YbCrO_4 decomposes in this first step. In the second step the weight loss is about 4.82 %, which corresponds to the removal of oxygen giving as final product at 1100 K the distorted YbCrO_3 perovskite, as it was confirmed from X-ray diffraction data. The total weight loss observed in the two mentioned steps agrees well the theoretical value of 5.82% expected for the decomposition process of YbCrO_4 to YbCrO_3 . Similar behavior has been obtained for the remaining RCrO_4 -scheelite polymorphs. These results indicate that the thermal decomposition of RCrO_4 -scheelite polymorphs takes place through the zircon-phase as intermediate product, distorted RCrO_3 perovskites being the final product.

Table 1. Rietveld refined lattice parameters, agreement factors and atomic positions for the zircon- and scheelite-type RCrO_4 (R= Ho and Tb) oxides.

RCrO_4			<i>Ho</i>		<i>Tb</i>	
Structural type			Zircon	Scheelite	Zircon	Scheelite
Space group			$I4_1/amd$	$I4_1/a$	$I4_1/amd$	$I4_1/a$
Cell parameters (Å)	<i>a</i>		7.119(10)	5.0017(10)	7.1650(17)	5.0316(10)
	<i>c</i>		6.2557(5)	11.2664(2)	6.2282(15)	11.3740(2)
Rietveld R-factors	R_p		0.134	0.133	0.0204	0.0156
	R_{wp}		0.156	0.149	0.0287	0.0214
	χ^2		4.08	4.19	1.90	1.55
Bragg R-factors	R_B		0.0398	0.0372	0.0320	0.0236
	R_f		0.0221	0.0182	0.0258	0.0160
Atoms,	R	1	0, 3/4, 1/8	0, 1/4, 5/8	0, 3/4, 1/8	0, 1/4, 5/8
occupations,	Cr	1	0, 1/4, 3/8	0, 1/4, 1/8	0, 1/4, 3/8	0, 1/4, 1/8
x/a, y/b, z/c	O	1	0, 0.4308(8), 0.2065(8)	0.1420(17), 0.0074(13), 0.2017(7)	0, 0.4399(8), 0.2058(9)	0.2456(11), 0.6104(16), 0.5501(6)
Overall tem. factor (Å ²)			0.16(3)	0.50(4)	0.10(4)	0.10(3)

Table 2. Volume, selected distances and angles for the zircon- and scheelite-type RCrO_4 (R= Ho and Tb) oxides.

RCrO_4	<i>Ho</i>		<i>Tb</i>	
Structural type	Zircon	Scheelite	Zircon	Scheelite
Volume (Å ³)	317.07(4)	281.850(9)	322.813 (13)	287.965 (10)
d(Cr-O) (Å)	1.664(5)×4	1.650(7)×4	1.727(4)×4	1.690(7)×4
d(R-O) (Å)	2.329(6)×4	2.369(8)×4	2.279(6)×4	2.354(6)×4
	2.441(4)×4	2.444(8)×4	2.481(5)×4	2.447(7)×4
O-Cr-O (°)	113.7(4)×4	116.8(7)×2	112.3(2)×2	119.5(7)×2
	101.4(5)×2	105.9(7)×4	103.9(2)×4	104.7(7)×4
O-R-O (°)	154.7(4)×2	137.2(6)×2	154.24(16)×2	137.6(5)×2
	92.7(3)×4	97.6(4)×4	92.85(16)×4	97.5(4)×4
	136.2(3)×4	129.7(5)×4	134.46(15)×4	131.5(5)×4
	63.66(14)×2	74.0(4)×2	66.38(15)×2	70.2(2)×2
Cr-O-R (°)	153.3(2)×1	122.3(3)×1	154.8(3)×1	122.4(3)×1
	97.5(2)×1	132.9(3)×1	94.84(20)×1	132.3(3)×1

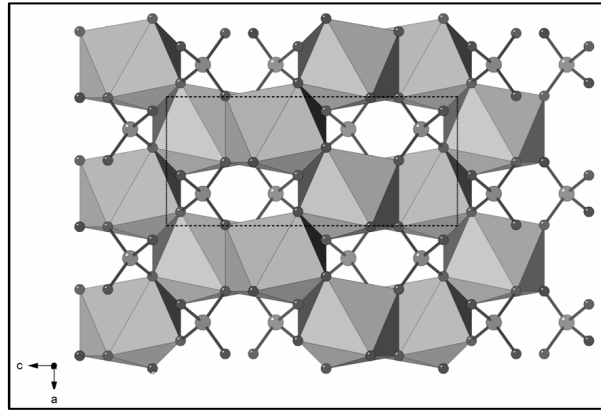


Figure 3. Perspective view of the scheelite-type structure.

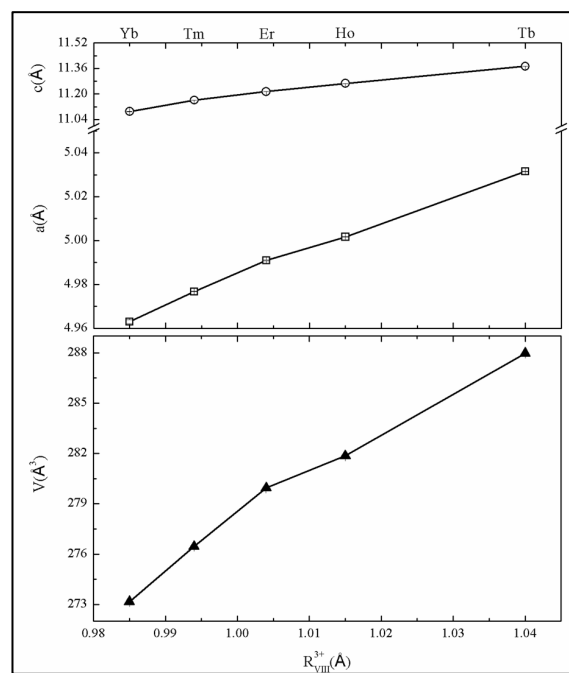


Figure 4. Variation of the lattice parameters for the scheelite-type $RCrO_4$ ($R = Tb, Ho, Er, Tm$ and Yb) oxides.

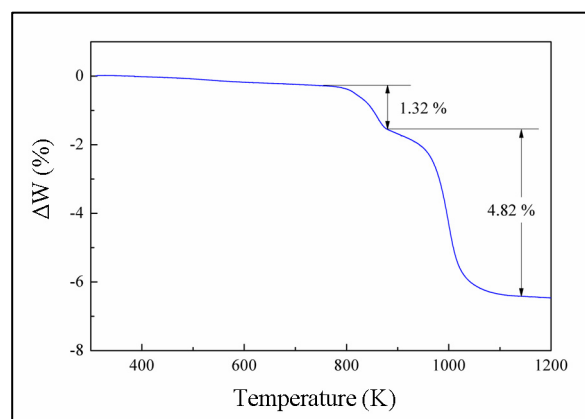


Figure 5. TG-diagram for scheelite-type $YbCrO_4$.

Magnetic properties

The temperature dependence of the magnetic susceptibility for the scheelite YbCrO_4 and HoCrO_4 oxides, as examples of these representative polymorphs, is given in Figure 6. The experimental data follow a Curie-Weiss behavior $\chi = \frac{C}{T - \theta}$ for both oxides in a wide range of temperatures (300-50 K). The magnetic parameters such as Weiss constant (θ), effective magnetic moment (μ_{eff}) and Néel temperature (T_N) for the different scheelite phases are collected in Table 3. A good agreement can be observed between the experimental μ_{eff} value and the theoretical one expected for R^{3+} ground state, calculated with the Hund's equation [31]. The experimental values of μ_{eff} have been corrected taking into account the Cr^{5+} contribution of $1.6 \mu_B$ [32]. It is worth noting that this value is lower than the calculated one considering the spin-only contribution for Cr^{5+} ($S = \frac{1}{2}$), which is $1.73 \mu_B$. This small difference can be explained by the mixing into the 2E electronic ground state of $\text{Cr}^{5+} 3d^1$ in a tetrahedral coordination with the higher lying 2T excited state by spin-orbit coupling. This gives rise to an μ_{eff} that depends on both the spin-orbit coupling constant λ and the $10Dq$ value [33]. Since Cr^{5+} has just one unpaired electron the λ constant is positive and thus the obtained μ_{eff} can be fully justified. Moreover, this value has been reported earlier for the LuCrO_4 and YCrO_4 zircon oxides [29,34]. On the other hand, the negative values of the Weiss constant for all samples, Table 3, can be ascribed to antiferromagnetic interactions.

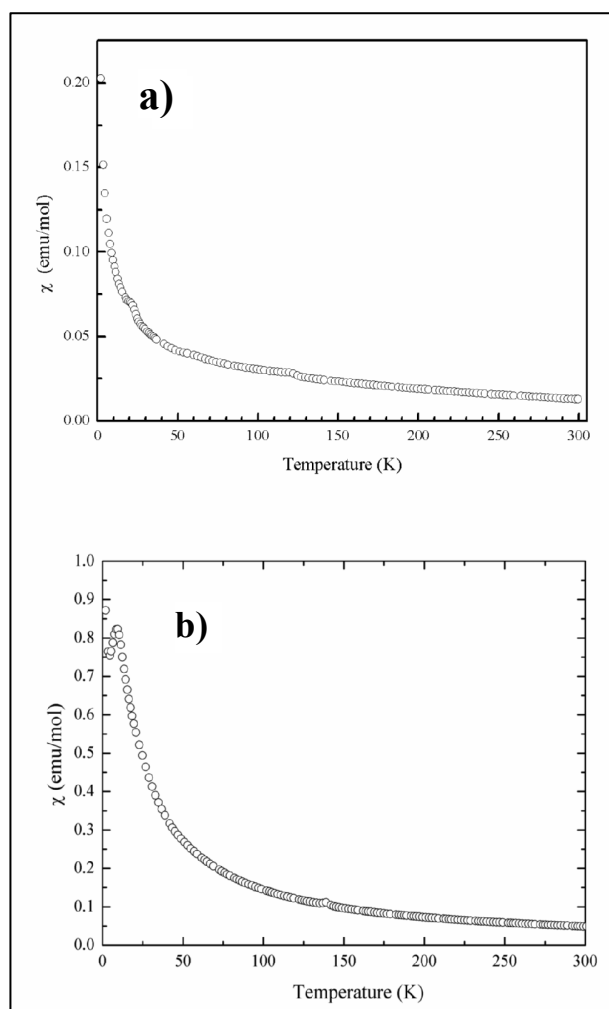


Figure 6. Magnetic susceptibility versus temperature for the scheelite-type YbCrO_4 (a) and HoCrO_4 (b) oxides.

Table 3. Magnetic parameters obtained for the scheelite-type RCrO_4 (R= Tb, Ho, Er, Tm and Yb) oxides.

RCrO_4 -scheelite	$\mu_{\text{eff}}^{\text{exp}} (\mu_{\text{B}})$	$\mu_{\text{eff}}^{\text{theor}} (\mu_{\text{B}})$	$T_{\text{N}}(\text{K})$	$\theta(\text{K})$
TbCrO ₄	9.63	9.72	29	-1.94
HoCrO ₄	10.67	10.58	8	-6.15
ErCrO ₄	9.66	9.59	11	-43.6
TmCrO ₄	7.87	7.55	27	-17.1
YbCrO ₄	4.60	4.54	21	-26.4

^aAfter subtraction of $\mu_{\text{eff}}^{\text{exp}} (\text{Cr}^{5+})$.

At low temperature the onset of a maximum can be observed at 21 and 9.4 K for YbCrO₄ and HoCrO₄, respectively, hence confirms the presence of antiferromagnetic interactions in which R^{3+} and Cr^{5+} sublattices are involved. The T_{N} values for the different RCrO_4 -scheelites are also included in Table 3. In the case of the YbCrO₄ the presence of a minor impurity of YbCrO₃ produces an increase in the susceptibility below the Neel temperature as result of Yb^{3+} behaving as paramagnetic in this distorted perovskite [35].

Magnetization curves as a function of magnetic field at selected temperatures are shown in Figure 7 for TbCrO₄ and HoCrO₄ scheelite-polymorphs. The magnetization curves in all cases exhibit a linear behavior above T_{N} as it was expected for an antiferromagnetic compound. Below the ordering temperature, M vs. H plots show the characteristic S-shape due to the onset of a metamagnetic transition that takes place in these two TbCrO₄ and HoCrO₄ scheelite-polymorphs, as it can be observed for the curves corresponding to 2 K. These field-induced transitions take place at 2.6 and 1 T, respectively. Similar results have been also found for the ErCrO₄ oxide.

Specific heat (C_{p}) measurements have been also carried out to investigate further the nature of the antiferromagnetic transitions taking place in these RCrO_4 scheelite polymorphs. Figure 8 shows the thermal evolution of C_{p} at different applied magnetic fields for HoCrO₄-scheelite. In all cases at zero magnetic field there is a λ -type anomaly at ordering temperatures which is coincident with those previously determined from the magnetic susceptibility measurements. In addition, it can be observed that this λ -type anomaly is magnetic field dependent and at the highest field strength it almost disappears, a fact that confirms the magnetic origin of this transition.

On the other hand, it has been previously reported that the most of the zircon- RCrO_4 phases behave as ferromagnets and it has been also indicated the prominent role that the Cr^{5+} ($3d^1$) plays as promoter of the interactions in the R^{3+} sublattice [19].

As it was discussed earlier [18], the magnetic interaction, either ferromagnetic for the zircon or antiferromagnetic for the scheelite-forms, mainly involves a super-exchange mechanism of the R^{3+} -O- Cr^{5+} -type. The change of the sign of the exchange integral accompanying this phase transition is mostly due to the changes in the bond angles in going from zircon to scheelite, since the R-O and Cr-O distances remains almost constant for both polymorphs as it can be observed in Table 2.

We are currently undertaken the analysis of the neutron diffraction data obtained at different temperatures in order to determine the magnetic structures that present this family of new RCrO_4 -scheelites.

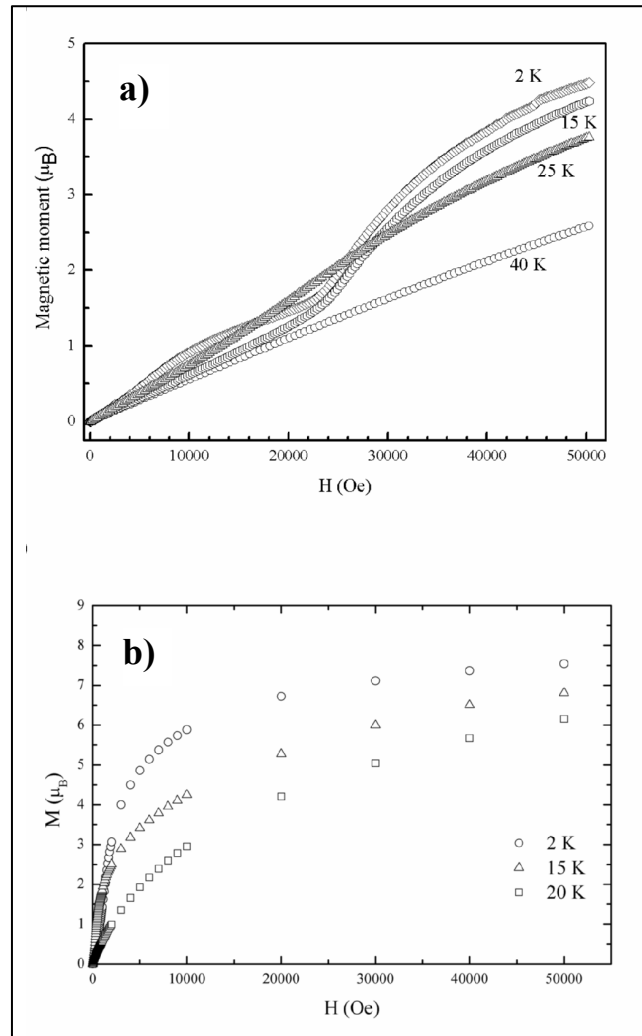


Figure 7. Magnetic field dependence of the magnetization for scheelite-type $TbCrO_4$ (a) and $HoCrO_4$ (b) obtained at different temperatures.

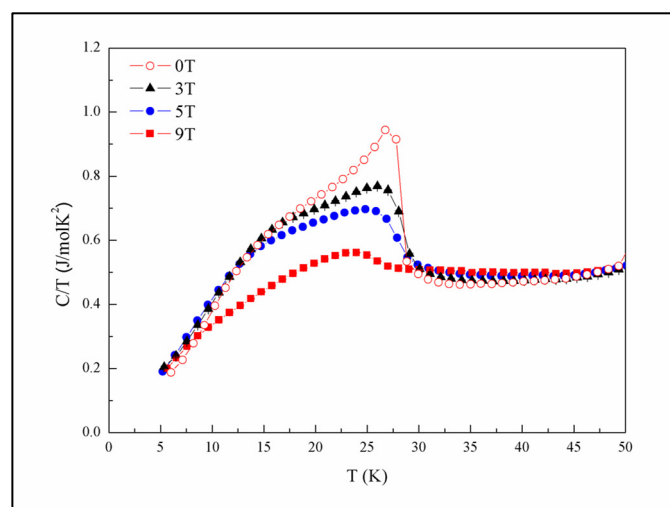


Figure 8. Temperature dependence of the total specific heat measured at different magnetic fields for scheelite-type $HoCrO_4$.

Conclusions

The scheelite- RCrO_4 oxides have been prepared from their zircon forms at the high pressures and temperatures in the 4-5 GPa and 773-873 K ranges, depending of the rare earth trivalent cation R^{3+} . These high pressure scheelite- RCrO_4 phases can be quenched at ambient conditions and the study of the magnetic properties reveals an antiferromagnetic behaviour and metamagnetic transitions were found for most of the samples below the Neel temperature. By contrast, the zircon phases are ferromagnetic. This different magnetic behaviour has been correlated with the differences found in the bond angles and distances for the R-O-Cr superexchange pathway through which the predominant magnetic interactions take place.

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