Neutron diffraction characterization and magnetic properties of the scheelite-type ErCrO$_4$ polymorph

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Abstract. The new scheelite-type ErCrO$_4$ polymorph has been obtained from the zircon-type ErCrO$_4$ phase by a treatment at 4 GPa and 823 K. X-ray and neutron diffraction studies reveal that this scheelite-type polymorph crystallizes with tetragonal symmetry, space group $I\bar{4}1/a$ being the lattice parameters $a=4.9989(10)$ Å and $c=11.2332(23)$ Å. Although bisdisphenoids [ErO$_8$] and tetrahedra [CrO$_4$] polyhedra are present in both compounds, dramatic changes have been observed in the magnetic properties of both polymorphs of ErCrO$_4$. The zircon one is ferromagnetic with $T_C \approx 15$ K; while the corresponding scheelite-type polymorph behaves as antiferromagnetic with $T_N \approx 21$ K. The observed change of sign in these compounds could be explained by considering the differences found in the superexchange Er–O–Cr bond angles through which the magnetic interactions take place in both polymorphs.

1. Introduction

The $R$XO$_4$ oxides, where $R$= rare earth and $X$= P, As, Cr and V, crystallize in the zircon or monazite-type structures at ambient conditions and transform to scheelite-type at high pressures and moderate temperatures [1]. These phases are quenchable to ambient conditions [2] except for YbPO$_4$ and LuPO$_4$, where a non-quenchable pressure induced transition has been observed [3].

Regarding the zircon-$R$CrO$_4$, high pressure phase transitions have only been studied for YCrO$_4$ [4], HoCrO$_4$ [5] and TbCrO$_4$ [6]. This structural phase transition from zircon to scheelite produces important changes in the magnetic properties. In this sense, most of the zircon-type $R$CrO$_4$ oxides being ferromagnetic become antiferromagnetic for the corresponding scheelite-type polymorph [7].

In this paper, we report the synthesis conditions used in the preparation of the scheelite-type ErCrO$_4$ oxide and its structural characterization by means of X-ray and neutron powder diffraction data as well as the study of the magnetic properties.

2. Experimental

Zircon-type ErCrO$_4$ polymorph was prepared using stoichiometric amounts of Er(NO$_3$)$_3$·6H$_2$O and Cr(NO$_3$)$_3$·9H$_2$O according to the experimental procedure described elsewhere [7]. The obtained zircon-type ErCrO$_4$ oxide was placed in a gold container and treated in a belt-type press at different pressures and temperatures in order to optimize the synthesis conditions to yield the scheelite-ErCrO$_4$ phase. The optimized conditions were 4 GPa and 833 K for 40 min. The sample obtained from the high-pressure experiment was tested by means of X-ray diffraction measurements.
Neutron powder diffraction data were collected in the temperature range of 2-100 K using the medium resolution powder diffractometer D1B ($\lambda$= 2.5251 Å, $20 (\text{deg.}) \leq 90$) at the Institut Laue Langevin (Grenoble, France). The data were analyzed by the Rietveld method using the program FullProf integrated in the software package WinPlotr [8].

Magnetic susceptibility and magnetization measurements were performed in a Quantum Design MPMS-XL magnetometer in the temperature range of 2-300 K at different applied magnetic fields.

3. Results and discussion

Figures 1(a) and (b) show the Rietveld refinement of the neutron diffraction data for the obtained scheelite-type ErCrO$_4$ oxide at 100 and 2 K, respectively. The data have been refined according to the scheelite-type structure, space group $I4_1/a$. The oxygen atoms are located in the general positions 16f $(x, y, z)$, while the Er$^{3+}$ and Cr$^{5+}$ ions are placed in the special 4b $(0,1/4,5/8)$ and 4a $(0,1/4,1/8)$ sites, respectively. Note that the impurities Cr$_2$O$_3$ (4 wt %) and ErCrO$_3$ (10 wt %) have been also included in the refinement. The structural parameters obtained from the Rietveld refinement, main bond distances, angles and agreement factors are included in Table 1.

The temperature dependence of the magnetic susceptibility for ErCrO$_4$ is shown in figure 2. The onset of a net maximum found around 11 K is indicative of the appearance of antiferromagnetic interactions in which both Cr$^{5+}$ and Er$^{3+}$ sublattices appear to be involved. The small anomaly found around 133 K is due to the magnetic behavior of the detected ErCrO$_3$ impurity, a canted antiferromagnetism, but no further low temperature anomaly due to this impurity is observed [9]. Figure 3 shows the magnetization versus magnetic field curves obtained at different temperatures. Note that below the ordering temperature the plot shows the typical S-shape feature characteristic for an antiferromagnet that undergoes a metamagnetic transition, in this case with a critical field of 1.4 T.

Figure 1. Rietveld refinement of neutron diffraction patterns obtained at (a) 100 K and (b) 2 K for scheelite-type ErCrO$_4$. Observed, calculated and difference profiles are denoted by circles, the upper solid line and the lower solid line, respectively. Vertical marks denote the position of (a) nuclear allowed reflections for the scheelite polymorph (first line), Cr$_2$O$_3$ (third line, 4 wt %) and ErCrO$_3$ (fourth line, 10 wt %); and (b) nuclear and magnetic reflections for the scheelite-type polymorph (first and second lines), Cr$_2$O$_3$ (fourth line), ErCrO$_3$ (fifth line) and magnetic reflections for ErCrO$_3$ (sixth line). Nevertheless, the second row of vertical marks in (a) and the third in (b) refer to the shoulder in the main reflection resulting from the sample environment equipment during the experiment.
TABLE 1. Atomic parameters, main interatomic distances and bond angles for the scheelite-type ErCrO₄ polymorph, calculated from the Rietveld refinement of neutron diffraction data obtained at 100 K. The corresponding reliability factors are also included.

| Space group | \( I \ 4_1/a \) |
|-------------|------------------|
| Cell parameters (Å) | \( a \) 4.9989(10) \( c \) 11.2332(23) |
| Rietveld R-factors | \( R_p \) 0.0115 \( R_w \) 0.0146 \( \chi^2 \) 1.90 |
| Bragg R-factors | \( R_B \) 0.0140 \( R_F \) 0.0202 |
| Atoms, wyckoff | Er 4\( b \) 1 0.1/4.5/8 |
| Positions | Cr 4\( a \) 1 0.1/4.1/8 |
| \( x/a, y/b, z/c \) | O 16\( f \) 1 0.2352(26), 0.6044(20), 0.5478(6) |
| \( B_{iso} \) (Å²) | 0.065(3) |
| Main interatomic distances (Å) and bond angles (deg.) | |
| \( d \) (Cr-O) | 1.744(10)×4 d (Er-O) 2.295(11)×4 2.382(9)×4 |
| \( \angle \) (O-Cr-O) | 120.3(13)×2 \( \angle \) (O-Er-O) 135.5(9)×2 98.2(8)×4 131.5(6)×4 71.0(5)×2 |
| \( \angle \) (Cr-O-Er) | 121.5(5)×1 130.7(5)×1 |

Neutron powder diffraction patterns show the onset of new reflections forbidden for the space group \( I \ 4_1/a \) along with a progressive increase of certain reflections below \( T_N \approx 20 \) K. These magnetic reflections, see Fig. 1(b), have been indexed on the basis of the coincidence between the crystal and magnetic cells, with the propagation vector \( \mathbf{k} = (0,0,0) \). The thermal evolution of the integrated intensity of the (002) and (011) magnetic reflections reveals that these magnetic reflections disappear at 22 K, a higher ordering temperature than the observed one from the magnetic susceptibility measurements. The magnetic structure is defined in the primitive \( P1 \) space group and the best agreement (\( R_M = 0.032 \)) between the experimental and calculated neutron diffraction profiles was obtained when Cr\(^{5+}\) and Er\(^{3+}\) magnetic moments are aligned parallel to the \( ab \)-plane [10]. The saturation moments obtained from the Rietveld refinement are 0.62(4) \( \mu_B \) and 5.11(7) \( \mu_B \) for the Cr\(^{5+}\) and Er\(^{3+}\), respectively.

The different magnetic behavior observed between the zircon-type and the scheelite-type polymorphs of ErCrO₄ oxide could be explained by considering the changes in the Er-O-Cr superexchange pathways through which the magnetic interactions take place in both compounds. These changes are mostly due to the changes in the Er-O-Cr bond angles, since the bond distances remain almost constant in both polymorphs. Such bond angles take the values of 152.67(20)° and 96.27(15)° for the zircon-type phase, while in the case of the scheelite-type phase they are 121.5(5)° and 130.7(5)°. 
Figure 2. Thermal variation of the magnetic susceptibility for the scheelite- ErCrO$_4$ polymorph.

Figure 3. Magnetization versus magnetic field plot for the scheelite-type ErCrO$_4$.

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