Structure and magnetic properties of multiferroic $YCr_{1-x}Fe_xO_3$ (0≤x≤1)♣

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Samples from the mixed oxide system $YCr_{1-x}Fe_xO_3$ (0≤x≤1) were prepared by self-propagation combustion techniques and studied by neutron and X-ray diffraction at 290 K and by magnetic measurements in the range 2–800 K. The average observed metal-oxygen distances based on refinements in the space group Pnma are in agreement with the expected distances from the valence bond approach. The non-collinear spin arrangement (mode Γ4) of $YFeO_3$ and $YCrO_3$ is preserved for the rest (x ≥0.33) of the compounds magnetic at 290 K. The findings indicate that $YCrO_3$ and $YFeO_3$ form a solid solution with strongly frustrated magnetic interactions.

1. Introduction

In multiferroic materials the magnetic and ferroelectric orderings coexist and are coupled [1]. Beside important implications for novel electronic devices [2], the physics behind the expected complex magnetoelectric phenomena is of great current interest [3]. Few multiferroic compounds with effective magnetoelectric properties are known (e.g. $BiFeO_3$, $BiMnO_3$, $YMnO_3$), since proper ferroelectricity and magnetism are usually antithetic [1,3]. Much of the current interest is in the so-called improper multiferroics (with magnetically induced ferroelectricity) such as $RMnO_3$, RMn_2O_5 (R= rare earth) and other perovskite-like materials with frustrated magnetic interactions and non-collinear spin ordering [3,4].

In this paper, the subjects of investigation are mixed oxides Y-Fe-Cr-O (0≤x≤1) whose end members $YFeO_3$ and $YCrO_3$ display intriguing magnetic and electric properties (ferroelectric data for $YCrO_3$ are given in [3]). Previous research work drew attention to the great complexity of the magnetic properties in the system [5-7]. We found the structural information for the system very limited and undertook a systematic structural and magnetic characterization of phases in the system.

2. Sample preparation

Materials with the general formula $YCr_{1-x}Fe_xO_3$ (x = 1.0, 0.875, 0.75, 0.67, 0.5, 0.33, 0.25, 0.125, 0.0) were obtained as polycrystalline powders by implementing a modified self-propagation combustion method [8]. The reaction products were characterized by X-Ray diffraction (XRD) for phase identification and to assess phase purity.

$YCrO_3$ was synthesized by slow evaporation and self-ignition of a stoichiometric reaction mixture of $Y(NO_3)_3.5H_2O$, $Cr(NO_3)_3.9H_2O$ and an organic component (sucrose – $C_{12}H_{22}O_{11}$). The other members of the series were prepared by the same method, where a stoichiometric amount of $Fe(NO_3)_3.9H_2O$ was added. In contrast to $YCrO_3$, the synthesis of $YCr_{1-x}Fe_xO_3$ (0<x<1) material proceeded without intermediate forming of $YCrO_4$.

3. Experimental

The X-Ray powder diffraction (XPD) patterns for structural refinement were recorded on a Brucker D8 Advance powder diffractometer (CuKα radiation, SolX energy dispersive detector) in the 10°-130° 2θ range, with a 0.02^o 2θ step and a counting time of 10 sec/step. Neutron powder diffraction (NPD) patterns (5°-113° in 2θ, steps of 0.1^o, wavelength of 1.065 Å) were measured on the PSD diffractometer at the Budapest Neutron Centre. The crystal and magnetic structure refinements of the XRD and NPD patterns were carried out by the Rietveld method, implemented in the FullProf package [9].

The dc magnetic susceptibility was measured by means of a Faraday-type magnetic balance in the temperature range 300–800 K in a magnetic field of 7 kOe and with a commercial SQUID magnetometer in the temperature range 2–400 K.

4. Results

Fig. 1 shows that the main XRD peaks have nearly equal intensities and angular positions, indicating that similarly to $YFeO_3$ and $YCrO_3$ all the members of the system are orthorhombically distorted perovskites. Correspondingly, all spectra could be indexed within the space group Pnma.
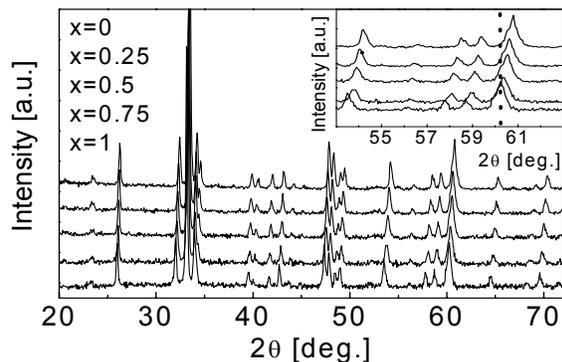

Fig. 1. XRD patterns of the $Ycr_{1-x}Fe_xO_3$ series. Inset: limited angular part with reflections 311, 321, 240 and 042.

Fig. 2 presents evidence for long range antiferromagnetic ordering at room temperature in the compositions with x>0.25; neutron diffraction revealed the presence of additional peaks with diffracted intensity depending on Fe-concentration.

Fig. 3 illustrates for $YCrO_3$ the crystal structure determination from the simultaneous refinement of the XRD and NPD patterns. The structural parameters are set out in Table 1.

The monotonic expansion of the unit cell volume with increasing x matches the refined mean metal-oxygen distances. This can be explained assuming that Fe^{3+} (ionic radius r_i = 0.645 Å) substitutes smaller Cr^{3+} (r_i = 0.615 Å) [10] and both ions are randomly distributed over the B-sites of the structure. This corroborates the findings for polycrystalline samples with $0.5 \le x \le 1$ obtained by solid

state synthesis [7], and the data on single crystals and powders [6]. Remarkably, the lattice constants of our samples, after being treated at 800^oC, are close to the values in [7] for samples with similar nominal compositions but heated at temperatures as high as 1350^oC.
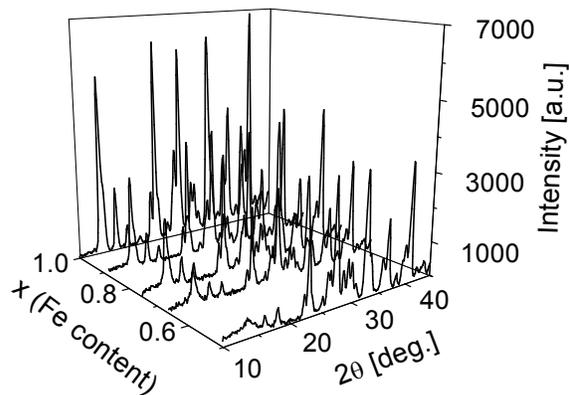

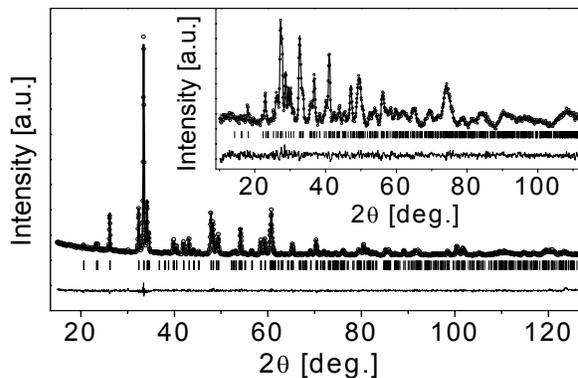Fig. 2. Low angle part of the room temperature NPD patterns of $YCr_{1-x}Fe_xO_3$.

Fig. 3. XRD and NPD (inset) Rietveld plots of $YCrO_3$ at room temperature.

Table 1. Positional and isotropic thermal parameters of $YCrO_3$ (lattice constants in Å: a= 5.5223(5), b=7.5338(6), c=5.2415(4)).

Ion	x	y	z	B_{iso}
Y^{+3}	0.0663_4	0.25	0.9818_6	0.55_7
Cr^{+3}	0.00	0.00	0.50	0.22_8
O_1^{-2}	0.464_1	0.25	0.106_1	0.5_1
O_2^{-2}	0.1992_9	-0.0537_6	0.1953_8	0.52_5

The XRD and NPD patterns, as well as the smooth changes in the unit cell volume and measured magnetic

moment versus x depicted in Fig. 4, indicate that the formation of a solid solution of $YCrO_3$ and $YFeO_3$ occurs in the whole concentration range. However, the evaluation of the MeO_6 (Me=Fe,Cr) distortions points to anomalies for $0.33 \leq x \leq 0.67$.
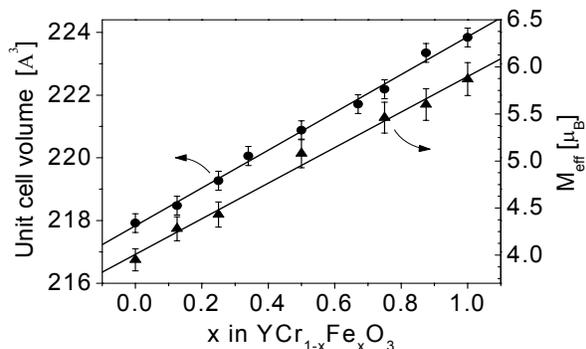

Fig. 4. Dependence of the unit cell volume and the effective magnetic moment on Fe content, x: experimental data with error bars and linear fits

In both $YFeO_3$ and $YCrO_3$ below the Neel temperatures T_N=648K and 141K, respectively, the non-collinear antiferromagnetic state Γ_4 ($G_cF_bA_a$) is established. In this spin arrangement, the basic vector of antiferromagnetism $G=M_1-M_2+M_3-M_4$ (M_i denotes the magnetization of the i-th transition metal ion sublattice) is directed along the c-axis and there is a small admixture of the vector of weak ferromagnetism $F=M_1+M_2+M_3+M_4$ and the vector of weak antiferromagnetism $A=M_1-M_2-M_3+M_4$, which point along the b- and a- crystal axes, respectively. The presence of the constituents F_b and A_a is permitted by crystal symmetry arguments, and their magnitudes are determined mainly by the antisymmetric exchange interaction of Dzialoshinski-Moryia (D-M) between the Fe^{3+} (or Cr^{3+}) ions, which is about two orders of magnitude lower than the isotropic exchange interaction [11]. The D-M interaction is very sensitive to the crystal symmetry and results in the ferromagnetic or antiferromagnetic spin canting.

As exemplified in Fig. 5, we found that the G-type magnetic ordering scheme is preserved for the Fe-rich compositions. Fig. 6 gives a schematic representation of the refined magnetic structures.

In the refinements, Cr atoms (Cr^{3+} spins S = 3/2) were allowed to occupy at random the 4b positions together with Fe (Fe^{3+} spins S = 5/2), and the complementary occupancy factors were refined, constrained to the full occupancy.

Weak ferromagnetic moment due to the D-M interaction can be easily observed and is well studied [12]. In contrast, the evaluation of A_a is commonly difficult, because of the relatively rather small scattered intensity associated with this magnetic component and spurious effects due to double Bragg reflections when working with

single crystals. Consequently, polarization analysis was needed to overcome the difficulties [13] or to perform careful time of flight neutron scattering experiments [14]. In our $YFeO_3$ sample, the diffraction peak (021) associated with the weak component A_a was visible. For the patterns in Fig. 2, this and other magnetic components disappear with increasing Cr content, most probably in accordance with the decreasing T_N.

Fig. 7 presents selected plots of the inverse susceptibility and Fig. 8 compares the experimental and calculated Curie constants from the corresponding Curie-Weiss plots, by considering the ideal stoichiometries of the compounds and the commonly used effective magnetic moments of the ions: μ_{eff} (Cr^{3+}) = 3.8 μ_B, μ_{eff} (Fe^{3+}) = 5.9 μ_B [15].

Fig. 9 demonstrates, for the example of x=0.33, the complex behaviour of the magnetization with temperature. Small amounts of Cr in $YFeO_3$ or Fe in $YCrO_3$ were found to lead to a considerable decrease in the magnitude of the component F [5,6]. Moreover, in the intermediate concentration interval a partial or full reorientation of the vector F takes place from the c-axis (at high temperature) to the a-axis (at low temperature) [16].
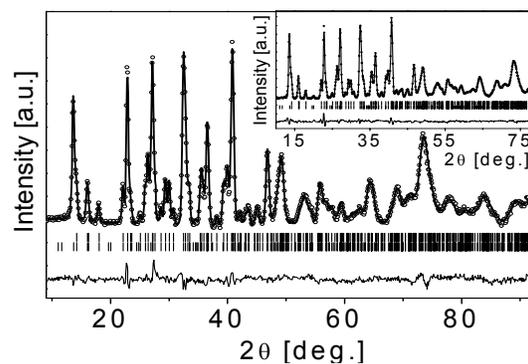

Fig. 5. Room temperature Rietveld plots of $YFe_{0.875}Cr_{0.125}O_3$ and $YFeO_3$ (inset)

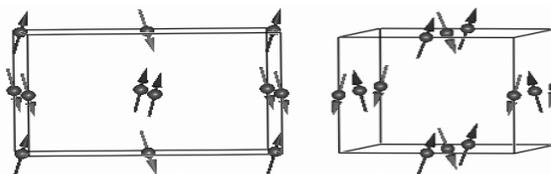*Fig. 6. Schematic view of the magnetic structure at room temperature of $YCr_{1-x}Fe_xO_3$ ($0.33<x<1$): (left) along the a-axis, (right) along the b-axis.*

The considerations [5,6,16] of the anomalous (for solid solutions) magnetic behaviour came to the

conclusion that the matrix-impurity model fails. Spin glass formation mechanisms could be involved, but our data present additional arguments to those in [7] for discarding such a model, as well.
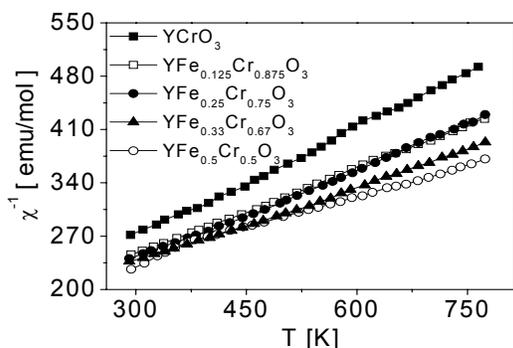

Fig. 7. Dependence of the inverse magnetic susceptibility on temperature for *T>300 K for YCr$_{1-x}$Fe$_x$O$_3$ (0≤x≤0.5).*
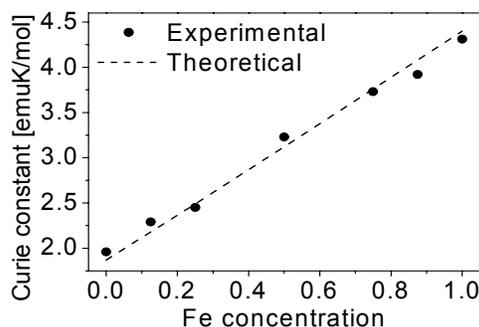

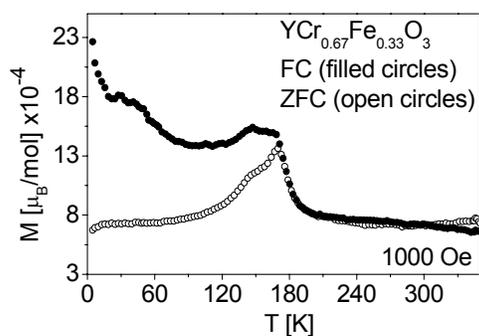*Fig. 8. Curie constant versus Fe concentration x.*

Fig. 9. x=0.33: magnetization vs temperature

5. Conclusions

The structural results for YCr$_{1-x}$Fe$_x$O$_3$ and the specific thermomagnetic behaviour of the system give a strong indication that replacement of Cr with Fe entails a substantially modified antisymmetric exchange and frustrated magnetic interactions.

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