Journal of Solid State Chemistry 221 (2015) 173–177

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

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

High-pressure transformation in the cobalt spinel ferrites

J. Blasco [a,*], G. Subías [a], J. García [a], C. Popescu [b], V. Cuartero [c]

[a] Instituto de Ciencia de Materiales de Aragón and Departamento de Física de la Materia Condensada, Consejo Superior de Investigaciones Científicas y Universidad de Zaragoza, 50009 Zaragoza, Spain
[b] CELLS-ALBA Synchrotron Light Facility, Ctra. BP1413 km 3.3, 08290 Cerdanyola del Vallès, Barcelona, Spain
[c] European Synchrotron Radiation Facility, F-38043 Grenoble Cedex 9, France

ARTICLE INFO

Article history:
Received 27 June 2014
Received in revised form
24 September 2014
Accepted 25 September 2014
Available online 2 October 2014

Keywords:
Ferrite spinels
Pressure induced transformation
Postspinel phase
Irreversible transformation
Bulk modulus

ABSTRACT

We report high pressure angle-dispersive x-ray diffraction measurements on $Co_xFe_{3-x}O_4$ ($x=1, 1.5, 1.75$) spinels at room temperature up to 34 GPa. The three samples show a similar structural phase transformation from the cubic spinel structure to an analogous post-spinel phase at around 20 GPa. Spinel and post-spinel phases coexist in a wide pressure range ($\sim$20–25 GPa) and the transformation is irreversible. The equation of state of the three cubic spinel ferrites was determined and our results agree with the data obtained in related oxide spinels showing the role of the pressure-transmitting medium for the accurate determination of the equation of state.

Measurements releasing pressure revealed that the post-spinel phase is stable down to 4 GPa when it decomposes yielding a new phase with poor crystallinity. Later compression does not recover either the spinel or the post-spinel phases. This phase transformation induced by pressure explains the irreversible lost of the ferrimagnetic behavior reported in these spinels.

1. Introduction

Mixed transition-metal oxides with cubic spinel structure (AB_2O_4; A tetrahedral and B octahedral sites) have been widely studied in the past because of its wide spread over the Earth and its use in different technological applications due to their magnetic and electric properties that can be modulated by changing the cationic composition [1]. The spinel structure can be viewed as a cubic close-packing of oxygen atoms with transition metals occupying ½ and ¼ of the octahedral and tetrahedral sites, respectively. The presence of occupied tetrahedral sites inhibits further compaction of the oxygen sublattice and lattice compression under external pressure lead to structural transitions [2–4] which strongly affects their electrical and magnetic properties [5–7]. Pioneering studies on the high pressure structural properties of cubic spinels were focused in understanding the behavior of Earth constituents in the crust and mantle [8] revealing that upon compression the spinels can adopt orthorhombic structures denoted as postspinels. The structure and properties of postspinels are still under debate. The reason is the great similarity of the possible high-pressure phases that can be isostructural to $CaMn_2O_4$, $CaFe_2O_4$ or $CaTi_2O_4$ [4]. The three phases have orthorhombic cells with similar lattice parameters and the transformation from spinel to one of these phases imply that cations change their coordination from tetrahedral and octahedral to octahedral and dodecahedral, respectively. Consequently, a more compact structure is formed and the phase transition occurs together with a small volume collapse. An example of the ambiguities that appear in the literature is the case of magnetite. High-pressure XRD patterns of Fe_3O_4 have been analyzed using the $CaMn_2O_4$-type [9] and the $CaTi_2O_4$-type [10,11] structures.

Regarding the magnetic properties, one of the most studied compounds are spinel ferrites. An interesting fact observed in these spinel ferrites is that pressure induces the disappearance of magnetism [12,13]. Some authors point out a structural phase transition into a non-magnetic phase stable at high pressure whereas other models argue about the magnetic collapse due to the 3d band widening induced by the pressure [12]. The latter effect decreases the density of states at the Fermi level below the stability limit for ferromagnetism given by the Stoner criterion [14]. Recently we have studied the stability of ferrimagnetism in the $Co_xFe_{3-x}O_4$ ($x=1$, 1.5, and 2) family showing pressure-induced transitions above 20 GPa [13]. Our results clearly discard any role of the magnetic collapse in $CoFe_2O_4$ and show that a structural phase transition is intimately correlated with the suppression of the ferrimagnetic order into either paramagnetic or antiferromagnetic high-pressure state. The other spinel ferrites also showed correlated pressure-induced magnetic and structural phase transitions. The high pressure non-magnetic phase of Co_2FeO_4 was found to be isostructural to the $CaMn_2O_4$-type structure but the ascription of the high-pressure phases for the other two studied

---

[*] Corresponding author. Fax: +34 976 761229.
E-mail address: jbc@posta.unizar.es (J. Blasco).

http://dx.doi.org/10.1016/j.jssc.2014.09.028
0022-4596/© 2014 Elsevier Inc. All rights reserved.

ferrites was ambiguous due to the occurrence of texture in the XRD patterns. In this paper we report a new structural study performed on a new set of samples prepared by a sol–gel method, which allows the preparation of more homogeneous samples than standard ceramic procedures. Our aim is to verify if all of these cobalt–iron spinels develop the same type of pressured-induced transitions or there exists some difference depending on their chemical composition.

2. Experimental section

Polycrystalline samples of $CoFe_2O_4$, $Co_{1.5}Fe_{1.5}O_4$, and $Co_{1.75}Fe_{1.25}O_4$ were synthesized by a sol-gel method using the citrate route. Stoichiometric amounts of Fe and Co were dissolved in a 0.1 M solution of nitric acid. Then, citric acid and ethylene–glycol were added in a ratio of 4 g:2 ml per gram of the resulting oxide. The solution was heated until the gel formation followed by desiccation. The resulting powder was heated overnight at 650 °C. The powders were ground and pressed into pellets. The sintering process was adapted to the chemical composition of the sample. $CoFe_2O_4$ was then sintered at 1100 °C for 48 h in air and cooled down to room temperature. $Co_{1.5}Fe_{1.5}O_4$ and $Co_{1.75}Fe_{1.25}O_4$ were sintered at 1100 °C in the same conditions, but they were slowly cooled (1 °C/min) down to 925 °C and quenched into air to prevent decomposition into two spinel phases [15]. The samples were characterized by x-ray powder diffraction (XRD) using a Rigaku D-system and Cu K_α radiation. The chemical composition of the samples was tested by using the wavelength dispersive x-ray fluorescence spectrometry technique (advant'XP+ model manufactured by ARL). The Fe:Co ratio agreed with the nominal one for all samples. Magnetic measurements were carried out between 5 and 300 K by using a commercial Quantum Design (SQUID). These properties agreed with samples with the right oxygen stoichiometry.

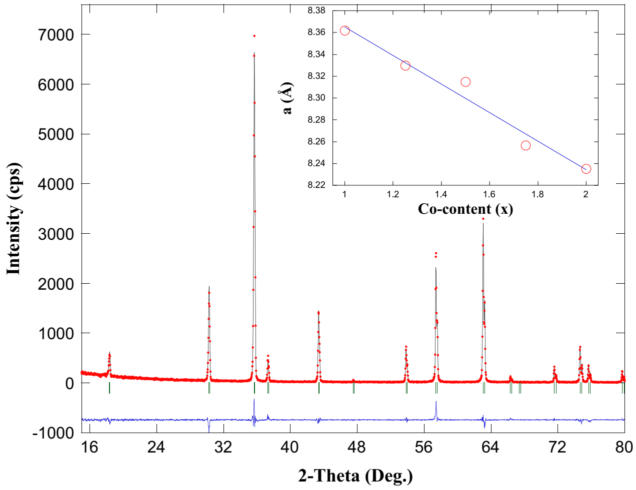

Fig. 1. Rietveld refinement ($\lambda = 1.5418$ Å) of $Co_{1.5}Fe_{1.5}O_4$ at ambient conditions (space group $Fd\bar{3}m$). Points and line stands for experimental and calculated patterns, respectively. The difference is plotted at the bottom together to the allowed reflections. Inset: Evolution of the cubic lattice parameter *vs.* co-content in the $Co_xFe_{3-x}O_4$ series ($1 \le x \le 2$).

Synchrotron XRD experiments under pressure using a membrane diamond-anvil cell (DAC) were carried out at the beam line MSPD in the ALBA synchrotron [16]. The measurements were performed at room temperature in angle dispersive mode with an incident monochromatic wavelength of 0.4246 Å. Samples were loaded in 130 μm diameter holes of 40 μm thick stainless steel gaskets in DAC with diamond culet sizes of 300 μm. Two ruby grains were loaded with the sample for pressure determination [17]. A mixture of methanol and ethanol (4:1) was used as the pressure-transmitting medium. Diffraction images were recorded on a fast scanning CCD camera (Rayonix SX 165). The image data were integrated using the FIT2D software package [18], and the resulting diffraction patterns were analyzed with the Fullprof program [19].

3. Results and discussion

Powder XRD were measured on $Co_xFe_{3-x}O_4$ samples ($x = 1$, 1.25, 1.5, 1.75 and 2) synthesized by the abovementioned sol-gel method at room temperature. All samples were successfully

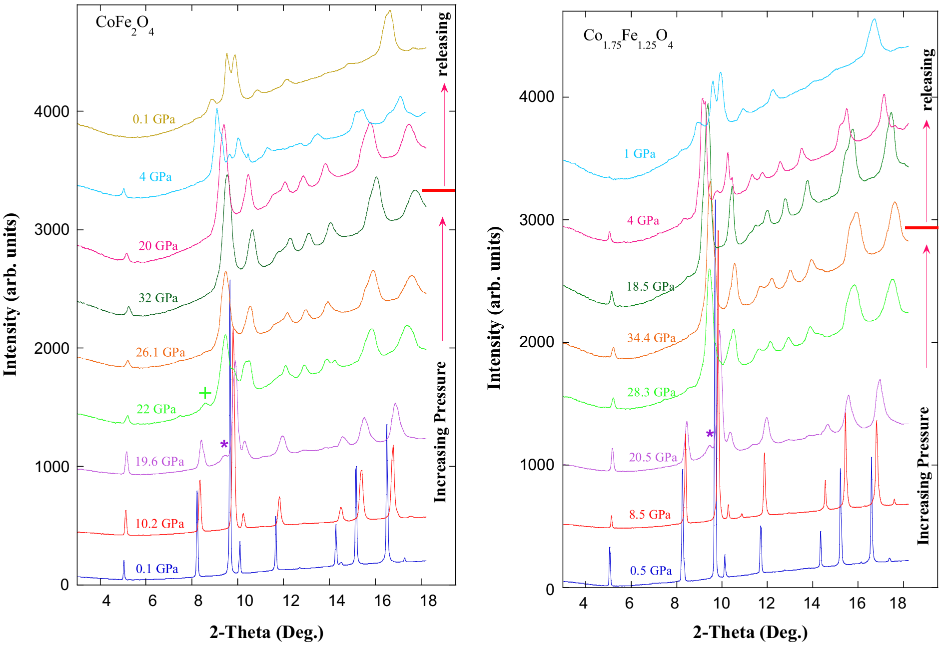

Fig. 2. Powder x-ray diffraction patterns of $CoFe_2O_4$ (left) and $Co_{1.75}Fe_{1.25}O_4$ (right) at selected pressures. The asterisk marks the appearance of contribution from postspinel phase while cross indicate the vanishing spinel phase. The pressure was increased and released as indicated by arrows on the right of the picture.