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Structural, ^{57}Fe Mössbauer and XPS studies of mechanosynthesized nanocrystalline $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Fe}_{1-x}\text{Cr}_x\text{O}_3$ particles

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Structural, ^{57}Fe Mössbauer and XPS studies of mechanosynthesized nanocrystalline $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Fe}_{1-x}\text{Cr}_x\text{O}_3$ particles

K. S. Al-Rashdi¹, H. M. Widatallah^{1,*} hishammw@squ.edu.om, M. E. Elzain¹, A. M. Gismelseed¹, A. D. Al-Rawas¹, M. T. Z. Myint¹, F. Al Mawali¹, S. H. Al-Harhi¹

¹*Department of Physics, College of Science, Sultan Qaboos University, P. o. Box 36, Al-Khoudh, Muscat 123, Oman*

E. A. Moore², E.M. Crabb²

²*Department of Life, Health and Chemical Sciences, The Open University, Walton Hall, Milton Keynes, MK7 6AA, UK*

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Graphical Abstract

Highlights

- Mechanosynthesis lower the formation temperature of $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Fe}_{1-x}\text{Cr}_x\text{O}_3$ nanoparticles by $\sim (470^\circ\text{C} - 700^\circ\text{C})$ relative to conventional processing routes.
- The lattice parameters of the nanoparticles decrease and the distortion of their orthorhombic structure reduces with increasing x .
- About $\sim 5\%$ of $\text{Eu}^{3+}/\text{Nd}^{3+}$ and $\text{Fe}^{3+}/\text{Cr}^{3+}$ cations exchange their normal A- and B-perovskite-related sites.
- Partial superparamagnetism is revealed, which enhances with increasing x .
- The $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Fe}_{1-x}\text{Cr}_x\text{O}_3$ nanoparticles exhibit a complex surface structure.

Abstract

We report on the structure and surface composition of $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Fe}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.0, 0.3, 0.5, 0.7, 0.9$ and 1.0) nanoparticles (~ 30 nm) mechanosynthesized at temperatures that are $\sim 470\text{--}700^\circ\text{C}$ lower than those at which the pure and doped pristine materials conventionally form. XRD Rietveld and FT-IR analyses show that with increasing x the lattice parameters decrease and the bond lengths and angles vary in a way that

reduces crystalline distortion. Whilst the majority of the $\text{Eu}^{3+}/\text{Nd}^{3+}$ and $\text{Fe}^{3+}/\text{Cr}^{3+}$ cations occupy the normal perovskite-related A- and B-sites, respectively, $\sim 5\%$ of them exchange sites. ^{57}Fe Mössbauer spectroscopy confirms the presence of these antisites and reveals a superparamagnetic behaviour at 298 K that enhances with increasing x . XPS measurement reveals a complex surface composition of the nanoparticles with traces of Eu_2O_3 , Nd_2O_3 , Cr_2O_3 and Fe_2O_3 as well as partial O^{2-} -deficiency.

Keywords: Orthoferrites; Mechano-synthesis; XRD; Mössbauer Spectroscopy; XPS.

Introduction

The physical and chemical properties of the perovskite-related europium ferrite EuFeO_3 and europium chromite EuCrO_3 are attractive from an applied viewpoint [1-4]. For instance the multiferroicity, low temperature canted antiferromagnetism, high dielectric constants, low dielectric losses and the high temperature stability render them potential in applications that include magnetic storage devices, spin switches, multifunctional smart devices, magneto-electric coupling devices, gas sensing devices and solid oxide fuel cells among others [1-11]. Both solids crystallize in a distorted orthorhombic crystalline structure (SG: $Pbnm$; #62) where the rare earth (RE) Eu^{3+} cation and the transition metal (TM) cations, respectively, occupy the cuboctahedral (A) and the corner-sharing octahedral (B) sites [1-5]. The Néel temperatures (T_N) of these G-type antiferromagnets are ~ 662 K (EuFeO_3) and ~ 181 K (EuCrO_3) [6].

It has been demonstrated that the magnetic and electrical properties of bulk EuFeO_3 and EuCrO_3 may be tangibly tuned when they are RE/TM cation-doped and/or have their average particle size reduced to the nanometer scale [1,3,7,8]. The partial substitution of the A-site Eu^{3+} in EuFeO_3 with RE ions was addressed by few workers. For instance, doping with Sm^{3+} was found to increase the EuFeO_3 conductivity [10]. Taheri *et al* have shown that doping EuCrO_3 with Ce^{3+} to form $\text{Eu}_{1-x}\text{Ce}_x\text{CrO}_3$ nanoparticles has significantly increased T_N and resulted in novel magnetic and electric properties including magnetic exchange bias effect, magnetization reversal, and relaxor-type dielectric properties [7,8]. In an earlier study, Liu *et al* reported a Mössbauer study on the effect of Gd^{3+} -doping on the hyperfine properties of bulk EuFeO_3 [12]. The influence on the structural and magnetic properties of EuFeO_3 when the Fe^{3+} ions at the B-site are substituted with a TM ion such as Co^{3+} , Sc^{3+} , Ca^{2+} and Mn^{3+} has also been reported [11,13-16]. Among the various TM cations, however, Cr^{3+} and Fe^{3+} appear to be the most attractive cationic substituents in EuFeO_3 and EuCrO_3 , respectively. This is partially related to the fact that the magnetic super-exchange interaction between both cations could be monitored as a function of cationic

concentration and the particle size [1,4,9]. Of special interest to us in this work is a previous study on the structural and magnetic properties of mechano-synthesized $\text{EuCr}_x\text{Fe}_{1-x}\text{O}_3$ ($x = 0.0-1.0$) nanocrystalline particles in which we reported an unusual $\text{Eu}^{3+}/\text{Cr}^{3+}\text{-Fe}^{3+}$ cationic A-B site exchange (antisite defects), unit cell expansion, enhanced structural distortion and a reduction in T_N with increasing Cr^{3+} content [1,4,6]. Whilst antisite disorder in perovskite-related solids has been reported to be externally-induced, such as when the solids are radiation-damaged [17], it is interesting to note how the effect was induced by the use of the mechano-synthesis route in EuCrO_3 and $\text{EuCr}_x\text{Fe}_{1-x}\text{O}_3$ [1,4,6]. Intriguingly a magnetocaloric effect augmented by magneto-electric coupling was reported recently for the isostructural $\text{DyFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$ compound [18]. Such an effect is, to the best of our knowledge, not hitherto reported for $\text{EuFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$ or any other $\text{EuCr}_x\text{Fe}_{1-x}\text{O}_3$ ($x \neq 0.5$) compound. This hints on the role that could be played by the effective magnetic moment of some RE-substituents for Eu^{3+} ions in the $\text{EuCr}_x\text{Fe}_{1-x}\text{O}_3$ solid solution. Despite the huge interest in EuFeO_3 , EuCrO_3 and their cation-doped derivatives, to our knowledge there are no published studies where either EuFeO_3 or EuCrO_3 in the form of bulk or nanoparticles, has been co-substituted with a TM cation and RE one simultaneously.

Conventionally, pure and cation-doped bulk and microcrystalline EuFeO_3 and EuCrO_3 are prepared with the solid-state reaction (ceramic) route wherein the reactants, either oxides and/or carbonates, are pre-heated during two or more prolonged heating sessions (12-24 h) at elevated temperatures ($\sim 1000-1380$ °C) [1-4]. The materials have also been prepared using the self-propagating high-temperature synthesis routes where temperatures in the range of ~ 1400 to ~ 2200 °C were used [5,6]. Alternatively, the sol-gel preparation method, which involves double sintering a dried gel powder at 800 °C and 1000 °C (6 h) has also been used [10]. In addition, a combustion reaction technique, where a heating treatment at 950 °C under an atmosphere of mixed argon and hydrogen has been reported [8]. These methods, apart from being both resource consuming, could lead to typical adverse effects associated with bulk ferrites prepared under prolonged exposure to elevated temperatures. For example, the conductivity of the ferrite may get enhanced due to the possible reduction of Fe^{3+} to Fe^{2+} which could limit the usability of the material in microwave applications where high resistivity and minimum dielectric loss are required [19]. Over the past decades, ample experimental evidence has revealed oxide nanoparticles to exhibit physical properties that are different from those of their corresponding bulk [20,21]. In this respect we have, for some time, been investigating the structure, magnetic and electrical properties of cation-doped ferrite

nanoparticles synthesized using non-conventional low-temperature processing routes [1,4,6,19]. One such route that is simple and low-cost is mechanosynthesis where the reactants are mechanically milled to form nanoparticles with large surface area that are tightly pressed together [1,4,6,22,23]. The large interfaces between the particles facilitate the induction of the sought reaction with or without subsequent calcination. Similar to other routes, mechanosynthesis has its drawbacks that include, for instance, contamination due to possible reaction with the milling media [22]. This could be minimized by using milling media that are hardened enough to resist wearing during mechanical activation. It could, also, be reduced if the solid precursors used in the conventional ceramic preparation routes are used as the starting milling materials [23]. The presence of amorphous phases that escape detection with normal diffraction techniques is sometimes an inevitable drawback of mechanosynthesis. Often these amorphous materials stick to the surfaces of produced particles and are associated with extremely small amounts of un-reacted precursors or intermediate phases. This often leads to complex surface structures of the produced nanomaterials and reflects both the bottom-up nature of the technique and the extreme difficulty in using precursor amounts that result in an ideal stoichiometric product [1,6].

While core-probing techniques, such as X-ray diffraction and transmission Mössbauer spectroscopy, could reveal the mechanosynthesized nanoparticles to be structurally single-phased, the bottom-up nature of mechanosynthesis could lead to reminiscences of un-reacted materials or intermediate phases on the surfaces of the nanoparticles. These, while normally are smaller than the detection limit of the core-probing methods, could be investigated with surface-sensitive techniques such as X-ray photoelectron spectroscopy. It is worth noting here that mechanosynthesized nanocrystalline particles of NdFeO_3 are reported to form at room temperature, possess modified crystal structure and exhibit larger magnetization saturation relative to other RE orthoferrites [24]. This suggests that mechnosynthesis could lead to the production of Nd^{3+} -doped or co-doped versions of EuFeO_3 nanoparticles with modified structural and magnetic properties at low temperatures.

In this paper, we report on the low temperature mechano-synthesis of nanocrystalline particles of Nd^{3+} and Cr^{3+} co-substituted EuFeO_3 of the composition $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ ($x = 0.0-1.0$) and their core and surface structural analysis with X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), ^{57}Fe Mössbauer spectroscopy, and X-ray photoelectron spectroscopy (XPS). We first study the structural phase evolution during the formation of the

particles. This will be followed by a detailed structural investigation of the crystal structure of the cores of the nanoparticles. Finally, the structure and composition of the surfaces of the nanoparticles will be probed by analyzing their XPS data.

2.1. Experimental

Powder samples of $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ ($x = 0.0, 0.3, 0.5, 0.7, 0.9$ and 1.0) were prepared using the mechanochemical synthesis route, as we detailed in [1], using mixtures of highly pure Nd_2O_3 , Eu_2O_3 , Cr_2O_3 , and $\alpha\text{-Fe}_2\text{O}_3$ reagents ($> 99\%$; Sigma Aldrich) in the molar ratios of $0.17: 0.33: x/2: (1-x)/2$. The prepared mixed powders were subjected to mechanical milling for different times using a Fritsch D-55743 P6 milling machine with tungsten carbide vial (250 mL) and balls (10 mm in diameter). The ball-to-powder mass ratio was 22:1. The milling was performed for pre-set time intervals with a speed of 300 rpm. A Carbolite (HTF 1800) furnace was used to sinter the pre-milled mixtures at different temperatures for periods of 6 h. The phase evolution as the reaction proceeded was monitored with an X'Pert PRO PANalytical X-ray diffractometer equipped with a scintillation counter and an exit beam graphite monochromator. $\text{Cu-}k\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) was used in 2θ - range of 20° to 80° in angular steps of 0.014° and a counting time of 0.02 s per step. Rietveld refinement structural analysis of the XRD patterns (e.g. ionic site occupancies of fractional coordinates, lattice parameters, phase abundance,...,etc.) was performed using the MAUD analysis code [25]. In this context, we note that the Rietveld method, as implemented in the MAUD software, can help in estimating the crystallite size and strain. This is because the XRD peaks are assumed to be tunable Voigt, pseudo-Voigt or the Pearson VII functions whose Gaussian and Lorentzian components could be, respectively, used to compute the crystallite size [26] and strain [27] when the whole diffraction pattern is simultaneously fitted. High resolution transmission electron microscopy (HRTEM) was performed using a JEM 2100F system operating at 200 kV. A Perkin-Elmer spectrometer was used to collect FT-IR spectra. ^{57}Fe Mössbauer spectra were recorded at 298 K and 78 K using a conventional constant acceleration and the isomer shift values are quoted relative to $\alpha\text{-Fe}$ foil at 298 K. XPS measurements were performed using an Omicron Nanotechnology XPS system with $\text{Al } K\alpha$ radiation ($h\nu = 1486.6 \text{ eV}$). All scans were done at a base pressure of 1.2×10^{-9} mbar. As charging effects are unavoidable in XPS measurements of non-conducting samples, charge compensation was performed by electron

flooding of the samples' surfaces using a built-in neutralizer. The binding energies were calibrated according to the C 1s reference peak at the binding energy of 284.6 eV.

3. Results & Discussion

3.1. Formation

Figure 1(a) shows the XRD patterns recorded from the 0.17: 0.33: 0.5 molar mixture of Nd_2O_3 , Eu_2O_3 and $\alpha\text{-Fe}_2\text{O}_3$, intended to form $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{FeO}_3$ (i.e. $x = 0.0$), milled for 1, 10 and 20 h. After just 1 h of milling, the peaks indexable to both Nd_2O_3 and Eu_2O_3 almost disappear implying a milling-induced transformation of both oxides into an amorphous state, possibly in the form of thin films on the surface of the size-reduced $\alpha\text{-Fe}_2\text{O}_3$ whose reflection peaks substantially become broader and weaker in intensity. Further milling of the mixture for 10 h induced a reaction resulting in nearly a complete formation of a nanocrystalline perovskite-related $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{FeO}_3$ phase as is evident from the dominant broad reflection peaks. However, a small amount of unreacted $\alpha\text{-Fe}_2\text{O}_3$ was present, which remained even after 20 h of milling. To complete the reaction leading to the single-phased $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{FeO}_3$, the 20 h pre-milled reactant mixture was calcined in air at 400 °C and 500 °C. The XRD patterns of the calcined mixtures are shown in Figure 1 (b). Calcination at 500 °C is required to form the sought single-phased $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{FeO}_3$. This temperature is significantly lower (~ 470 °C – 700 °C) than those previously reported for the formation of doped rare-earth orthoferrites [9,28,29]. Turning to the material at the other end of the $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ series, namely $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{CrO}_3$ (i.e. $x = 1.0$), Figure 2 (a) and (b) show the XRD patterns recorded from the appropriate molar mixture of Nd_2O_3 , Eu_2O_3 and Cr_2O_3 . To produce the single-phased $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{CrO}_3$ the reactant mixture was pre-milled for 40 h and then calcined at 800 °C (6 h). To synthesize the remaining samples in the $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ series ($x = 0.3, 0.5, 0.7, \text{ and } 0.9$), the milling of the reactants was halted when it was realized that further milling results in no further reaction. The required reaction was then completed by subjecting the finally-milled mixture to calcination at different temperatures until a single-phased final product was attained. In Figure 3, we present the XRD patterns of the obtained single-phased $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ ($x = 0.0, 0.3, 0.5, 0.7, 0.9$ and 1.0).

In general the formation of $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ nanoparticles, required longer milling times for the reactants as x increased, rising from 20 h ($x \leq 0.5$) to 30 h ($x = 0.7$) to 40 h ($x = 0.9$ and 1.0). The calcination temperature of the pre-milled reactant mixture increased from 500 °C ($x \leq 0.9$) to 800 °C ($x = 1.0$). The inset of Figure 3 shows how the progressive substitution of the

larger Fe^{3+} ion by the smaller Cr^{3+} one [35] in the structure of $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ consistently shifts the (112) x-ray reflection peak towards a larger Bragg angles. The TEM images (Figure 4) show all the samples to be composed of nearly spherical and irregular-shaped nanoparticles that tend to aggregate. All samples with ($x < 1.0$) show generally a broad size distribution with an average particle size of (30 ± 3) nm for the samples with ($x \leq 0.5$) and (33 ± 6) nm for the sample with ($x = 0.9$). The particle size distribution of the sample with no Fe^{3+} content, ($x = 1.0$), is narrower than the rest with an average particle size of (26 ± 3) nm.

Figure 5 shows the FT-IR spectra recorded for all $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ samples to have two broad cation (M) - anion (O) vibrational bands that are characteristics of perovskite-related materials in the $800\text{-}400\text{ cm}^{-1}$ wavenumber range. These bands arise from the overlapping of the Eu/Nd-O stretching and Fe/Cr-O stretching and deformation of the FeO_6 vibrational modes [30-34]. In the spectrum of the sample with $x = 0.0$ ($\text{Nd}_{0.33}\text{Eu}_{0.67}\text{FeO}_3$) the first band at $\square 564\text{ cm}^{-1}$ is similar to but slightly higher than those ascribed to Fe-O in both EuFeO_3 (560 cm^{-1}) and NdFeO_3 (550 cm^{-1}) [30,33-35,]. Both bands in the FT-IR spectra of the samples with $x = 0.3\text{-}0.9$ shift gradually with increasing Cr^{3+} concentrations (x) towards higher wavenumbers up to $x = 0.9$. The positive band shift ceases to exist for the sample with $x = 1.0$ ($\text{Nd}_{0.33}\text{Eu}_{0.67}\text{CrO}_3$) that only features Cr-O, O-Cr-O and Eu/Nd-O bands. The reported wavenumber ranges for these bands in pure EuCrO_3 are in the ranges of $\square 540\text{-}600\text{ cm}^{-1}$, $420\text{-}457\text{ cm}^{-1}$ and $473\text{-}584\text{ cm}^{-1}$ respectively [31,34,35]. The lower mass of Cr^{3+} ion relative to Fe^{3+} one may contribute to the increase in frequency going from $x = 0.0$ to $x = 1.0$. The effect of random substitution may be allowance of bands not seen in the $x = 0.0$ and 1.0 samples due to lowering of the site symmetry of the MO_6 octahedra as a result of differing neighbouring atoms. These vibrations may contain contributions from symmetric stretches which lie at higher wavenumbers than the allowed asymmetric stretches in the non-substituted materials.

3.2. XRD Rietveld structural analysis

It is evident from Figure 3 that the intensity of certain reflection peaks in the XRD profiles of $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ materials, such as those of the (112) planes, systematically change and their positions shift with increasing Cr^{3+} concentration (x). A careful Rietveld analysis was performed for the XRD patterns of all samples starting from the crystallographic data of orthorhombic EuFeO_3 (space group $Pnma$ (# 62)) where the Cr^{3+} ions are introduced as substituents for the Fe^{3+} cation. The results of the best refinements are presented in Table 1. Figure

6 shows only the refined XRD patterns for the samples with $x = 0.0$ and $x = 1.0$ as the refined structural features of the remaining samples are intermediate between these (see supplementary information).

Generally, the Nd^{3+} ions substitute for Eu^{3+} at the (4c) cuboctahedral A-sites whereas the Cr^{3+} ions replace Fe^{3+} at the (4a) octahedral B-sites. The XRD patterns were found amenable to best fits with structural models with antisite defects where the $\sim 5\%$ of the $\text{Eu}^{3+}/\text{Nd}^{3+}$ partly exchange their A-sites with the B-site $\text{Fe}^{3+}/\text{Cr}^{3+}$ ions. Assuming similar $\text{Eu}^{3+}/\text{Nd}^{3+}$ and $\text{Fe}^{3+}/\text{Cr}^{3+}$ atom form factors and taking into account the very small number of the antisites, the $\text{Eu}^{3+}\text{-Cr}^{3+}$ antisites given in Table 1 should be taken as equivalent to those involving any of $\text{Nd}^{3+}\text{-Fe}^{3+}$, $\text{Nd}^{3+}\text{-Cr}^{3+}$ and $\text{Eu}^{3+}\text{-Fe}^{3+}$ cationic pairs. This cationic site exchange is similar to that we previously reported for $\text{EuFe}_x\text{Cr}_{1-x}\text{O}_3$ nanocrystalline particles using an identical mechano-synthesis regime [1,4,6] and could be a consequence of the initial milling process that led to the intercalation of the $\text{Eu}^{3+}/\text{Nd}^{3+}$ ions in the octahedral voids of the corundum-related $\alpha\text{-Fe}_2\text{O}_3$ and Cr_2O_3 structures. The estimated average crystallite size slightly increases with increasing (x) and is comparable, within experimental errors, to the TEM-estimated particle average size (Figure 4).

The lattice constant of all samples satisfy the relation $a < c/\sqrt{2} < b$, as is shown in Figure 7 indicating that these materials do not exhibit Jahn-Teller effect [36]. The lattice parameters for the sample with $x = 0.0$ ($\text{Nd}_{0.33}\text{Eu}_{0.67}\text{FeO}_3$) are slightly larger than those reported for EuFeO_3 [4], reflecting the partial substitution of the Eu^{3+} ion (1.066 Å) with the larger Nd^{3+} ions (1.27 Å) [37]. With increasing Cr^{3+} content (x), the lattice parameters decrease monotonically in such a way that the rate of decrease in the lattice constant c is more pronounced than a and b . These results bear good agreement with those reported for $\text{EuFe}_x\text{Cr}_{1-x}\text{O}_3$ prepared using a similar route to that used in the present study [4] and imply that the Fe^{3+} ions (0.645 Å) are substituted with the smaller Cr^{3+} ones (0.615 Å) [37].

The lattice strain (Table 1) generally increases with increasing Cr^{3+} content (x) which may be related to the apparent shrinkage of the lattice parameters of the samples shown in Figure 7 and Table 1 as well as their bond strengthening deduced from the FTIR measurements as discussed above. Additionally for the sample with $x = 1.0$, which shows the highest strain value, the apparent reduction in the average particle size relative to the rest of the samples (Figure 4), implies a larger surface area-to-volume ratio which could enhance the crystalline lattice strain due to a complex interplay between bond contractions and expansions.

It is seen in Table 1 that with increasing Cr^{3+} concentration in the $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ materials, the x - and y - fractional coordinates of the A-site cations and those of the O^{2-} anions slightly vary in response to the mismatch of the ionic radii between the A-site RE cations and the B-site Fe^{3+} cations and the Cr^{3+} substituents. This leads to the bond lengths and angles given. Within experimental error, the A-B cationic bond lengths remain almost constant and those of the metal-oxygen ligands (A–O1, B–O1, and A–O2) generally decrease with increasing x before increasing for the Fe^{3+} -free sample ($x = 1.0$). In contrast, the lengths of the (B–O2) bonds monotonically increase as x increases and decreases for the sample with $x = 1.0$. With increasing Cr^{3+} concentrations, the tilting of octahedra is generally reduced as the bond angles B–O1–B and B–O2–B increase. This, in turn, reflects a shift towards a structure with higher symmetry. Figure 8 shows the degree of structural distortion for each of the end $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ samples, i.e. $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{FeO}_3$ with $x = 0.0$ and $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{CrO}_3$ with $x = 1.0$. This is illustrated by distances between the central A-site $\text{Eu}^{3+}/\text{Nd}^{3+}$ cation and its four nearest O^{2-} anionic neighbours. The distances and angles show that orientation of the surrounding FeO_6 octahedra ($x = 0.0$) to be more asymmetric relative to that of the CrO_6 octahedra ($x = 1.0$). We recall that the body diagonals connecting adjacent octahedra in the ideal perovskite structure are collinear [38].

A special note here goes for the very weak peak at $2\theta \sim 36^\circ$ in the XRD profile of the pre-milled mixture for the sample with $x = 1.0$ calcined at 800°C (Figure 2). This very weak peak, while indexable to the perovskite-related $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{CrO}_3$ particles as indicated by the bar diagram of Figure 2, also coincides with the most intense reflection peak of Cr_2O_3 . This suggests the possibility of having un-reacted Cr_2O_3 on the surface of the nanoparticles as hinted before. Additionally, for the other samples in the series, it is possible to find surface traces of un-reacted $\alpha\text{-Fe}_2\text{O}_3$, whose most intense XRD reflection peak is also at $2\theta \sim 36^\circ$. This will be elucidated further using the XPS surface analysis.

3.3. Mössbauer spectral analysis

Figure 9 and Figure 10, respectively, show the ^{57}Fe Mössbauer spectra of $\text{Eu}_{0.67}\text{Nd}_{0.33}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ nanocrystalline particles recorded at 298 K and 78 K, with the exception of the sample with $x = 1.0$. The corresponding fitted hyperfine parameters are shown in Table 2. The Mössbauer spectra recorded for the sample with $x = 0.0$ at 298 K show a well-defined magnetic sextet superimposed on a central paramagnetic broad component. This spectrum was best fitted

with one magnetic six-line pattern and three doublets. These doublets, which amount to ~ 39% of the total spectral area, reduce to one doublet with an intensity of ~ 3% in the 78 K spectrum. This is indicative that 36 % of the nanoparticles are superparamagnetic with blocking temperature (T_B) in the range between 78 K and 298 K. The very weak doublet at 78 K could be associated either with distorted $\text{Fe}^{3+}/\text{Eu}^{3+}$ configurations in some particles leading to Néel temperatures < 78 K or a superparamagnetic behaviour due to very fine particles with $T_B < 78$ K [4,21]. Combining this observation with the XRD Rietveld refinement where weak cationic site exchange was concluded, this paramagnetic doublet is likely to be due to a distorted $\text{Fe}^{3+}/\text{Cr}^{3+}$ and $\text{Eu}^{3+}/\text{Nd}^{3+}$ configurations in some nanoparticles. It is pertinent to mention that “superparamagnetism” is generally associated with nanoparticles of ferromagnetic and ferrimagnetic systems rather than antiferromagnetic ones [30]. The fitting of the magnetic spectral component, at 298 K and 78 K, with one sextet suggests a unique B-site environment around the Fe nuclei in the majority of the particles. It also suggests that the $\text{Eu}^{3+}/\text{Fe}^{3+}$ cationic antisite exchange, deduced from the XRD data, is generally random as a localized presence of the Fe^{3+} ions at the A-site would require at least an additional spectral component with different Mossbauer parameters. The isomer shifts (δ) of all spectral components at both temperatures are characteristic of Fe^{3+} cations at high spin-state [39]. The values of the effective hyperfine field (H_{eff}) obtained at both temperatures are slightly lower than those reported (50.2 T - 54.0 T) for EuFeO_3 [4]. This could be explained in terms of the small particle sizes and the inevitable surface effects that lead to weakening in the Fe^{3+} - Fe^{3+} magnetic exchange interaction. It could reflect the presence of Nd^{3+} together with Eu^{3+} cations in the crystal structure, although this has to be better investigated and confirmed.

Considering the Mössbauer spectra of the $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ samples with $x \neq 1.0$ (Figure 9), the 298 K Mössbauer spectrum of the sample with $x = 0.3$ shows a broad and weak magnetic component superimposed on a central paramagnetic one whose area amounts to ~ 52% of the whole spectrum. The magnetic component weakens, both in the value of H_{eff} and its intensity, as x increases collapsing completely for the samples with $x \geq 0.5$. The 298 K spectra of the samples with $x = 0.3$ was best fitted with three doubles and two sextets with the hyperfine parameters listed in Table 2. Sextet 1 with larger H_{eff} and smaller δ is assigned to Fe^{3+} ions with poor Cr^{3+} and Eu^{3+} environments (i.e. as in un-doped EuFeO_3) whereas sextet 2 with smaller H_{eff} and larger δ represents environments of the Fe^{3+} ions that are rich in Cr^{3+} and Eu^{3+} . The reduction, here, in H_{eff} reflects a weakening in the Fe-Cr exchange interaction whereas the increase of δ is

implicative of a change in the chemical environment surrounding the Fe^{3+} ions following the incorporation of the Cr^{3+} dopant ions instead of the expelled Fe^{3+} ions. The 298 K Mössbauer spectra of the samples with $x = 0.5-0.9$ were fitted, each, with two paramagnetic doublets. The quadrupole splitting values for these doublets generally decrease with increasing x and are indicative of reduced lattice distortion with increasing Cr^{3+} content and a more symmetric crystal structure, agreeing with the XRD analysis discussed above.

The 78 K Mössbauer spectra of the $\text{Eu}_{0.67}\text{Nd}_{0.33}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ nanoparticles with $x \neq 1.0$, shown in Figure 10, indicate magnetic ordering at this temperature. Well-resolved six-line magnetic patterns were attained for the samples with $x = 0.3, 0.5$, and 0.7 , and each of which was fitted with two sextets (Table 2). These spectra were fitted using a similar scheme to that used for the 298 K counterparts and the fitting parameters are given in Table 2. The sextet with the higher magnetic field (sextet 1) can be attributed to nuclei of Fe^{3+} ions in B-sites having a majority Fe^{3+} nearest cationic neighbors. The sextets with lower fields are associated with B-site Fe^{3+} and possibly A-site Fe^{3+} , as implied by the XRD analysis, that are surrounded with $\text{Eu}^{3+}/\text{Nd}^{3+}$ and/or Cr^{3+} nearest neighbours. It is to be noted that the spectral area of the doublet in the 298 K spectrum of the sample with $x = 0.3$ ($\sim 52\%$) has reduced in the 78 K spectrum to only $\sim 8\%$. This indicates that $\sim 44\%$ of the nanoparticles in the sample are superparamagnetic with $78 \text{ K} < T_B \leq 298 \text{ K}$. Using the same reasoning $\sim 13\%$ of the nanoparticles in that samples with $x = 0.5$ and $x = 0.7$ are superparamagnetic with $78 \text{ K} < T_B \leq 298 \text{ K}$. Evidently the small area of the doublets in the spectra of the $\text{Eu}_{0.67}\text{Nd}_{0.33}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ nanoparticles with ($x = 0.3, 0.5$ and 0.7) are a consequence of particle size suggesting values of $T_B < 78 \text{ K}$ as explained above. The sample with $x = 0.9$ shows a very poorly resolved magnetic spectrum which reflects the very small number of ^{57}Fe nuclei and the associated limited magnetic exchange interactions.

3.4. XPS analysis

Figure 11 shows the Eu 3d and Nd 3d core-level XPS spectra recorded from representative nanocrystalline $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ particles, namely those with $x = 0.0, 0.5$ and 1.0 . Resolved doublets related to the spin orbit coupling of $3d_{5/2}$ and $3d_{3/2}$ are evident. For the sample with $x = 0.0$ ($\text{Nd}_{0.33}\text{Eu}_{0.67}\text{FeO}_3$), the Eu $3d_{5/2}$ and $3d_{3/2}$ binding energies at $\sim 1131.9 \text{ eV}$ and $\sim 1161.7 \text{ eV}$ with a spin-orbit splitting of 29.8 eV and the associated satellite peak at $\sim 1140.8 \text{ eV}$ are characteristic of Eu^{3+} compounds [6,40-43]. To identify the origin of the Eu^{3+} species, the $3d_{5/2}$ ($3d_{3/2}$) envelopes were deconvoluted into two components. The dominant component at binding energies of 1132.1

eV (1161.9) eV is related to Eu^{3+} in an un-reacted Eu_2O_3 at the surface of the $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ nanoparticles [41-43]. The small difference between the binding energies of the samples presented here and those reported for Eu^{3+} in pure Eu_2O_3 (1133.5 eV (1162.0) eV) could be associated with the presence of Nd^{3+} dopant ions shifting the energies to smaller values. The other smaller Eu^{3+} spectral component with $3d_{5/2}$ ($3d_{3/2}$) binding energies of ~ 1129.0 eV (1159.3) eV does not match any reported compound, hence we associate it to Eu^{3+} in EuFeO_3 . No traces of Eu^{2+} ions, whose binding energies are expected to be in the vicinities of ~ 1124 and ~ 1154 eV, are observed in the XPS spectrum [6]. The Eu $3d_{5/2}$ and $3d_{3/2}$ XPS spectral doublets for the samples with $0.0 < x < 1.0$ shift towards higher binding energies with increasing Cr^{3+} content (x) reflecting the change in the environment around Eu ions as is exemplified by the spectrum of the sample with $x = 0.5$ (Figure 10). For the sample with $x = 1.0$ ($\text{Nd}_{0.33}\text{Eu}_{0.67}\text{CrO}_3$), the $3d_{5/2}$ binding energies of the two components at 1133.8 eV and 1135.8 eV could be assigned to Eu^{3+} in Eu_2O_3 and/or EuCrO_3 compounds respectively [6,40,41,44,45]. Hence, as it is shown in Table 3, the Eu 3d spectrum implies a complex surface structure for the $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ where traces of Eu_2O_3 , EuFeO_3 and EuCrO_3 are presenting.

The Nd $3d_{5/2}$ and $3d_{3/2}$ core-level XPS spectra (Figure 11), which exhibits broad doublets, follow a similar trend to those of Eu $3d_{5/2}$ ($3d_{3/2}$) as x increases. The Nd $3d_{5/2}$ envelop for the material at $x = 0.0$ ($\text{Nd}_{0.33}\text{Eu}_{0.67}\text{FeO}_3$) is fitted with two components at binding energies of 971.3 eV and 978.5 eV that are attributed to Nd^{3+} in Nd_2O_3 compounds [46], whereas those for the sample with $x = 1.0$ ($\text{Nd}_{0.33}\text{Eu}_{0.67}\text{CrO}_3$), the binding energies at 978.3 eV and 984.2 eV are attributed to Nd^{3+} in Nd_2O_3 and $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{CrO}_3$ compounds [46,47] with no traces of Nd^{2+} ions at the surface of the nanoparticles. Thus the Nd 3d spectrum implies the presence of some traces of un-reacted Nd_2O_3 species.

Figure 12 shows examples of Fe 2p and Cr 2p core-level XPS spectra of selected $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ nanoparticles. For the sample with $x = 0.0$ ($\text{Nd}_{0.33}\text{Eu}_{0.67}\text{FeO}_3$), it was readily noticed that the Fe $2p_{3/2}$ and $2p_{1/2}$ spectral peaks are not typical of Fe^{3+} compounds. Accordingly the spectrum was fitted with one component having binding energies at 708.5 eV and 721.9 eV. These values are in good agreement with those previously reported for Fe_3O_4 which has both Fe^{2+} and Fe^{3+} ions in the ratio of 1: 2 [48]. It goes without saying that at the surface of the nanoparticles, the bonding of both ions and O^{2-} need not be that of the ideal Fe_3O_4 . Such a reduction of Fe^{3+} to Fe^{2+} at the surface has indeed been reported for other rare earth orthoferrites prepared by

mechanical milling such as PrFeO_3 [49] or by the conventional ceramic technique such as ErFeO_3 [50] and Ir-doped YbFeO_3 [51]. Li *et al* have attributed the existence of Fe^{2+} ions at the surfaces of the orthoferrite particles to the presence of oxygen vacancy as inevitable point defects in these perovskite-related materials [50]. These defects are likely to exist in materials like the present ones where the ingredients were mechanically-milled and subjected subsequently to calcination. To charge-balance the oxygen vacancy (+2e), a reduction of Fe^{3+} to Fe^{2+} is likely.

For the samples with $x \neq 0$ it is seen in Figure 12 that the peaks of the Fe $2p_{3/2}$ and $2p_{1/2}$ spectrum shift towards higher binding energies with increasing x . This is shown in Figure 11 for the sample with $x = 0.7$ where the peaks are deconvoluted into two components at binding energies of 709.9 eV and 711.9 eV that are related to Fe_3O_4 and Fe_2O_3 compounds respectively [44,52]. The ratios of the two components reflect a decrease in Fe^{2+} surface population and an increase in that of Fe^{3+} with increasing x . For the sample with $x = 0.9$ no Fe^{2+} traces are detected in the Fe 2p core-level XPS spectra of the $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ particles and the binding energies match with those of Fe^{3+} as in Fe_2O_3 . Thus, the Fe 2p XPS data suggest the presence of unreacted traces Fe_2O_3 on the surface of the $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ nanoparticles. It also suggests the presence of the oxygen-deficient perovskite-related $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Fe}_{1-x}\text{Cr}_x\text{O}_{3-\delta}$.

The binding energies associated with Cr $2p_{3/2}$ ($2p_{1/2}$) spectral doublets for the samples with $x > 0.0$ are typical of Cr^{3+} compounds and shift towards higher values from 575.8 eV (587.4) eV at $x = 0.1$ to 577.0 (587.3) eV at $x = 1.0$. Fitting the Cr $2p_{3/2}$ peak with two components. The first at binding energies in the ranges of 573.4 eV – 575.5 eV is attributed to Cr^{3+} in Cr_2O_3 [6,49]. The second, at binding energies in the range 578.3 eV – 579.6 eV, is associated with Cr^{3+} in $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ in [6]. As mentioned previously, the slight difference in the binding energies from those previously reported for $\text{EuCr}_x\text{Fe}_{1-x}\text{O}_3$ is attributed to the presence of Nd^{3+} ions.

The existence of the complex surface composition of the $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ nanoparticles was confirmed by the O 1s XPS spectra as shown for compounds in Figure 13. The O1s peak for the sample with $x = 0.0$ ($\text{Nd}_{0.33}\text{Eu}_{0.67}\text{FeO}_3$) is deconvoluted into the three components 1, 2 and 3. Components 1 and 2, at binding energies of ~ 529 eV and 530.5 eV are attributed to Fe_2O_3 and the Fe^{2+} -containing species, respectively. Component 3, at the binding energy of 532.4 eV, is assigned to Eu_2O_3 and Nd_2O_3 as well as the perovskite-related $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Fe}_1\text{O}_3$. As more Cr^{3+} was introduced in the perovskite-related structure, the O1s peak shifts toward higher binding

energies and is fitted with three components that are assigned to Eu_2O_3 , Nd_2O_3 , the Fe^{2+} -containing species, Cr_2O_3 and $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ in varying ratios as depicted in Figure 13.

So, XPS studies for the $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ nanoparticles have revealed a complex surface structure dominated by the presence of cations ascribed to the initial reactants' mixture (Eu_2O_3 , Nd_2O_3 , Fe_2O_3 , Cr_2O_3) that we assume to have not reacted during milling and subsequent sintering processes.

4. Conclusions

Nanocrystalline particles of $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Fe}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.0, 0.3, 0.5, 0.7, 0.9$ and 1.0) with average particle size of ($\square 30$ nm) were found to form using the mechanochemical synthesis route at temperatures that are $\sim 470^\circ\text{C} - 700^\circ\text{C}$ lower than those at which their bulk counterparts form using conventional high temperature routes. With increasing Cr^{3+} concentration (x), the lattice parameters of the $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Fe}_{1-x}\text{Cr}_x\text{O}_3$ nanoparticles decreases whereas the bond lengths and angles vary slightly to reduce the distortion of the orthorhombic structure. The majority of the $\text{Eu}^{3+}/\text{Nd}^{3+}$ and $\text{Fe}^{3+}/\text{Cr}^{3+}$ cations, respectively, occupy the A- and B-sites in the perovskite-related structure in a random fashion. Both XRD and ^{57}Fe Mössbauer spectroscopy, however, suggest that $\sim 5\%$ of these cations to exchange these usual sites. The $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Fe}_{1-x}\text{Cr}_x\text{O}_3$ nanoparticles exhibit a superparamagnetic behaviour at 298 K that becomes more evident with increasing x . A complex surface structure of the $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Fe}_{1-x}\text{Cr}_x\text{O}_3$ nanoparticles was detected with the XPS technique where traces of un-reacted Eu_2O_3 , Nd_2O_3 , Cr_2O_3 and Fe_2O_3 exist, which are to be expected owing to the nature of the mechanochemical synthesis route. An Fe^{2+} -containing surface species on the surface of the samples with $x \neq 1.0$ was associated with an oxygen-deficiency on the surface of the nanoparticles.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Figure Captions:

Figure 1: The XRD patterns recorded for the 0.67: 0.33: 1- x : x molar mixture of Eu_2O_3 , Nd_2O_3 , $\alpha\text{-Fe}_2\text{O}_3$ and Cr_2O_3 with ($x = 0.0$): (a) milled for different times and (b) the finally pre-milled mixture heated at the temperatures indicated. The bars above the XRD profiles refer to the positions of major reflection peaks of the phase indicated. The symbol (*) indicates peaks indexable to unreacted of $\alpha\text{-Fe}_2\text{O}_3$.

Figure 2 The XRD patterns recorded for the 0.67: 0.33: 1- x : x molar mixture of Eu_2O_3 , Nd_2O_3 , $\alpha\text{-Fe}_2\text{O}_3$ and Cr_2O_3 with ($x = 1.0$): (*left*) milled for different times and (*right*) the finally pre-milled mixture heated at the temperatures indicated. The bars above the XRD profiles refer to the positions of major reflection peaks of the phase indicated. The symbol (*) indicates peaks indexable to unreacted of $\alpha\text{-Cr}_2\text{O}_3$.

Figure 3: The XRD patterns of all mechanosynthesized $\text{Eu}_{0.67}\text{Nd}_{0.33}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ (*see text*). The inset illustrates how the main (112) peak gradually shifts with increasing the (x).

Figure 4: The TEM images of selected $\text{Eu}_{0.67}\text{Nd}_{0.33}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ nanoparticles.

Figure 5: FT-IR spectra recorded for the nanocrystalline $\text{Eu}_{0.67}\text{Nd}_{0.33}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ particles.

Figure 6: Observed (points), fitted (solid line) and difference XRD patterns of the $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Fe}_{1-x}\text{Cr}_x\text{O}_3$ with $x = 0.0$ and 1.0. The bars refer to the positions of the Bragg's reflection.

Figure 7: The variation of lattice parameters of $\text{Eu}_{0.67}\text{Nd}_{0.33}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ with x .

Figure 8: The crystal structures of the $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Fe}_{1-x}\text{Cr}_x\text{O}_3$ nanoparticles with $x = 0.0$ ($\text{Nd}_{0.33}\text{Eu}_{0.67}\text{FeO}_3$) and $x = 1.0$ ($\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Cr}_x\text{O}_3$) derived from the XRD Rietveld refinement. Ionic distances are given in Angstroms. The large spheres represent $\text{Eu}^{3+}/\text{Nd}^{3+}$ ions and the red spheres represent O^{2-} ions on the corners of the Fe/CrO_6 octahedra.

Figure 9: The 298 K ^{57}Fe Mössbauer spectrum recorded for the nanocrystalline $\text{Eu}_{0.67}\text{Nd}_{0.33}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ particles at $x = 0.0$, where the solid-lines represent the best fit of the spectrum.

Figure 10: The 78 K ^{57}Fe Mössbauer spectra recorded for the nanocrystalline $\text{Eu}_{0.67}\text{Nd}_{0.33}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ particles at different x indicated in the figure, where the solid-lines represent the best fit of the spectrum.

Figure 11: The Eu-and Nd- $3d_{5/2}$ and $3d_{3/2}$ core-level XPS spectra recorded for the $\text{Eu}_{0.67}\text{Nd}_{0.33}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ nanocrystalline particles with the indicated values of x . The solid-lines represent the best fit of XPS spectra.

Figure 12: The Fe- and Cr-2p_{3/2} and 2p_{1/2} core-level XPS spectra recorded for the Eu_{0.67}Nd_{0.33}Cr_xFe_{1-x}O₃ nanocrystalline particles with the indicated values of x . The solid-lines represent the best fit of XPS spectra.

Figure 13: The O 1s core-level XPS spectra recorded from Eu_{0.67}Nd_{0.33}Cr_xFe_{1-x}O₃ nanoparticles with the indicated x values. The solid-lines represent the best fit of XPS spectra.

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Table Captions:

Table 1: Refined parameters from powder XRD for the nanocrystalline $\text{Nd}_{0.33}\text{Eu}_{0.67}\text{Fe}_{1-x}\text{Cr}_x\text{O}_3$ particles. Space group: *Pnma* (#62). The cell parameters a , b and c are given in units of Å. $\text{Eu}^{3+}:\text{Nd}^{3+}:\text{Cr}^{3+}$ and $\text{Fe}^{3+}:\text{Cr}^{3+}:\text{Nd}^{3+}$ are the occupancy ratios of the ions in the A- and B- sites, respectively. The fractional coordinates are x/a , y/b and z/c . The units for the crystallite size are (nm), for the bond lengths are (Å) and for the bond angles are ($^\circ$). Fitting parameters: R_B and R_{exp} are, respectively, the reflection intensity-based Bragg factors and expected R factor.

Table 2: Table 2: The fitted Mössbauer hyperfine parameters for the spectra of the $\text{Eu}_{0.67}\text{Nd}_{0.33}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ nanoparticles recorded at 298 K and 78 K. The 78 K values represented inside brackets and in *italic* font.

Table 1

<i>x</i>	<i>x</i> = 0.0	<i>x</i> = 0.3	<i>x</i> = 0.5	<i>x</i> = 0.7	<i>x</i> = 0.9	<i>x</i> = 1.0
<i>a</i> (Å)	5.387(1)	5.388(1)	5.383(1)	5.372(1)	5.375(1)	5.366(2)
<i>b</i> (Å)	5.578(1)	5.566(1)	5.551(1)	5.523(1)	5.510(1)	5.486(2)
$\frac{c}{\sqrt{2}}$ (Å)	5.442(1)	5.437(1)	5.429(1)	5.415(2)	5.414(1)	5.401(2)
A-site (4c)						
Eu ³⁺ :Nd ³⁺ :Cr ³⁺	0.67:0.33:0.00	0.67:0.28:0.05	0.67:0.28:0.05	0.67:0.28:0.05	0.67:0.28:0.05	0.67:0.27:0.06
<i>x/a</i>	0.9855	0.9884	0.9884	0.9884	0.9884	0.9888
<i>y/b</i>	0.0540	0.0523	0.0518	0.0504	0.0495	0.0490
<i>z/c</i>	0.2500	0.2500	0.2500	0.2500	0.2500	0.2500
B-site (4a)						
Fe ³⁺ :Cr ³⁺ :Nd ³⁺	1.00:0.00:0.00	0.70:0.25:0.05	0.50:0.45:0.05	0.30:0.65:0.05	0.10:0.85:0.05	0.00:0.94:0.06
<i>x/a</i>	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
<i>y/b</i>	0.5000	0.5000	0.5000	0.5000	0.5000	0.5000
<i>z/c</i>	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
O²⁻ (4c)						
<i>x/a</i>	0.0904	0.08884	0.1007	0.0910	0.0873	0.0776
<i>y/b</i>	0.4542	0.4524	0.4513	0.4537	0.4628	0.4635
<i>z/c</i>	0.2500	0.2500	0.2500	0.2500	0.2500	0.2500
O²⁻ (8d)						
<i>x/a</i>	0.7240	0.72078	0.7207	0.7187	0.7155	0.7192
<i>y/b</i>	0.3118	0.31143	0.3059	0.3036	0.2972	0.2976
<i>z/c</i>	0.0533	0.05528	0.0518	0.0501	0.0510	0.0530
Crystal. Size (nm)	27.8(2)	27.7(2)	28.5(2)	28.7(2)	33.0(4)	34.2(4)
Microstrain x10 ⁻⁴	1.0(1)	3.9(1)	8.5(6)	8.0(2)	13.4(7)	14.1(4)
Bond Lengths (Å) & Angles (°)						
Fe/Cr – O1	2.00	2.00	2.01	1.99	1.98	1.97
Fe/Cr – O2	1.87	1.88	1.89	1.90	1.93	1.91
Eu/Nd – O1	2.35	2.35	2.28	2.32	2.33	2.37
Eu/Nd – O2	2.77	2.76	2.75	2.73	2.74	2.77
Fe/Cr – Eu/Nd	3.26	3.27	3.27	3.26	3.26	3.26
Fe/Cr – O1 – Fe/Cr	148.1	148.5	145.0	147.9	151.1	152.5
Fe/Cr – O2 – Fe/Cr	149.1	148.0	150.0	150.6	150.7	150.5
O1 – Fe/Cr – O2	95.1	95.8	93.6	94.1	93.9	95.8
R-factors						
R _B	8.76	9.00	9.06	8.69	8.52	8.75
R _{exp}	10.04	9.86	10.23	9.70	10.02	10.18

Table 2

X	Component	δ (mm/s) ± 0.02	$2\varepsilon/\Delta$ (mm/s) ± 0.02	H_{eff} (T) ± 0.2	Γ (mm/s) ± 0.02	A (%) ± 1
0.0	Doublet 1	0.27 (0.41)	0.73 (0.80)		0.81 (0.70)	11 (3)
	Doublet 2	0.38	2.45		0.36	12
	Doublet 3	0.46	4.09		2.60	16
	Sextet 1	0.36 (0.48)	-0.01 (0.00)	49.4 (54.2)	0.59 (0.48)	61 (97)
0.3	Doublet 1	0.21 (0.14)	1.05 (0.56)		1.27 (0.30)	4 (5)
	Doublet 2	0.26 (0.45)	2.51 (2.55)		0.84 (0.20)	41 (3)
	Doublet 3	0.31	7.50		0.80	7
	Sextet 1	0.27 (0.47)	-0.12 (-0.03)	43.4 (52.8)	0.80 (0.56)	39 (72)
	Sextet 2	0.45 (0.51)	0.43 (0.00)	42.9 (49.2)	1.38 (0.84)	9 (20)
0.5	Doublet 1	0.35 (0.13)	0.63 (0.56)		0.72 (0.72)	17 (8)
	Doublet 2	0.37 (0.46)	0.34 (3.86)		0.52 (0.59)	83 (5)
	Sextet 1	(0.45)	(0.00)	(48.5)	(0.69)	(71)
	Sextet 2	(0.55)	(0.04)	(45.2)	(0.75)	(16)
0.7	Doublet 1	0.32 (0.11)	0.73 (0.75)		0.46 (0.59)	22 (7)
	Doublet 2	0.36 (0.42)	0.24 (3.23)		0.46 (0.61)	78 (6)
	Sextet 1	(0.42)	(-0.03)	(45.2)	(1.22)	(71)
	Sextet 2	(0.64)	(-0.03)	(41.8)	(1.04)	(16)
0.9	Doublet 1	0.28	0.56		0.46	50
	Doublet 2	0.36	0.17		0.34	50