Exceptional layered ordering of cobalt and iron in perovskites

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Exceptional Layered Ordering of Cobalt and Iron in Perovskites.


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ABSTRACT: An exceptional layered ordering of cobalt and iron in perovskites, in spite of the same valence, size and coordination of these two cations, has been observed using TEM and EELS. This unique 3:2 stacking of Fe and Co layers, which appears in a perovskite matrix with composition $Y_2Ba_3Fe_5Co_2O_{12+\delta}$, can be described as a regular intergrowth of the “123” ferrate with the “112” cobaltate, [$YBa_2Fe_5O_{13+\delta}$] [$YBaCo_2O_{5+\delta}$]. It is closely related to the simultaneous presence of two other types of layered orderings: The 1:1 and 1:2 ordered stacking of the Y and Ba layers and the preferential localization of anionic vacancies in the Y layers sandwiched between one Fe and one Co layer.

The ordering of two sorts of transition metal elements in the B-sites of the ABO$_3$ perovskite structure is a rare phenomenon, which requires that particular conditions, such as size or valence difference, be fulfilled. For this reason in layered perovskites or derivatives containing two different transition cations, the latter are always distributed at random, except if they are elaborated as thin films, allowing super-lattices to be built. In this respect, layered oxygen deficient ABO$_{3-\delta}$ perovskites containing cobalt or iron on the B sites and combining rare earth and barium cations on the A sites are of great interest, due to the fact that besides the Ln/Ba layered ordering, there exists a clear ordering of the oxygen and anionic vacancies, which may possibly generate Fe/Co ordering. Moreover, this large family has been studied for its attractive properties, ranging from oxygen storage in view of the realization of solid oxide fuel cell cathodes (SOFC) to magnetic and magnetoresistance properties.

The layered perovskites of the Ln-Ba-Co-O and Ln-Ba-Fe-O systems are mainly represented by two classes, the double perovskites LnBa$_2$Co$_2$O$_{5+\delta}$ and LnBaFe$_2$O$_{5+\delta}$, called “112” and the triple perovskites LnBa$_2$Fe$_3$O$_{6+\delta}$, called “123”.

These oxides are characterized by a regular ordering of the layers of rare earth (or lanthanide Ln) and barium cations, which originates from the size difference between these two sorts of cations. Importantly, these oxygen deficient perovskites show simultaneously a specific ordering of their oxygen vacancies on the anionic sites. The latter seems to be correlated to the size of the A-site cation: the anionic vacancies are displayed in the Ln layers, whereas no oxygen deficiency is observed in the BaO layers. Recently, we observed a unique nanoscale ordering in quintuple perovskites Ln$_7$Ba$_2$Fe$_5$Co$_3$O$_{15+\delta}$ with Ln=Sm, Eu, Nd, Gd. In the latter compounds, the ordering of the Ba and Ln layers according to the five-fold sequence “Ba-Ln-Ba-A-A-Ba”, where A is a mixed layer containing 50% Ba/50% Ln, suggests that the “112” BaLnCo$_2$Fe$_2$O$_{5-\delta}$ structure is the base of this new ordering (Ba-Ln-Ba), whereas the “123” Ba$_2$LnFe$_2$O$_{13+\delta}$ component is partly disordered (Ba-A-A-Ba). These results raise a first question about the possibility of complete ordering of the Ln and Ba layers in the quintuple perovskites according to the sequence “Ba-Ln-Ba-Ba-Ln-Ba” and a second question concerning the associated oxygen content and ordering of oxygen vacancies in such oxides if they exist. Bearing in mind that that the “112” structure is easily obtained for both, cobaltates and ferrates, but that the “123” phase is only synthesized for ferrates containing smaller cations (Y, Ho, Dy) we embarked in the investigation of perovskites of the system Y-Ba-Fe-Co-O.  In the present study, we show that the oxide Y$_2$Ba$_2$Fe$_3$Co$_2$O$_{13+\delta}$ ($\delta$=0.36) exhibits a unique perovskite-nanostructure involving a double layered cationic ordering of both Y/Ba and Fe/Co layers, and simultaneously layered ordering of oxygen vacancies in the quintuple perovskite matrix, corresponding to the ideal intergrowth [YBaCo$_2$O$_3$][YBaFe$_2$O$_3$], with oxygen excess (0.36 O) sandwiched between one cobalt and one Fe layer at the level of the Y layer.

Similarly to Ln$_7$Ba$_2$Fe$_5$Co$_3$O$_{15+\delta}$ phases with Ln=Nd, Sm, Eu, Gd, the presence of cobalt in the Y phase plays an important role for the stabilization of the ordered quintuple perovskite structure. However, the chemical analysis of our sample of nominal cationic composition “Y$_2$Ba$_2$Fe$_5$Co$_2$” prepared in air shows that its oxygen content is significantly smaller. In fact, we prefer to formulate it as Y$_{2.1}$Ba$_{2.9}$Fe$_{2.8}$Co$_{2.2}$, with $\delta$=0.36, for structural reasons that will be developed further. The powder X-ray diffraction pattern of this phase (Fig S1 in the supporting information) shows that similar to the Sm, Eu and Nd-homologues, the peaks can be indexed in a cubic perovskite, but that differently from the latter they are broader, suggesting a possible tetragonal symmetry involving order-disorder phenomena. Based on these observations, electron diffraction (ED) investigation of this oxide was performed, showing that two sorts of crystals with a closely related perovskite structure were coexisting. A large number of crystals exhibit a perfectly ordered tetragonal perovskite structure characterized by the presence of...
pattern; (b) ED patterns along main zone axis of disordered perfectly ordered crystals, suggests that the latter exhibit a other members, Ln quintuple layer ordering similar to that previously shown for columns are severely displaced with respect to the standard octaf axial and that the oxygen positions close to the Y columns are severely displaced with respect to the standard octahedral symmetry positions along the c-axis.

The five-fold “a_p x a_p x 5a_p” superstructure observed for the perfectly ordered crystals, suggests that the latter exhibit a quintuple layer ordering similar to that previously shown for other members, Ln_{0.5}Ba_{3}Fe_{5}O_{15.5} \text{ (49-51)}. However, differently from the latter, this oxide is not chemically twinned at a nanoscale. One indeed observes five-fold superstructure reflections only along one a_p direction with respect to the basic cubic sub-cell. This feature is corroborated by the [100] high resolution transmission electron microscopy (HRTEM) images (Fig. 1a) which show a quite regular 1:1 stacking of double and triple perovskite cells along c alternately and confirm the absence of 90° oriented twinned domains, contrary to the other Ln homologues of the series \text{[49]}. The [100] high angle annular dark field scanning TEM (HAADF-STEM) image (Fig. 1d) clearly shows that the nature and the stacking of the Ba and Y layers is also significantly different from the other Ln quintuple perovskites. One observes only two sorts of layers (very bright dots and much less bright dots corresponding to Ba and Y respectively) with the stacking sequence “Y-Ba-Ba-Y-Ba-Y” along the c-axis. Instead, the other Ln quintuple perovskites exhibit three sorts of layers Ln, Ba and mixed A (Ba_{0.5}Ln_{0.5}), with the stacking sequence “Ln-Ba-A-A-Ba-Ln”. This suggests that Y_{2}Ba_{3}Fe_{5}Co_{2}O_{13+δ} can be described as an intergrowth of a triple (Y-Ba-Ba-Y) and a double (Y-Ba-Y) perovskite.

**Figure 1.** Y_{2}Ba_{3}Fe_{5}Co_{2}O_{13+δ} : (a) [100]HAADF-STEM image of perfect ordered Y_{2}Ba_{3}Fe_{5}Co_{2}O_{13.36} structure and corresponding ED pattern; (b) ED patterns along main zone axis of disordered Y_{2}Ba_{3}Fe_{5}Co_{2}O_{13.36} structure: [001]*, [100]* and [110]*. Note the presence of streaks along the [001] direction; (c) [100] HRTEM image and corresponding FT pattern of the disordered Y2Ba3Fe3Co2013.36 structure containing numbers of stacking faults along the c-axis marked by white arrows; (d) HAADF-STEM and simultaneously acquired ABF-STEM images along the [100] zone axis of the ordered Y_{2}Ba_{3}Fe_{5}Co_{2}O_{13.50}; (e) enlargement of HAADF-STEM and ABF-STEM images and overlaid heavy atoms position (Y-red, Ba-yellow, Co-green and Fe-gray) and light atoms (O-blue) in HAADF-STEM and ABF-STEM images respectively. The corresponding structural model is given as insert. Note that oxygen vacancies are located between Y columns along a-axis and that the oxygen positions close to the Y columns are severely displaced with respect to the standard octahedral symmetry positions along the c-axis.

This perfect ordering between the Ba and Y layers is clearly confirmed by elemental electron energy loss spectroscopy (EELS) mapping (Fig.2a). One indeed observes that pure double Ba-layers (Ba2) are stacked with single Ba-layers (Ba1) along c and that single Y-layers are sandwiched between one double and one single Ba-layer. But the most remarkable feature deals with the ordering of Fe and Co in the form of layers: for the first time a perfect stacking of triple Fe layers (Fe3) with double Co layers (Co2) within a perovskite matrix (Fig.2a) is observed, in spite of the similar size of Co and Fe and of their ability to accommodate the same type of coordination. Moreover, one observes that the double Ba2 layers are sandwiched between the triple Fe3 layers, whereas the single Ba1 layers are sandwiched between the double Co2 layers. This double cationic ordering corresponds to the following stacking sequence along c: “Fe-Ba-Fe-Ba-Fe-Y-Co-Ba-Co-Y-Fe” This exceptional type of cationic ordering suggests that the oxygen stoichiometry may play a role in its stabilization, resulting from the alternate stacking of double perovskite slices.

**Figure 2.** (a) EELS elemental mapping of ordered Y_{2}Ba_{3}Fe_{5}Co_{2}O_{13.90} : overview HAADF-STEM image , Fe-L_{2-3} map , Co- L_{2-3} map , Ba-M_{45} map , O-K map. Colour overlays with Fe in red and Co in green and also overlays with Y in red and Ba in green, together with a structural model with Y in red, Fe in grey, Ba in yellow, Co in green and O in blue. (b) EELS fine structure of Y_{2}Ba_{3}Fe_{5}Co_{2}O_{13.50} obtained from the regions indicated as Fe and Co in the mapping.
YBaCoO$_5$ (Fig. 3a) and triple perovskite slices with the ideal composition YBa$_2$Fe$_3$O$_8$ (Fig. 3b). The ideal composition of such a triply ordered perovskite, Y$_2$Ba$_2$Fe$_5$CoO$_{13.50}$, close to that observed experimentally, Y$_2$Ba$_2$Fe$_5$CoO$_{13.56}$, with δ = 0.36 supports this hypothesis. In order to understand the distribution of oxygen vacancies in the structure, annular bright field STEM (ABF-STEM) imaging has been carried out. Bearing in mind that the brightest big dots on the HAADF-STEM image correspond to barium (Fig. 1d) and that the reverse contrast is obtained on the ABF-STEM image (Fig. 1e, g) one can easily see from the enlarged ABF-STEM image (Fig. 1g) that at the level of the Ba layers (largest dark dots) the anionic sites between two barium cations are fully occupied by oxygen (smallest well resolved dark dots), forming stoichiometric (001) BaO layers. In contrast, at the level of the Y layers (intermediate size dark dots on the ABF-STEM image) the anionic sites between two yttrium cations are very weakly occupied (weak and diffuse grey spots) forming YO$_{0.5}$ layers, with partially occupied anionic sites (δ = 0.36). These observations demonstrate that the Y$_2$Ba$_2$Fe$_5$CoO$_{13.50}$ structure corresponds to the perfect intergrowth [Y$_2$Ba$_2$Fe$_5$O$_{13.50}$] [YBa$_2$CoO$_5$] of the “123” ferrite and “112” cobaltate (Fig. 3c), with oxygen excess (δ) distributed at the boundary of the two blocks, sandwiched between FeO$_6$ and CoO$_5$ pyramids.

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Y$_2$Ba$_3$Fe$_7$O$_{13.36}$ is different from the other members of the series with Ln=Nd, Sm, Eu, which also exhibit all the same “a”, x a$_p$ x 5a$_p$. The second one concerns the oxygen stoichiometry/ordering. In fact, the ordered “123” YBa$_2$Fe$_8$O$_{16}$ structure is the foundation stone of this long range ordering, since it has the highest stability and can only be obtained for LnBa$_2$Fe$_8$O$_{16}$ oxides with small rare earths (Ln=Dy, Ho, Er, Y) [45-48], whereas for larger size (Ln=Nd, Sm, Eu) partial oxygen oxygen leading to a cubic or pseudo-cubic symmetry of the YBa$_2$Fe$_8$O$_{16}$ ferrite is obtained [45,52]. The absence of Co-Fe mixing within the triple iron layers at the benefit of separated double cobalt layers is in agreement with the fact that YBa$_2$Co$_3$O$_{5+x}$ is not obtained in normal synthesis conditions and that the level of Co for Fe substitution in the triple perovskite YBa$_2$Fe$_8$O$_{16}$ was shown to be smaller than 50%, even in special synthesis conditions using soft chemistry synthesis and higher oxygen pressure in one atmosphere [53]. The high stability of double perovskites YBa$_2$Co$_3$O$_{5+x}$ supports also this ability of Co to form double layers rather than to be distributed at random with Fe. These results open the road to the investigation of various superlattices in bulk perovskites and derivatives for the generation of new physical properties.

The oxide Y$_2$Ba$_3$Fe$_7$O$_{13.36}$ was synthesized by solid state reaction in air, using Y$_2$O$_3$ or Eu$_2$O$_3$, Fe$_2$O$_3$, “CoO$_{1.36}$” and BaCO$_3$ as starting materials. The compounds were first intimately mixed in required proportions, and de-carbonated at 1000°C for 24 hrs. The mixtures were then ground and pressed in the form of bars and heated at 1100°C for 48 hrs. The oxygen content in the single phase oxide was determined by both, isometric titration and thermogravimetric analysis TGA (STA 409PC, Netzsch Gmbh) (see supporting information S3).

TEM, including HRTEM and ED experiments were carried out on a JEOL ARM-200F cold FEG double aberration corrected microscope operated at 200 kV. HAADF-STEM and ABF-STEM were performed on a JEOL ARM-200F cold FEG double aberration corrected microscope operated at 200 kV and equipped with a large solid-angle CENTURIO EDX detector. EELS experiments were performed on a Titan “cubed” double aberration corrected electron microscope equipped with a high-brightness gun, electron monochromator excited to provide 250 meV energy resolution and a high resolution EELS spectrometer (Gatan Enfinium) operated at 120 kV for the EELS. For experimental setting see supporting information S2.

ASSOCIATED CONTENT
Supporting Information. Additional experimental data and XRD data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.”

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ABBREVIATIONS

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