

The Ba-Fe-O2 system revisited: the crystal structure of BaFeCl_{0.25}O_{2.4}

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The system BaFeO_{3-y}, with $0 \leq y \leq 0.5$, is well known to comprise several highly complicated perovskite related superstructures. The member $y=0$ has never been synthesized and the most oxidized known compounds are only accessible through high oxygen pressure and high temperature. When approaching the other end composition, $y=0.5$, several different compounds condense out. In the composition range BaFeO_{2.52-2.64} up to four different phases have been reported depending on the synthetic method. Much more surprising is the fact that two of these compounds are related to a basic cubic perovskite structure, with orthorhombic and monoclinic symmetries, while the other two correspond to the 6H and 10H hexagonal perovskite related structures. Furthermore, the 10-layered hexagonal structure, 10H, presents a wide range non-stoichiometric region due to oxygen vacancies [1,2]. Finally, and probably the most exotic compound in this system, BaFeO_{2.5} [3] adopts a unique crystal structure where Fe is distributed in up to three different coordination polyhedra. Besides, a compound with this composition and the brownmillerite type structure can also be found described in the literature.

All these data suggest that even though the early reports in this system are from more than 60 years ago, i.e. [4], little is known about the crystalchemistry behaviour of this system. Taken into account that these compounds are known to present interesting electrical, magnetic and catalytic properties, it would be desirable to be able to explain the apparition of all those crystal structures based on some kind of clear, and preferably simple, crystalchemistry rule.

The complexity in this system resides in the peculiar distribution of the oxygen vacancies, what it must be indeed tightly connected with the presence of Fe in at least two different oxidation states. Up to date, transmission electron microscopy has not been able to resolve these problems due to the resolution achievable. However, the newly available spherical aberration correctors, either in the probe forming system or in the objective lens, constitute a new era in transmission electron microscopy that allow us to easily tackle problems that need resolution below 1 Å. This communication is part of a broad project concerning a re-investigation of the BaFeO_{3-y} system by using sub-angstrom resolution transmission electron microscopy.

In this context, we have obtained a new compound which seems to be closely related to these superstructures by using BaCl₂·2H₂O as flux for the solid state reaction. A 1:1/2:2 molar mixture of BaCO₃, Fe₂O₃ and BaCl₂·2H₂O was well ground and heated at 1000 °C for 48 h in alumina crucible. The mixture was then slowly cooled to 800 °C at 0.1 °C/min and then the furnace was switched off, allowing gradual cooling to room temperature. One type of single crystal was extracted from the preparation. Microprobe quantitative analysis performed in several points of the crystal showed a Ba:Fe:Cl ratio of 1:1:0.25, which gives rise to the composition: BaFeCl_{0.25}O_{2.4}. Single crystal X-Ray diffraction data showed a unit cell of $a=28.869(8)$ Å, $b=28.852(14)$ Å, $c=10.001(4)$ Å, $\alpha=90.019(3)^\circ$, $\beta=90.053(4)^\circ$, $\gamma=119.93(4)^\circ$. However, tilting experiments in the TEM allowed us to confirm that such a unit cell is fictitious and it stems from the presence of quite intriguing twinning. The basic structure is hexagonal and this compound adopts a five-fold superstructure along one of the equivalent $\langle 10\bar{1}0 \rangle$, Fig 1. Perfectly balanced twinning with the superstructure running along all symmetry equivalent directions in the basic hexagonal structure render the unit cell obtained in the single crystal diffractometer. The superstructure is well ordered and free of defects, Fig. 2. The crystal structure of this new compound will be presented and discussed.

References

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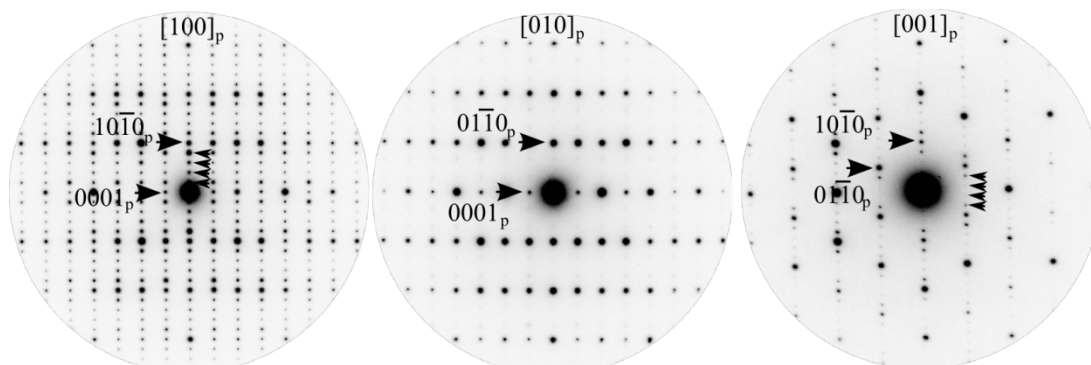


Figure 1. $[100]_p$, $[010]_p$ and $[001]_p$ zone axis electron diffraction patterns of the title compound. Indexing is done according to the basic hexagonal structure (indicated by subscript p).

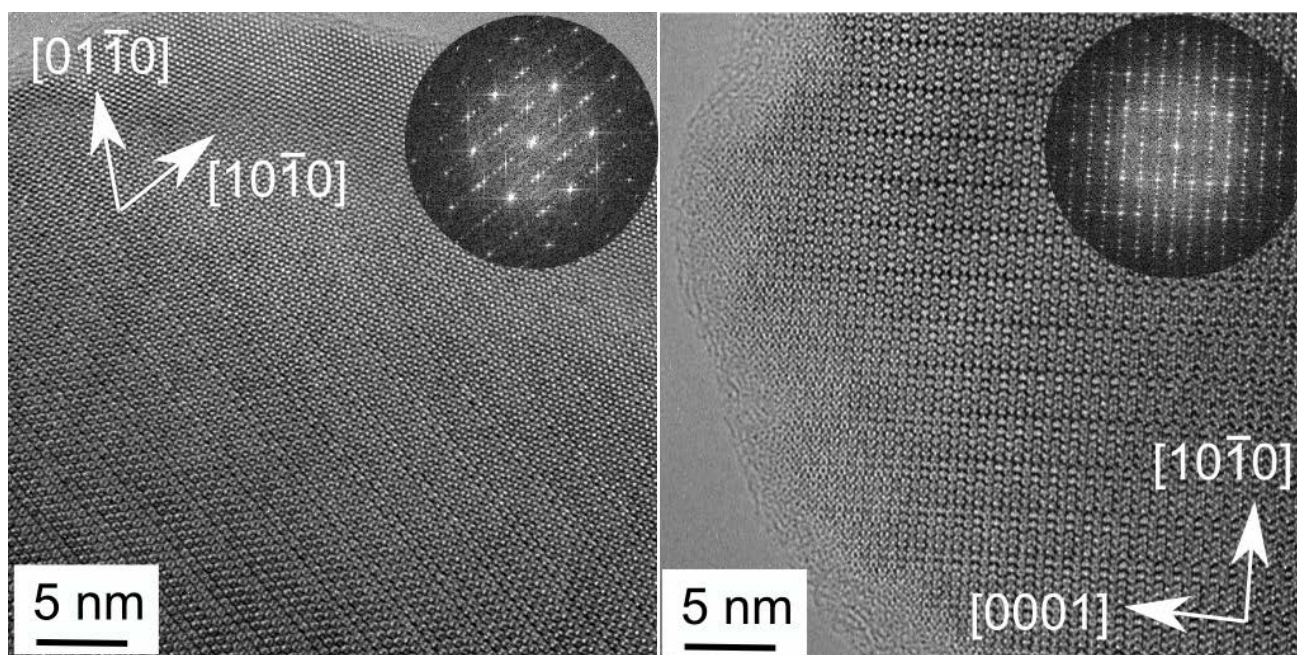


Figure 2. HREM images of the title compound down $[001]_p$ and $[100]_p$. The images show perfectly well ordered crystals of the superstructure.