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Synthesis and structural mechanisms of the 2201-type ferrites and polytypes: Fe$_2$(Sr$_{2-x}$A$_x$)FeO$_{6.5-\delta/2}$ (A = Ba, La, Tl, Pb and Bi)

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ABSTRACT

The Fe$_2$(Sr$_{2-x}$A$_x$)FeO$_{6.5-\delta/2}$ systems have been investigated, by doping the iron rich 2201-type parent structure with Ba^{2+}, La^{3+} and 5d^{10} post-transition cations. The syntheses have been carried out up to the limit of the 2201-type solid solutions, in order to test the role of the double iron layer Fe$_2$O$_{2.5-\delta/2}$. The localisation of the charge carriers in these compounds is consistent with their strong antiferro-magnetism. The investigation was then carried out in the transition part of the diagram up to the formation of stable phases. The study of structural mechanisms was carried using high resolution electron microscopy (transmission and scanning transmission), electron diffraction and energy dispersive spectroscopy. Different non-stoichiometry mechanisms are observed, depending on the electronic structure and chemical properties of the doping elements. The specific behavior of the modulated double iron layer is discussed.

1. Introduction

Transition metal oxides with perovskite-related structures have been intensively studied in recent years because of their unusual electric and magnetic properties. Among the atoms occupying the B site, iron is the source of a rich chemistry because of its aptitude to adopt different valence states and coordination numbers, able to generate complex structures. The Ae–Fe–O systems (Ae = Sr and Ca) are exceptionally rich, as evidenced by the existence of the oxygen deficient perovskites and numerous families of perovskite-related families, where iron atoms adopt the IV, V and VI coordinations. Among these interesting ferrites, Sr$_4$Fe$_6$O$_{13}$ [1] has been shown to be an oxygen deficient material, with a mixed-conducting behaviour and potential applications to high temperature electrochemical processes and the study of the related solid solution (Sr$_{4-y}$Ca$_y$)(Fe$_{6-x}$Co$_x$)$_{13\pm\delta}$ obtained by doping the two cation sites has revealed the stability of the materials and thermoelectric power [2]. However, as evidenced by recent studies [3–6], Sr$_4$Fe$_6$O$_{13-\delta}$ phases exhibit modulated structures, commensurate or incommensurate, where the modulation vector is clearly correlated to the oxygen stoichiometry. Moreover, the analysis of the structure highlighted that its average structure can be directly compared to the RP's phases Sr$_{m+1}$Fe$_m$O$_{3m+1}$ [7–9] and derivatives of the high Tc superconducting cuprates [10]. All these oxides correspond to the intergrowth of single or multiple perovskite layers with single or double or even triple distorted rock salt (RS)-type layers.

Numerous members of these RP-derivatives have been discovered in the pseudo-ternary metal oxides diagram Bi–Sr–Fe–O, demonstrating the exceptional ability of the ferrites to form layered structures [11–15]. These layered compounds Bi$_2$(Sr$_{2-x}$A$_x$)Sr$_{m-1}$Fe$_m$O$_{3m+3+w}$ are denoted as **22(*m* − 1)*m***, ***m*** indicating the number of perovskite layers. The rock salt-type block is built up from one double [BiO][BiO] layer sandwiched between two [SrO] layers, to form one triple (RS)-type block. The description of Sr$_4$Fe$_6$O$_{13-\delta}$ as the intergrowth of one perovskite layer [SrFeO$_{3-y}$] ($y \approx 0$) with three distorted rock salt-type layers [Fe$_2$SrO$_{3.5-\delta/2}$] shows that it belongs to the 2201-type members with a highly original character: the intermediate layers are double [FeO][FeO] layers [5] instead of [BiO][BiO] layers. This specificity, together with the presence of extra oxygen located in between the two [FeO] layers, leads to the developed formula Fe$_2$(Sr$_2$)FeO$_{(3-y)+(3.5-\delta/2)}$. This description of the Sr$_4$Fe$_6$O$_{13-\delta}$ compound as a 2201-type structure provided clues to head towards a large family of new ferrites, i.e. to increase the number of perovskite layers according to the general formula Fe$_2$(A$_2$)Sr$_{m-1}$Fe$_m$O$_{(3-y)m+(3.5-\delta/2)}$. At present, the members ***m*** = 2 Fe$_2$(Bi$_{0.7}$Sr$_{1.3}$)SrFe$_2$O$_{9.33}$ and ***m*** = 4 Fe$_2$(Sr$_{1.9}$Tl$_{0.1}$)Sr$_3$Fe$_4$O$_{14.65}$ have been isolated [16,17]. The latter ferrites are denoted as Fe$_{\text{Bi}}$-2212 and Fe$_{\text{Tl}}$-2234 to highlight the structural characteristics of the

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intermediate double layer of the RS block, with regard to the Bi-based compounds, denoted Bi-2212 for example [12,13]. In a more general way, any member belonging to the present ferrite family is denoted as $\mathbf{Fe}_\mathrm{A}$-$(\boldsymbol{n}-\mathbf{1})\mathbf{2}(\boldsymbol{m}-\mathbf{1})\boldsymbol{m}$, the suffix A indicating the nature of the cation associated with the alkaline earth.

The structural mechanisms of the RP-derivatives are highly complex [10]; they have been intensively investigated, especially in the systems of the Bi- and Tl-based cuprates, ferrites and manganites. The complex non-stoichiometry mechanisms which take place in these systems associated to the modulated character of the structures increase the difficulty to determine the limits of solid solutions in order to understand the properties. As a consequence, it is straightforward that a large amount of structural work, down to the nano-structural scale, would be necessary for understanding perfectly their mechanisms.

The goal of the present paper is to present the structural behaviour of the Fe-2201-type phases, $Fe_2(Sr_{2-x}A_x)FeO_{6.5-\delta/2}$ when they are doped with La^{3+}, Ba^{2+} and $5d^{10}$ post-transition cations, Tl^{3+}, Pb^{2+} and Bi^{3+}. The syntheses have been first carried out up to the limit of the different solid solutions, in order to test the role of the double iron layer $Fe_2O_{2.5-\delta/2}$. The investigation was then carried out beyond these limits, in the transition part of the diagrams, up to the formation of stable phases.

2. Experimental section

The syntheses have been carried out by increasing x up to the limit of the solid solutions and the formation of stable phases. According to our first attempts, the nominal A content $Fe_2(Sr_{2-x}A_x)FeO_{6.5-\delta/2}$ was varied from 0 to 0.5, by $x = 0.01$ steps, for A = Bi, Tl, La, Pb, Ba. The Bi-based samples have been prepared from mixtures of the starting materials Bi_2O_3, Fe_2O_3 and SrO in a glove box. The different oxide powders, in the stoichiometric ratio, were ground, pressed into bars and sealed in a silica tube. The mixtures were heated at 1100 °C for 48 h, with a heating rate of 2 °C/min and slow cooled at the same rate. The Tl-based samples were prepared, in the same way, from mixtures of the starting materials Tl_2O_3, Fe_2O_3 and SrO. The Pb and Ba based samples from PbO or BaO, Fe_2O_3 and SrO, in a glove box. The silica tubes were introduced in an alumina tube in order to avoid contamination in case they should explode. The first energy dispersive spectroscopy (EDS) analyses carried out on the thallium based samples showed that the thallium content of the crystallites was way below the nominal one. Due to its volatility, a large part of the thallium oxide was deposited on the tube walls.

The powder X-ray diffraction (PXRD) analyses were carried out at RT with a Philips diffractometer working with the Cu Kα ($\lambda = 1.5406$ Å) in the range $5° \le 2\theta \le 105°$.

The samples were studied by different transmission electron microscopy (TEM) techniques. For this work, a small piece of sample was crushed in a mortar containing alcohol, and then a droplet was deposited on a copper grid covered with holey carbon film. Electron diffraction (ED) was carried out with a JEOL 200CX electron microscope, equipped with an energy dispersive spectroscopy (EDS) analyzer. The microscopes used for high resolution TEM (HRTEM) were a JEOL 4000EX operating at 400 kV and a TOPCON 002B microscope operating at 200 kV. The Z-contrast images were obtained on a JEOL 3000F microscope equipped with a scanning transmission electron microscopy (STEM) unit and a high-angle annular dark field (HAADF) detector.

The magnetic measurements were performed by SQUID magnetometry ($T < 400$ K) and the susceptibility measurements on a Faraday balance (0.3 T). The resistivity measurements were carried out by the four probes method on a Physical Properties measurements System (PPMS).

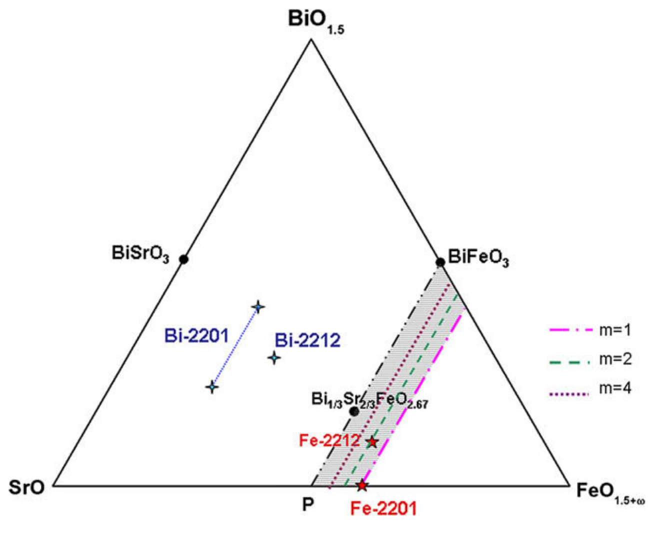

Fig. 1. Bi–Sr–Fe–O diagram showing the Bi- and Fe-based 2201 and 2212-type phases. The hatched zone represents the theoretical existence domain of the $22(m-1)m$-type ferrites.

3. Results

The structure of the double iron layer $[Fe_2O_{2.5-\delta/2}]$ is one of the key factors of the stabilisation of the present ferrites and the A^{3+} for Sr^{2+} substitution one way to increase the oxygen stoichiometry. This is a potential test of the upper limit of oxygen $[Fe_2O_{2.5\pm\delta/2}]$. La and Bi are good candidates because their substitution for Sr has been carried out successfully in numerous perovskite systems, leading to complete solid solutions, as in $La_{1-x}Sr_xMO_{3-x/2}$ (with M = Fe, Mn, Co···) [18–20] or $Bi_{1-x}Sr_xFeO_{3-x/2}$ [21,22]. Pb^{2+} and Ba^{2+}, isovalent with Sr^{2+}, were selected for the size effect. The first step was to determine the limits of the $Fe_2(Sr_{2-x}A_x)FeO_{6.5-\delta/2}$ solid solutions.

Another interesting point is the possible stabilisation of two 2201- and two 2212-type structures within one system. This point is illustrated by the Bi–Sr–Fe–O diagram given in Fig. 1, with the relative distribution of the different phases in the "ternary" system.

- The bismuth rich Bi-2212 and Bi-2201 compounds are represented by blue stars; $(Bi_{2-x}Sr_x)Sr_2FeO_{6.5-x/2}$ [11] is stabilized in the domain $0 \le x \le 0.9$ (blue dotted line) (for interpretation of the references to colour in this figure, the reader is referred to the web version of this article).
- The iron rich Fe-2212 [16] and Fe-2201 compounds are represented by red stars.

The hatched zone is the theoretical existence domain of the $\mathbf{Fe}_\mathbf{A}$-$(\boldsymbol{n}-\mathbf{1})\mathbf{2}(\boldsymbol{m}-\mathbf{1})\boldsymbol{m}$ phases, from $\boldsymbol{m} = 1$ (pink line 2201's) to $\boldsymbol{m} = \infty$ (the perovskite limit); it is common to all the A cations (taking into account the possible mixed valences of Fe (Fe^{2+}, Fe^{3+} and Fe^{4+})). The second step was to understand the non-stoichiometry mechanisms of the A–Sr–Fe–O systems beyond the limits of the solid solutions, depending on the doping cation.

3.1. *The parent structure $Fe_2(Sr_2)FeO_{6.5-\delta/2}$: brief recall*

In the first member of the family ($m = 1$) $Fe_2(Sr_2)FeO_{(3-y)+(3.5-\delta/2)}$, y has been determined to be close to 0, in the accuracy limit of our techniques [2–5], leading to an oxygen content $O_{6.5-\delta/2}$. Its subcell is