Vacancies ordering in La$^{3+}_{1-x}$Ba$^{2+}_{x}$FeO$_{3-\delta}$ perovskites

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Abstract. Using powder X-ray diffraction the La$^{3+}_{1-x}$Ba$^{2+}_{x}$FeO$_{3-\delta}$ perovskite related solid solutions were investigated. A morphotropic phase transition from orthorhombic to cubic was shown for the sample with x ~ 0.3. High temperature XRD patterns of La$_{0.2}$Ba$_{0.8}$FeO$_{3-\delta}$ obtained under air and vacuum revealed new diffraction peaks related to local ordering of the oxygen vacancies. Such ordering remained at room temperature only after cooling in vacuum.

Introduction

In recent years catalysts for environmental protection operating at high temperatures in the reactions such as toxic wastes incineration, ammonia oxidation, etc. have attracted the attention of the researchers and technologists. Compared with expensive traditional noble metal supported catalysts, perovskite-related ABO$_3$ oxides [1,2], including nano-heterogeneous solid solutions [3,4], are regarded as promising since they show high activity for some hazardous reactions. Physical and chemical properties of these materials can be varied due to their ability of formation of numerous solid solution series. Additionally, by the varying of cationic substitution in the ABO$_3$ lattice, it is possible to tune the oxygen stoichiometry via aliovalent substitution. These substitutions result in the chemical composition A$'_{1-x}$$^{3+}A''_{x}$$^{2+}$(B$_{1-y}$$^{3+}$, B$_{y}$$^{4+}$)O$_{3-\delta}$. In some cases, the charge compensation is achieved by increasing the oxygen non-stoichiometry itself. Vacancies appear in the oxygen sublattice randomly [5] or specifically ordered in the form of extended defects [6], or as superstructures of different kinds [7] depending on the nature of ion A and conditions of sample synthesis. Also, vacancy ordering may result in the formation of nanostructured states [3]. In spite of a huge number of papers devoted to the non-stoichiometry of La$^{3+}_{1-x}$Me$^{2+}_{x}$FeO$_{3-\delta}$ (Me = Ca, Sr, Ba) solid solutions [3,8], the phenomena and mechanisms of the non-stoichiometry in these systems are far from being understood. The aim of this paper is to study conditions of vacancy order-

ing in $La^{3+}_{1-x}Ba^{2+}_xFeO_{3-\delta}$ solid solutions prepared via mechanochemical synthesis [9] that combines mechanochemical activation of the parent oxides in planetary mill followed by calcination at 1100^oC for 4 h.

Experimental

The samples were investigated using a Bruker D8 X-ray diffractometer D8 (Bruker, Germany) with CuKα radiation (λ ~ 1.5418 Å). High temperature experiments were carrying out in air and in vacuum using HTK-16 (Anton Paar, Austria) XRD camera. The diffractometer was equipped with Goebel Mirror (Bruker, Germany). The parallel X-ray radiation geometry avoids errors due to an uneven sample and sample displacement during the experiment.

Results

According to XRD data the substitution of La^{3+} with Ba^{2+} cation preserves the perovskite structure, but for the charge balance it is expected that either effective charge of the transition metal ions should increase or some oxygen vacancies should appear in the structure. By phase composition, all the samples are similar and have $La^{3+}_{1-x}Ba^{2+}_xFeO_{3-\delta}$ perovskite structure. At x < 0.3 there is orthorhombic perovskite whereas for x ≥ 0.3 XRD pattern shows cubic perovskite that reflects in the morphotropic first-order phase transition (MPT) of the orthorhombic structure into a cubic one without the appearance of a two-phase region. Physical size of the perovskite particles in these specimens is about 0.5 - 2 micrometers according to TEM observation, but XRD patterns exhibit pronounced peak broadening possibly due to the micrograin structure. Williamson-Hall plots were used as a first approximation to calculate sizes of the coherent scattering domains (CSD) and microstrain values. Instrument broadening function was determined by using SRM 676 powder. For sample with x = 0.4 the CSD is about 400 Å with ε = 0.001, and for sample with x = 0.6 the CSD is about 700 Å with ε = 0.004. Indeed, at x ~ 0.3 (region of the morphotropic phase transition, RMPT) grain structures, with minimal value of microstrains (ε = 0.001), is prevailed. For Ba contents lower than 0.4, the unit cell parameter does not change significantly as seen in figure 1, but higher Ba loadings lead to rapid growth of this parameter. A strong change of the parameter seems to be associated with appearance of numerous oxygen vacancies.

In contrast with $La^{3+}_{1-x}Ca^{2+}_xFeO_{3-\delta}$ ordering of oxygen vacancies was not revealed in $La^{3+}_{1-x}Ba^{2+}_xFeO_{3-\delta}$ perovskites at room temperature [10]. However, it is possible that vacancies are ordered at high temperature or in vacuum. For the sample with expected maximum of oxygen vacancies high-temperature investigations were carried out. A sample with x ~ 0.8 was studied in situ in the high temperature XRD chamber in air and in vacuum. During in situ calcinations in air at 1000^oC an additional diffraction peak appeared at ca. $32^o(2\theta)$ (figure 2, arrowed), but after cooling the sample down to the room temperature this peak disappeared and the resulting diffraction pattern looks practically the same as that of initial specimen.

According to thermogravimetry analysis, during cooling the sample becomes partially oxidized. TEM revealed that the surface of cooled specimen particles have a highly distorted grain structure with a grain size of 10 nm that could be considered as a consequence of the oxidation process (figure 3).

In addition to the peak at 32°, a new peak at 28° (figure 4, ▼) was formed during in situ calcination of the sample at 1000°C in vacuum. We assigned this feature to the ordering of oxygen vacancies in the perovskite structure. After cooling, the peak at 28° disappeared but peak at 32° remained. According to TEM data, in the cooled sample 1D highly ordered nanostructure was observed (figure 5).

As we reported earlier for $La_{1-x}Ca^{2+}_xFeO_{3-\delta}$ [11], the appearance of a satellite peak at 32° is caused by local ordering of vacancies with formation of the planar defects and 1D nanostructures.

In situ XRD experiments show that similar ordering in the structure of $La_{0.2}Ba_{0.8}FeO_{3-\delta}$ perovskites takes place at high temperature (at 1000°C) in air or in vacuum. However, after cooling down the sample heated in air re-oxidation leads to the appearance of the distorted nanostructured state. The surface of perovskite particles appears to have varying chemical compositions, but the bulk of the particle remains highly crystalline since we observed relatively narrow peaks of the perovskite structure. In the case of in situ calcination in vacuum, a highly ordered structure remains even after cooling down. The appearance of a peak at 28° may be associated with a long-scale ordering (superstructure) whereas peak at ca. 32° is responsible for the short-range arrangement – as a system of parallel planar defects. However, these diffraction phenomena should be considered more accurately in future, with taking into account observed ordering (figure 5), by modeling of diffraction patterns.
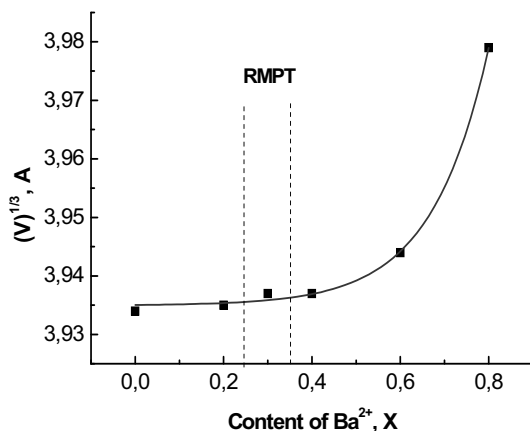

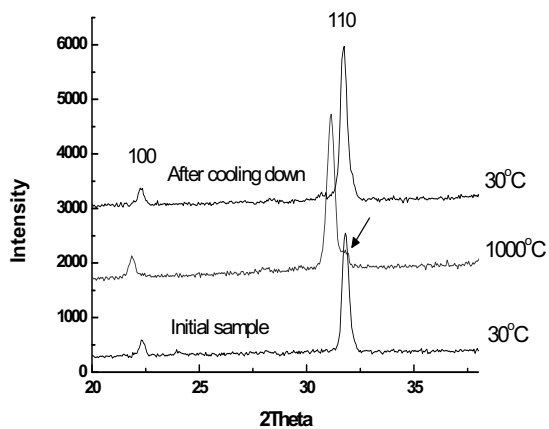*Figure 1. Parameter of cubic/pseudocubic $La_{1-x}Ba_xFeO_{3-\delta}$ unit cell versus Ba content.*

Figure 2. XRD patterns of $La_{0.2}Ba_{0.8}FeO_{3-\delta}$ obtained in situ in air.

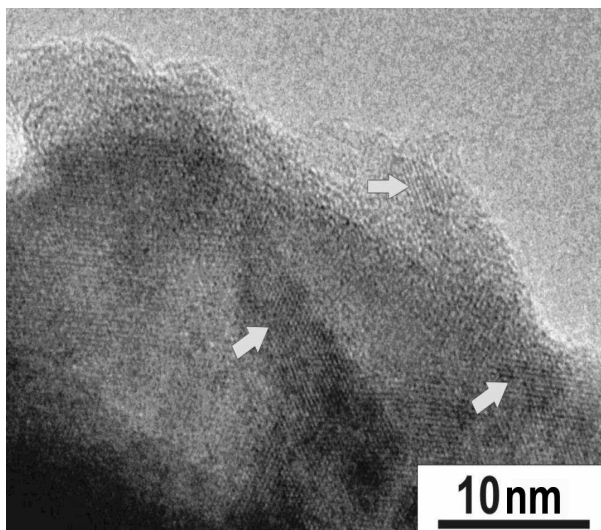*Figure 3. Microstructure of $La_{0.2}Ba_{0.8}FeO_{3-\delta}$ cooled down in air.*
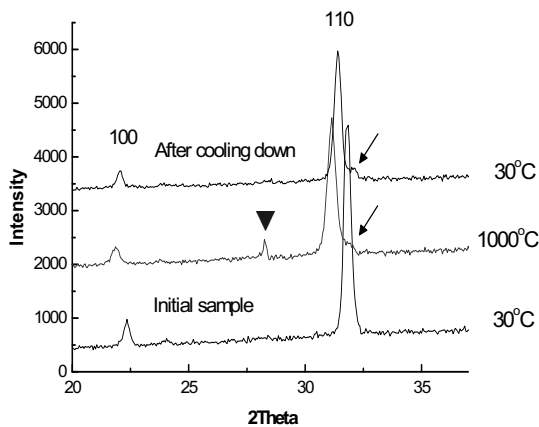
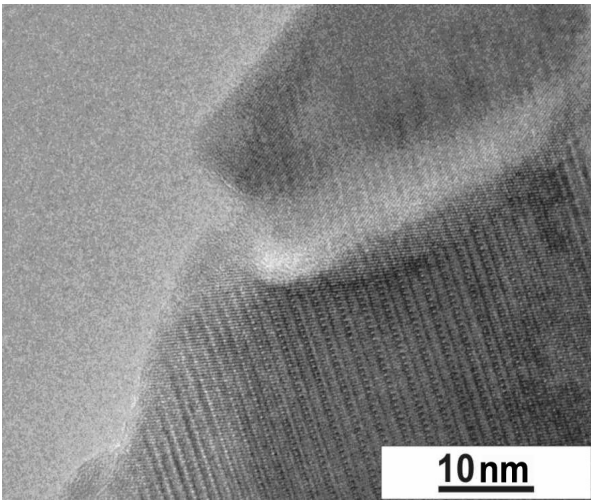Figure 4. XRD patterns of $La_{0.2}Ba_{0.8}FeO_{3-\delta}$ obtained in situ in vacuum.

Figure 5. Microstructure of $La_{0.2}Ba_{0.8}FeO_{3-\delta}$ cooled down in vacuum.

Conclusion

High-temperature XRD investigations showed that heating of $La_{0.2}Ba_{0.8}FeO_{3-\delta}$ results in some changes of the perovskite structure revealed by the appearance of new diffraction peaks. Changes in the diffraction pattern are due to the appearance and ordering of oxygen vacancies at $1000^{o}C$. In vacuum experiments a local ordering of oxygen vacancies is preserved down to room temperature, whereas a long ordering which may be associated with a peak at 28° disappears. Influence of oxygen ordering and superstructure formation on diffraction pattern is the aim of further investigation.

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