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Kinetics and thermodynamics of B-site cation order in (Sr,Ba)₂FeSbO₆ perovskite

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Abstract

Several sample series of the (Sr_{0.5}Ba_{0.5})₂FeSbO₆ double-perovskite compound are synthesized under various heat-treatment conditions starting from a sol-gel prepared precursor to investigate the kinetics and thermodynamics of the B-site cation ordering. The synthesis yields samples with different levels of Fe/Sb ordering ranging from essentially disordered up to fully ordered depending on the synthesis temperature and duration. In the temperature range 1050 – 1200 °C the degree of order is kinetically controlled following Johnson-Mehl-Avrami-Kolmogorov type kinetics, while at 1300 °C the thermodynamic equilibrium is quickly reached such that higher than 95% ordering degrees are obtained in heat-treatment periods as short as couple of hours. Also importantly, for the differently synthesized single-phase samples a linear relationship between the degree of order and the cubic sub-cell dimension is seen.

Keywords: double perovskite; crystal structure; cation ordering

1. Introduction

Perovskite oxides form an exciting group of functional materials as the basic ABO_3 perovskite composition/structure is highly flexible for chemical and structural modifications thus providing multiple ways for tailoring the important material properties. The ideal ABO_3 structure is cubic with space group $Pm-3m$ but even the archetype mineral perovskite $CaTiO_3$ actually shows orthorhombic distortion leading to space group $Pnma$ [1]. The simple ABO_3 structure itself is readily formed with a large number of different A and B cation components [2]. It is also notoriously prone to oxygen-content variations and thereby redox engineering [3]; another aspect of diversity related to the oxygen content is the possibility of the oxygen vacancies to order into different superstructures such as the famous brownmillerite structure [4,5]. Moreover, through partial cation substitutions at the A and B cation sites, a rich variety of solid solutions and ordered perovskite structures can be created [2,6,7]. Finally, the phases with unpaired electrons may show spin ordering leading to different magnetic structures [8].

In recent years the B-site ordered double perovskites of the $A_2B'B''O_6$ type have been intensely investigated [9], as they have shown a variety of exciting functional properties such as the room-temperature half-metallicity in Sr_2FeMoO_6 [10] and the mixed oxide-ion and electronic conductivity in Sr_2MgMoO_6 [11]. The most common but not the only pattern for the B-site order is the rock-salt type ordering known from e.g. the mineral elpasolite K_2NaAlF_6 [12]. In a perfectly rock-salt type ordered $A_2B'B''O_6$ structure the octahedral B-cation site is alternatively occupied with two cations, B' and B'' such that each $B'O_6$ octahedron is surrounded by six corner-sharing $B''O_6$ octahedra, and *vice versa*. The ideal face-centered cubic unit cell of $A_2B'B''O_6$ is eight ($2 \times 2 \times 2$) times larger than the primitive cubic ABO_3 single-perovskite cell, and possesses the space group $Fm-3m$. However, in practice pseudocubic perovskites with various lower symmetries are observed as the BO_6 octahedra are often tilted to compensate the cation size mismatch and distortion [13,14].

Cation ordering in $A_2B'B''O_6$ has different driving forces, the most obvious one being the charge difference between the two B cations [15,16]. As a measure for the degree of order (DoO), the Bragg-Williams long-range order parameter S is commonly used: this parameter is calculated as $S = 2g - 1$ from the occupancy factor g that is the probability of the B' (or B'') cations to reside on their primary crystallographic site. Typically, when the charge difference between the B' and B'' cations is more than two the fully-ordered phase with $S = 1$ ($g = 1$) is obtained, while for the systems where the charge difference is less than two essentially no ordering is seen, i.e. S is close to 0 ($g = 0.5$). The most interesting $B'-B''$ compositions in terms of ordering are those for which the charge difference is two; in these systems S may vary even from 0 to 1 depending on factors such as the difference between the B' and B'' ionic radii, the presence of Jahn-Teller active species and the nature of bonding (covalent versus ionic). Also important is the choice of the synthesis conditions (initial mixing and synthesis temperature, atmosphere and time). The synthesis temperature (under a given atmosphere) in particular controls the thermodynamic equilibrium value of S , such that the lower the temperature the higher the S value may be. At the same time, at too low synthesis temperatures the ordering process may be so slow that the equilibrium S value is not reached within the synthesis; in such cases the S value is rather controlled by the kinetics of the ordering process [17].

In $A_2B'B''O_6$ double perovskites the unideal ordering commonly results not only in the antisite (AS) point defects, i.e. individual B' cations occupying the B'' lattice site, or *vice versa*, but also in more extended defects, i.e. so-called antiphase boundaries (APBs) [18]. Such defects are formed at the interface of two well-ordered regions that may be crystallographically identical but in different phases in terms of the alternating stacking of the B' and B'' cations. Understanding and quantifying the presence of the different types of defects, e.g. AS and APB, and the capability to control the defect concentrations are of major importance – both scientific and technological – in the research on $A_2B'B''O_6$ double perovskites. For example, in case of the halfmetallic Sr_2FeMoO_6 the magnetic transition temperature sensitively depends on the DoO parameter S [19,20,21,22].

Here, we will use the $(\text{Sr}_{0.5}\text{Ba}_{0.5})_2\text{FeSbO}_6$ compound as a model system for a systematic evaluation and control of AS and APB defects in $\text{A}_2\text{B}'\text{B}''\text{O}_6$ double perovskites. The general interest in the $(\text{Sr},\text{Ba})_2\text{FeSbO}_6$ system stems from the fact that it is a member of a larger family of $(\text{A}',\text{A}'')_2\text{B}'\text{B}''\text{O}_6$ double perovskites ($\text{A}'/\text{A}'' = \text{Ca}, \text{Sr}, \text{Ba}, \text{La}$; $\text{B}' = \text{Mn}, \text{Fe}$; $\text{B}'' = \text{Nb}, \text{Sn}, \text{Sb}, \text{Te}$) where – as a common feature – only the B' cation is magnetic, either Mn^{II} or Fe^{III} with $3d^5$ high-spin electron configuration and a total spin angular moment of $5/2$ [23,24,25]. In our recent work we investigated the structure evolution in the $(\text{Sr},\text{Ba})_2\text{FeSbO}_6$ system upon the Sr-for-Ba isovalent substitution or so-called chemical pressure [26]. By selecting the 1:1 composition for the two A-site cations, Sr and Ba, we are able to stabilize the ideal cubic double-perovskite structure, which simplifies the structure analysis. Also, the X-ray scattering factors for Fe and Sb are reasonably different. In the diffraction patterns the sub- and supercell reflections are clearly separated allowing the straightforward determination not only the AS defect concentrations, i.e. the value of S , but also getting insight to the crystal and ordered-domain sizes. We will demonstrate that for our $(\text{Sr}_{0.5}\text{Ba}_{0.5})_2\text{FeSbO}_6$ model compound – as expected from charge difference two between Fe^{III} and Sb^{V} – excellent (thermodynamic and kinetic) control of the DoO is achieved in a wide range of S values.

2. Experimental

The $(\text{Sr},\text{Ba})_2\text{FeSbO}_6$ samples were prepared through sol-gel synthesis starting from dissolving Sb_2O_3 , SrCO_3 and BaCO_3 (in this order) in hot citric acid-water solution (5:1 acid to cation ratio). As the last step in the dissolution, metallic Fe was separately dissolved in citric acid-water solution (5:1 acid to Fe ratio), with a small amount of HNO_3 to aid the dissolution, and then added together with ethylene glycol (5:2 citric acid to ethylene glycol) in the solution containing the other metal cations for the gelation. The gel was first allowed to dry in open air on a hot plate, then in an oven in an air atmosphere at 135°C overnight and finally calcined at 650°C for 12 hours. The resultant precursor powder was briefly ground with acetone in a mortar, and after drying pressed uniaxially into pellets in a tungsten carbide die. The pellets were fired in the first sample series for 100 hours at different temperatures in the range of 750 to 1500°C , and in the second and third sample series at 1150 or 1300°C for a period ranging from 15 minutes to 100 hours. All samples were inserted in a furnace preheated to the synthesis temperature, and then quenched after the heating period to room temperature in an open Al_2O_3 crucible used for the synthesis.

From our previous systematic redox analysis works on B-site ordered double perovskites on the system [26] we know that $(\text{Sr},\text{Ba})_2\text{FeSbO}_6$ samples synthesized in air are essentially oxygen stoichiometric; hence, the samples were not analyzed for the oxygen content in the present work.

All samples were characterized with X-ray diffraction (XRD; PANalytical X'Pert PRO MPD α -1 powder diffractometer, programmable divergence slits, Johansson-monochromator, Cu $K\alpha$ -1 radiation). Rietveld refinements were carried out using the FullProf Suite software [27]. Instrumental peak broadening was taken into account by measuring and refining relevant parameters for a standard sample (LaB_6 ; NIST SRM 660b). For microstructural analysis, the strain-dependent broadening could be extracted from the Gaussian component of the profile and the size-dependent broadening from the Cauchy (Lorentz) component. To calculate the microstructural parameters, FullProf Suite utilizes size and strain equations by De Keijser et al. [28] In short, the Rietveld refinements were carried out using a dual-phase model. Both phases were set to have the same space group ($Fm\text{-}3m$) but the sub- and super-cell reflections were refined in separate phases. Parameters such as the scale and atomic positions were fixed to be the same in both phases and refined at the same time if required. Only the profile parameters were relaxed without constraints. In the initial refinements, the overall Debye-Waller thermal parameter was first refined for all the samples. These refinements gave quite consistently $B \approx 1$, and therefore we fixed the B to unity for the final refinements. This allowed us to determine the cation occupancies in a consistent manner for all the samples.

3. Results and discussion

Our sol-gel synthesis yields the mixed perovskite phase already at relatively low synthesis temperatures but initially with no ordering between the B-site cations; XRD patterns and Rietveld refinement results are systematically presented for all the samples investigated in the Supplementary data section. Here in Fig. 1 we display XRD patterns for representative samples only, heat-treated at different temperatures in air for 100 hours. From Fig. 1, the fundamental (sub-cell) diffraction peaks for the perovskite phase appear already for the sample synthesized at 650 °C, although the peaks are relatively broad and some secondary-phase peaks are seen as well. Even the sample heat-treated at 950 °C has a minor unknown impurity phase; also, no superlattice (super-cell) reflections are yet seen. For samples heat-treated at or above 1050 °C clear superlattice reflections appear, their intensity increasing with temperature as an indication of the gradually enhancing ordering.

With increasing synthesis temperature, a plateau appears around 1200–1400 °C where the DoO parameter S saturates to an essentially constant value, see the inset in Fig. 2. The value reached for S is very close to unity, and taking the estimated error bars into account we may claim that these samples are essentially fully ordered. Finally, for the sample synthesized at 1500 °C a shoulder appears to the sub-cell reflections from an unknown reason. As for the shapes of the superlattice reflection peaks, it seems that these peaks are relatively broader for the samples synthesized at the lower temperatures, indicating towards smaller ordered-domain sizes and higher strain values, and also higher concentrations of antiphase boundaries when compared to the samples synthesized at the higher temperatures.

Fig. 1. XRD patterns for samples synthesized at different temperatures for 100 hours; the inset shows details of some sub- and super-cell reflections for the same samples (in the same order).

Fig. 2. Degree-of-order parameter S for samples heat-treated at 1150 °C (white circles) or 1300 °C (black triangles) for various time periods; the inset shows the S values for samples heat-treated for 100 hours at different temperatures (black squares). Error bars are approximately of the same size as the markers.

According to thermodynamics, the DoO should decrease with increasing temperature when a certain phase-dependent temperature is achieved. At that temperature, the energy difference between the two B-cation sites vanishes and they become thermodynamically equivalent. From our data presented in the inset of Fig. 2, there is no downturn seen for the S parameter in the high temperature side. This indicates that for the present $(\text{Sr}_{0.5}\text{Ba}_{0.5})_2\text{FeSbO}_6$ compound the order-disorder temperature is higher than 1400 °C. For the sample 1500 °C supercell peaks were seen but the cation occupancies could not be reliably refined since the sample contained an unknown impurity. Unfortunately, with our furnace temperatures higher than 1500 °C could not be reached. Hence it is not clear if a temperature, where the DoO starts to decrease can be practically achieved for $(\text{Sr}_{0.5}\text{Ba}_{0.5})_2\text{FeSbO}_6$ before it decomposes. For $\text{A}_2\text{B}^{\text{III}}\text{B}^{\text{V}}\text{O}_6$ double perovskites in general, a range order-disorder temperatures starting from ca. 1000 °C upwards have been observed [15-17,29]. On the other hand, the inset of Fig. 2 shows that the S value increases with increasing synthesis temperature up to around 1200 °C. This means that for our samples synthesized below 1200 °C the thermodynamic equilibrium is not reached within the 100-hour heat-treatment period applied, and the DoO is rather controlled by the slow kinetics of the ordering process. To investigate the kinetics in more detail we synthesized two sample series, at 1150 and 1300 °C, using different heat-treatment periods up to 100 hours. The S values for these sample series are plotted in Fig. 2 as a function of the synthesis period. It is evident that the ordering proceeds – as expected – much faster at 1300 °C. On the other hand, using the lower synthesis temperature of 1150 °C allows us to precisely tune the DoO almost for the whole range of S values from zero to unity.

In Fig. 3 we plot the crystallite and ordered-domain sizes as obtained from Rietveld refinements for the samples synthesized at various temperatures for 100 hours; the crystallite size seems to remain relatively constant, but the ordered-domain size within the crystallites grows as the synthesis temperature increases up to around 1150 °C. For all samples the strain value was found to be within 2 to 8 %. For the sample series heat-treated at 1150 or 1300 °C for different time periods, rapid

crystallite (and ordered-domain) size growth was seen with increasing time, such that the maximal value was reached in even less than 2 hours. The detailed data are shown in the Supplementary material section.

Fig. 3. Crystallite (white circles) and ordered-domain (black circles) sizes for samples heat-treated for 100 hours at different temperatures. Error bars are approximately of the same size as the markers.

From Fig. 4 where we plot the cubic lattice parameter a against the degree of order parameter S for the different sample series a clear relationship is seen between the two parameters, such that the unit cell shrinks with increasing cation order. The data can be extrapolated to the lattice parameter $a \approx 8.012$ Å for the completely disordered phase and $a \approx 8.004$ Å for the fully ordered phase. Interestingly, since in the present $(\text{Sr}_{0.5}\text{Ba}_{0.5})_2\text{FeSbO}_6$ compound the DoO can be controlled in a wide range, also a large variation in the lattice parameter can be seen, and although the data show some scattering we may even use the lattice parameter value as a rough measure for the DoO in the sample. Similar trends have been previously observed for other double-perovskite systems as well [15-17]; however, in most these systems the data do not cover the whole range of S values from zero to unity as in the present case. For intermetallics very strong dependencies of the unit-cell volume on the DoO have been reported [30,31].

Fig. 4. Unit-cell parameter a against the DoO parameter S for samples synthesized for various time periods (white circles: at 1150 °C; black triangles: at 1300 °C) and for samples synthesized at various temperatures for 100 hours (black squares). Error bars are approximately of the same size as the markers.

The kinetics of the cation ordering process at a certain temperature may be directly followed by using the DoO parameter S . In cases where the process does not begin from the $S = 0$ situation or does not proceed to completion, the transformed fraction f is calculated as $f = S/S_{\text{end}}$, where S is the DoO at time t and S_{end} the DoO at the end of the process. Assuming that the ordering process follows Johnson-Mehl-Avrami-Kolmogorov (JMAK) kinetics [32], the $\ln(-\ln(1-f))$ versus $\ln t$ plot may be used to extract the kinetic parameters. In Fig. 5 we plot our data at the heat-treatment temperatures 1150 and 1300 °C. The parallel nature of the linear lines of the both sample series implies that the growth exponent (according to JMAK kinetics) is temperature independent and the decreasing abscissa intercept value with increasing temperature indicates the temperature dependent nature of the reaction rate coefficient. The slope is relatively constant for the samples synthesized at 1300 °C while for samples synthesized at 1150 °C there are two regions with the same slope, but with different time-axis intercepts (~ 8 (0.86 h) and ~ 10 (8.6 h)). This corresponds well with the observation that crystallite size growth decreases in the region where the intercept value changes. Since the crystallite size at 1300 °C is relatively constant for all samples, there is no change in the intercept value. The slight drop seen in the DoO at around 20 hours in Fig. 2 also corresponds well with the time region where the crystallite growth ceases.

Fig. 5. The $\ln(-\ln(1-f))$ vs. $\ln t$ (left) and crystallite size vs. $\ln t$ plots (right) (annealing time t) for samples synthesized at 1150 °C (black circles) and 1300 °C (white circles) for various time periods. Error bars are approximately of the same size as the markers.

4. Conclusions

The degree of the B-site cation order of the $(\text{Sr,Ba})_2\text{FeSbO}_6$ double perovskite can be tuned in an appreciably wide range and in a predictable fashion by selecting the synthesis time and temperature accordingly. The crystallite size is relatively constant at every synthesis temperature for samples synthesized for 100 hours. The size of the ordered domains starts to grow gradually reaching the maximum at 1150 °C. This implies that the long-range ordering starts from multiple individual nucleation centers. As the ordered domains remain smaller than the crystallites, ordering does not span over the whole crystallite and individual domains are coalesced within the crystal. Importantly, our data also clearly demonstrate the remarkable reverse dependency of the cubic lattice parameter a and the degree of order.

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