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Phase relation in the system $La_{1-x}Ba_xFeO_{3-y}$ $(0 \leqslant x \leqslant 0.70)$

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Samples of the system $La_{1-x}Ba_xFeO_{3-y}$ $(0 \leqslant x \leqslant 0.70)$ have been synthesized and investigated by means of X-ray diffraction and Mössbauer effect. Two different phases, i.e. a barium-poor orthorhombic perovskite phase and a barium-rich cubic perovskite phase, were found to exist in the system. The phase relation at room temperature is presented.

1. Introduction

Early, $LaFeO_3$ and $BaFeO_3$ were well studied. Their crystal structures and some properties are fairly well known. $LaFeO_3$ has an orthorhombic symmetry in the space group D_{2h}^{16}–$Pbnm$. Its unit cell with the lattice constants of $a = 0.5556$ nm, $b = 0.5565$ nm and $c = 0.7861$ nm consists of four perovskite-like monoclinic pseudo-cells with the dimension of $a = c = 0.3932$ nm, $b = 0.3931$ nm and $\beta = 90.2°$, where β is the angle between the axes a and c [1]. The magnetic ordering of the iron ions in $LaFeO_3$ is antiferromagnetic [2]. The Néel temperature of $LaFeO_3$ was determined to be 740 K [3, 4]. In the Mössbauer effect measurement of iron nuclei $LaFeO_3$ yields a 6-line spectrum having a hyperfine field splitting of 52.1 T at room temperature [5]. $BaFeO_3$ possesses a 12-layer hexagonal perovskite crystal structure [6] in the space group D_{3d}^{5}–$R\bar{3}m$ with the lattice constants of $a = 0.5700$ nm and $c = 2.803$ nm, and its Néel temperature is 270 K [7]. Recently, the structural characteristics and the electron transport properties of the oxygen-deficient perovskite $La_{0.50}Ba_{0.50}Fe_{1-x}Cu_x O_{2.75-x/2+\delta}$ have been reported [8]. We are interested in the system $LaFeO_3$–$BaFeO_3$, i.e. the system $La_{1-x}Ba_xFeO_{3-y}$. Our attention has first focused on the phase relation and the crystal structures of appearing phases in the system.

2. Experimental procedure

Samples of $La_{1-x}Ba_xFeO_{3-y}$ with various compositions between $x = 0$ and $x = 0.70$ were obtained by solid state reaction of pure La_2O_3, $BaCO_3$ and Fe_2O_3. The powders were rigorously mixed in the corresponding molar ratios of La:Ba:Fe $= (1-x):x:1$ and pre-fired in air at 950 °C for 20 h. They were then thoroughly ground, pressed into discs and fired by the following process: heating in air at a rate of 300 °C h^{-1} up to 1200 °C, keeping at 1200 °C for 15 h, and cooling slowly at a rate of 60 °C h^{-1} down to room temperature. Grinding played an important role, since a full reaction could be hindered under an inhomogeneous mixing. For this reason, after every firing the discs were pounded and reground. A full reaction was reached by repeating this firing process three times for $0 \leqslant x \leqslant 0.50$ and five times for $x = 0.60$ and 0.70. The sample preparation was controlled by X-ray diffraction analysis to examine whether the samples had completely reacted. A fully reacted sample gives the simplest diffraction pattern, and no diffraction peaks were found from the unreacted starting substances or an intermediate product which could be eliminated by elevating the firing temperature or repeating the aforementioned firing process even more times. In order to reduce the oxygen deficiency the well reacted ceramics were finally heated in 1×10^5 Pa pure oxygen at a rate of 300 °C h^{-1} up to 1200 °C, kept at this temperature for 5 h and cooled slowly at a rate of 60 °C h^{-1} down to 500 °C at which they were kept for 30 h and then cooled at a rate of 60 °C h^{-1} to room temperature. The produced discs were pulverized for X-ray diffraction and Mössbauer effect measurements.

X-ray diffraction was performed on a computer-controlled Siemens diffractometer D500 with CuK_α radiation using a step of 0.02 degree and a count time of 2.0 s. The measured data were recorded by DEC PDP 11 and analysed with the help of this computer.

Mössbauer effect experiments were carried out at room temperature in the standard transmission geometry using a ^{57}Co source in a Rh matrix. Spectra were fitted using Lorentzian lines by a least-square refinement program. Calibration of the velocity was made using pure iron metal.

3. Results

All samples were analysed by means of X-ray diffraction. Several X-ray diffraction patterns are plotted in Fig. 1. The result of our X-ray powder diffraction

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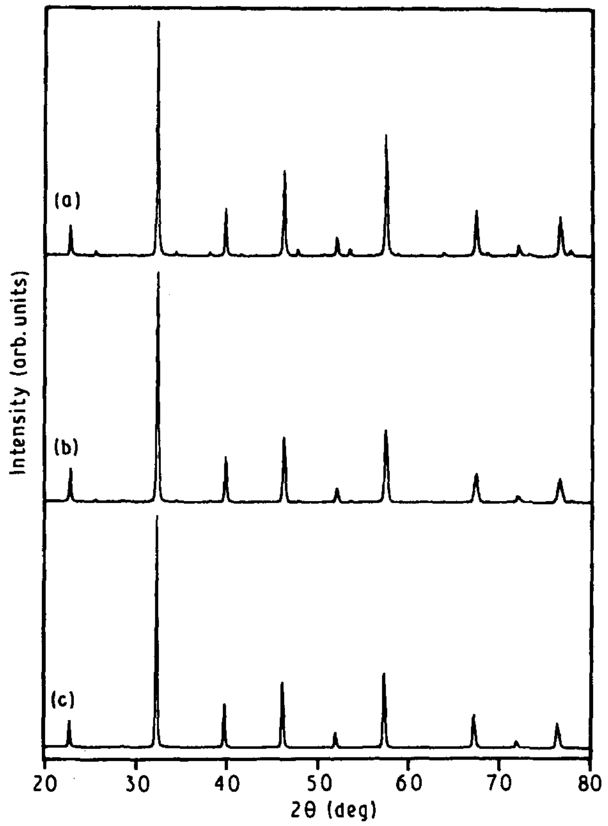

Figure 1 X-ray diffraction patterns of samples with x = (a) 0.05; (b) 0.30 and (c) 0.60.

analysis for the sample of $x = 0$ is in good agreement with the early crystallographic study of $LaFeO_3$ [1]. Magnifying every peak in the 2θ-axis and then comparing the corresponding peaks of X-ray diffraction patterns with the help of the computer, no detectable change in diffraction patterns could be found, as the Ba concentration was increased from $x = 0$ to $x = 0.10$. In other words, as Ba is substituted for La up to $x = 0.10$, the crystal structure keeps in an orthorhombic symmetry, and the cell dimension is little changed, though the introduction of Ba could theoretically enlarge the unit cell due to its large ion radius. The X-ray diffraction patterns of samples with $x = 0.20, 0.30$, and 0.40 are superposition of two patterns diffracted, respectively, from an orthorhombic perovskite phase and a cubic one. However, their main diffraction peaks overlap strongly. As x increases, the second peak, and other smaller peaks, from the orthorhombic perovskite phase decrease. Up to $x = 0.50$ the second peak, and other smaller peaks, from the orthorhombic phase have disappeared and the sample of $x = 0.50$ seems to be the one-phased cubic perovskite phase. The samples of $x = 0.60$ and 0.70 show the typical X-ray diffraction pattern of a cubic perovskite phase. $La_{0.40}Ba_{0.60}FeO_{3-y}$ was measured up to a high angle using a step of 0.02 degree and a count time of 5.0 s in order to determine its exact lattice parameter. All the peaks of its X-ray diffraction pattern were easily indexed by assuming a cubic perovskite structure. The $\{330\}$, $\{331\}$, $\{420\}$, $\{421\}$, and $\{332\}$ peaks at the high angles were chosen and fitted to obtain their exact peak positions. The lattice constant of the cubic perovskite $La_{0.40}Ba_{0.60}FeO_{3-y}$ was determined to be $a = 0.3941$ nm with $\cos^2\theta$-extrapolation method.

Mössbauer spectra of $La_{1-x}Ba_xFeO_{3-y}$ registered at 300 K for various compositions are shown in Fig. 2, and the data are reported in Table I. It is clear that samples with Ba concentrations of $x = 0$, 0.05 and 0.10 yield the characteristic 6-line spectra of the nuclear Zeeman effect of an antiferromagnetism. The best resolved lines are those of $x = 0$, and a Lorentzian fitting could be obtained with the intensity ratios of 3:2:1:1:2:3. As x increases up to 0.10, the absorption lines tend slightly to broaden asymmetrically in the direction of the reduction of the internal field, probably due to the introduction of Ba atoms in the vicinity of some iron atoms. However, their internal field, H_i, and isomer shift, IS, remain almost the same as those of $x = 0$, namely $H_i = 52$ T and $IS = 0.41$ mm s^{-1}, and the area ratios of the absorption peaks can be approximated to 3:2:1:1:2:3. The

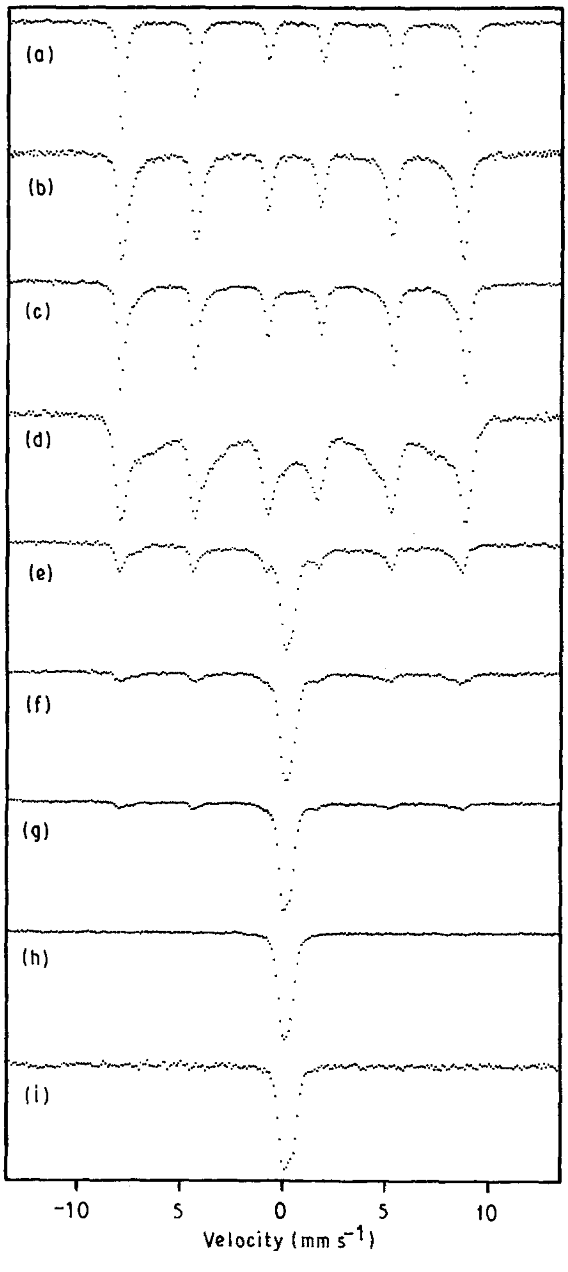

Figure 2 Mössbauer spectra of $La_{1-x}Ba_xFeO_{3-y}$ with various x: (a) 0; (b) 0.05; (c) 0.10; (d) 0.20; (e) 0.30; (f) 0.40; (g) 0.50; (h) 0.60 and (i) 0.70.

TABLE I Mössbauer data and related phases

Sample $x =$	IS ($\mathrm{mm\,s^{-1}}$)	H_i (T)	Area ratios (%)	Related phases
0	0.409	52.4	100	Orthorhombic
0.05	0.406	51.8	100	Orthorhombic
0.10	0.410	52.0	100	Orthorhombic
0.20	0.406	52.4	80.2	Orthorhombic
	0.172		19.8	Cubic
0.30	0.409	51.8	49.2	Orthorhombic
	0.170		50.8	Cubic
0.40	0.406	51.8	30.3	Orthorhombic
	0.172		69.7	Cubic
0.50	0.406	51.7	10.7	Orthorhombic
	0.172		89.3	Cubic
0.60	0.170		100	Cubic
0.70	0.170		100	Cubic
	0.410			

Mössbauer spectra of samples with $x = 0.20, 0.30, 0.40$ and 0.50 reveal both a 6-line sub-spectrum whose parameters are almost the same as those of the spectrum for $x = 0$, and an additional single line in the centre. This single-line sub-spectrum has an isomer shift of $0.17\ \mathrm{mm\,s^{-1}}$. As the Ba concentration increases from $x = 0.20$ to $x = 0.50$, the intensity of the 6-line sub-spectrum decreases and that of the single-line sub-spectrum increases. The ratios of the absorption areas of both these sub-spectra were calculated with the help of the fitting program (Fig. 3). Samples with Ba concentrations of $x = 0.60$ and 0.70 are paramagnetic at room temperature. Sample with $x = 0.60$ displays a single line having an isomer shift of $0.17\ \mathrm{mm\,s^{-1}}$. The spectrum for $x = 0.70$ shows a small peak at $0.41\ \mathrm{mm\,s^{-1}}$ on the positive-velocity slope of the dominant single peak at $0.17\ \mathrm{mm\,s^{-1}}$.

4. Discussion

Our X-ray diffraction measurements on $La_{1-x}Ba_xFeO_{3-y}$ $(0 \leqslant x \leqslant 0.70)$ reveal two phases, respectively, with an orthorhombic and a cubic symmetry in the system. $La_{1-x}Ba_xFeO_{3-y}$ with $x = 0$, 0.05 and 0.10 is the single-phased barium-poor orthorhombic perovskite phase. $La_{0.40}Ba_{0.60}FeO_{3-y}$ and $La_{0.30}Ba_{0.70}FeO_{3-y}$ are the single-phased barium-rich perovskite phase, however, with a cubic symmetry. The X-ray diffraction patterns for intermediate Ba concentrations of $x = 0.20$, 0.30 and 0.40 exhibit a coexistence of these two phases, and the relative amount of the barium-rich cubic perovskite phase increases, as the Ba concentration increases from $x = 0.20$ to $x = 0.40$. These two phases yield quite similar diffraction patterns on account of their very similar crystal structures and cell dimensions. As a result, the main peaks of their diffraction patterns overlap each other. That restricts the use of X-ray diffraction in phase analysis in certain cases. The sample with a Ba concentration of $x = 0.50$, for example, seems to be the one-phased barium-rich cubic perovskite phase. However, as described later, Mössbauer effect leads to another identification.

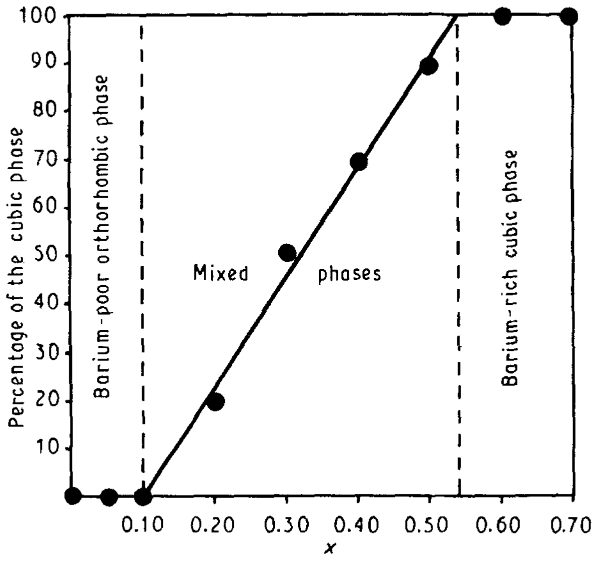

Figure 3 Variation of molar percentage of barium-rich cubic perovskite phase in $La_{1-x}Ba_xFeO_{3-y}$ with x.

Comparing Mössbauer spectra of $La_{1-x}Ba_xFeO_{3-y}$ with its X-ray diffraction analysis, it is obvious that the 6-line sub-spectrum and the single-line sub-spectrum arise not from iron atoms in two different sites in the same crystal but from iron atoms in two different phases, i.e. from the barium-poor orthorhombic perovskite phase and the barium-rich cubic one. The Mössbauer effect measurements for a Ba concentration of up to $x = 0.10$ show only 6-line patterns and those for Ba concentrations of $x = 0.60$ and 0.70 display only single lines. This supports the X-ray analysis result that samples with Ba concentrations from $x = 0$ to $x = 0.10$ are the single-phased barium-poor orthorhombic perovskite phase and samples with $x = 0.60$ and 0.70 are the single-phased barium-rich cubic perovskite phase. The 6-line sub-spectrum and the single-line sub-spectrum in the spectra of samples with Ba concentrations from $x = 0.20$ to $x = 0.50$ indicate that these samples are a mixture of the orthorhombic and cubic phase, which are antiferromagnetic and paramagnetic, respectively, at room temperature. Otherwise, one would expect a gradual collapse in these spectra from 6-line to single-line as a result of lowering the Néel temperature with increasing Ba concentration. However, this contradicts the experimental fact that a narrow single-line and a 6-line sub-spectrum with the intensity ratio of 3:2:1:1:2:3 are present in the spectra. According to the X-ray diffraction analysis the sample with $x = 0.50$ seems one-phased, but its Mössbauer spectrum clearly includes a 6-line sub-spectrum with a small intensity which results from the barium-poor orthorhombic phase, in addition to a predominant single-line sub-spectrum. The Mössbauer effect is very sensitive to the sites and environment of iron atoms in the crystal lattice, namely to different phases. Unfortunately, the X-ray diffraction patterns of the two concerned phases are quite similar to each other. Therefore, the Mössbauer effect is more convincing in this case: the sample with a Ba concentration of $x = 0.50$ is obviously still two-phased and consists of the barium-poor orthorhombic perovskite phase and the barium-rich cubic one.

Assuming that the difference in the Debye temperatures of the two phases can be neglected, the relative integral areas of the 6-line sub-spectrum and the single-line sub-spectrum reflect the molar percentages of the two corresponding phases in the two-phased samples. The molar percentage of the barium-poor orthorhombic perovskite phase and that of the barium-rich cubic perovskite phase were obtained for all samples and are given in Fig. 3. In the two-phased samples the molar percentage of the barium-rich cubic phase increases proportionally with the Ba concentration. This result conforms to the lever rule very well. The solubility of Ba in the orthorhombic perovskite phase is extrapolated to be $x = 0.10$, and that of La in the cubic perovskite phase is extrapolated to be $1 - x = 1 - 0.54 = 0.46$. Fig. 3 exhibits simultaneously the room temperature phase relation of the system $La_{1-x}Ba_xFeO_{3-y}$ $(0 \leqslant x \leqslant 0.70)$. Three phase regions are outlined in the phase diagram: the barium-poor orthorhombic perovskite phase for $0 \leqslant x \leqslant 0.10$, mixed phases for $0.10 \leqslant x \leqslant 0.54$, and the barium-rich cubic perovskite phase for $0.54 \leqslant x \leqslant 0.70$.

The existence of two phases in the system can probably be explained by considering the great difference in ion radii between La and Ba. Ba has a relatively large ion radius, and the orthorhombic perovskite phase has a relatively small unit cell. Thus, just a little amount of Ba atoms can dissolve in the orthorhombic phase. On the contrary, La has a relatively small ion radius, and the cubic perovskite phase has a relatively large unit cell. Therefore, a large amount of La atoms can dissolve in the cubic phase. Moreover, the substitution of divalent Ba for trivalent La may cause the change of oxidation state of iron. The single-line sub-spectrum with the isomer shift of about 0.17 $mm\,s^{-1}$ (Fig. 2 and Table I) appears to belong to neither the trivalent nor the tetravalent iron but an intermediate oxidation state. A systematic study in this aspect will be published elsewhere.

5. Summary

The results of the present investigation on the system $La_{1-x}Ba_xFeO_{3-y}$ $(0 \leqslant x \leqslant 0.70)$ can be outlined as follows. As La atoms are substituted by Ba up to $x = 0.10$, the barium-poor orthorhombic perovskite phase exists at room temperature. A further substitution of La by Ba atoms causes the formation of a second phase with a cubic symmetry. $La_{1-x}Ba_xFeO_{3-y}$ with a Ba concentration between $x = 0.10$ and $x = 0.54$ shows a coexistence of the barium-poor orthorhombic perovskite phase and the barium-rich cubic one. In the two-phase region the phase relation follows the lever rule. As more Ba than $x = 0.54$ is introduced, only the barium-rich cubic perovskite phase can be found. The lattice constant of the single-phased cubic perovskite $La_{0.40}Ba_{0.60}FeO_{3-y}$ was determined to be $a = 0.3941$ nm.

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