Subsolidus phase relation in the Bi_2O_3–Fe_2O_3–La_2O_3 system*

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Bismuth-containing semiconductor material is a hot topic in photocatalysts because of its effective absorption under the visible light. In this paper, we expect to explore a new bismuth-based photocatalyst by studying the subsolidus phase relations of the Bi_2O_3–Fe_2O_3–La_2O_3 system. The X-ray diffraction data shows that in this ternary system the ternary compound does not exist, while seven binary compounds (including one solid solution series $Bi_{1-x}La_xO_{1.5}$ with $0.167 \leq x \leq 0.339$) are obtained and eight compatibility triangles are determined.

Keywords: Bi_2O_3–Fe_2O_3–La_2O_3 system, phase diagram, X-ray diffraction, $BiFeO_3$

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1. Introduction

In the quest for environmental purification, the photocatalytic decomposition of organic pollutants by employing semiconductors is one of the most promising methods. To effectively harvest the visible light, constructing a photocatalysis system with high visible-light activity is essential. Bismuth-containing semiconductor material has attracted considerable attention because of its effective absorption under visible light.[1–3] Bismuth oxide (Bi_2O_3) is a visible-light-active semiconductor with a direct band-gap of 2.8 eV–2.9 eV, and has thus emerged as an alternative photocatalyst to conventional photocatalysts.[4] However, the photocatalytic efficiency of Bi_2O_3 must be further improved due to its low quantum efficiency and instability. This instability is attributed to the phase transformation and the reaction with aqueous solution during photocatalytic activity.[5,6]

Since ionic radii of La^{3+} and Bi^{3+} are similar, La^{3+} ions can enter into the lattice of Bi_2O_3, thus the optical response of Bi_2O_3 can be modulated.[7] In addition, doping Fe_2O_3 with a narrow band gap of 1.9 eV is expected to make up the shortage of composite material in utilizing visible-light.[8] The oxides of Bi^{3+}, La^{3+}, and Fe^{3+} possibly form perovskite or perovskite-related structure in an ideal chemical formula ABO_3, which has fascinating physical and structural properties.[9] Perovskite-type samples with the common formula ABO_3 have been studied extensively as promising photocatalysts.[10,11] Such materials could combine high visible-light photocatalytic activity with the merits of stability by structure regulation. The superior visible photocatalytic performance of $LaFeO_3$ has been confirmed,[9,12] implying that the perovskite-based materials are feasible and promising. Therefore, we choose to clarify the phase relations of the Bi_2O_3–Fe_2O_3–La_2O_3 system and hope to explore novel photocatalysts.

1.1. Bi_2O_3–Fe_2O_3 system

The Bi_2O_3–Fe_2O_3 binary system was intensively investigated,[13–15] and five compounds with Bi_2O_3:Fe_2O_3 molar ratios of 1:2 ($Bi_2Fe_4O_9$), 3:5 ($Bi_3Fe_5O_{12}$), 1:1 ($BiFeO_3$), 20:1 ($Bi_{40}Fe_2O_{63}$), and 25:1 ($Bi_{25}FeO_{40}$) were reported in Refs. [14], [16]–[25]. Their space groups and lattice parameters are listed in Table 1.

The phase diagram of this system was also determined by Koizumi *et al.*,[13] Speranskaya *et al.*,[14] and Maitre *et al.*[15] However, the determined phase equilibriums are different from each other. Only two compounds, $Bi_2Fe_4O_9$ and $BiFeO_3$, were found in the system Bi_2O_3–Fe_2O_3 according to Koizumi *et al.*'s[13] results. Speranskaya *et al.*[14] reported on three compounds $Bi_2Fe_4O_9$, $BiFeO_3$, and $Bi_{40}Fe_2O_{63}$. For the compound $Bi_{40}Fe_2O_{63}$, nothing else was reported except for the X-ray powder diffraction data. According to Maitre's results, $Bi_2Fe_4O_9$, $BiFeO_3$, and $Bi_{25}FeO_{40}$ were existent in this system.

The authors in Ref. [26] have thought that the compound $Bi_{25}FeO_{40}$, should be $Bi_{25}FeO_{39}$. But, according to the report of Craig and Stephenson,[25] $Bi_{25}FeO_{39}$ should be considered to be $Bi_{25}FeO_{40}$ ($Bi^{+3}_{24}Bi^{+5}Fe^{+3}O_{40}$) as the valence of one Bi ion changes to +5.

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The compound $BiFeO_3$ is intensively studied since it is a promising candidate of multiferroic materials.[27–29] However, its difficult synthesis and large current leakage have hampered its practical applications. Recently, some authors have reported that, by using a so-called rapid liquid-phase sintering method, single phase $BiFeO_3$ can be synthesized.[30,31] In addition, single phase $BiFeO_3$ has been synthesized by traditional solid-state reaction (SSR) using ultrapure grade raw material.[32] They considered that the impurities in the starting material crucially influenced the phase composition of the reaction product.[32]

1.2. Bi_2O_3–La_2O_3 system

In the Bi_2O_3–La_2O_3 system, six compounds $Bi_2La_4O_9$, $BiLa_2O_2$, $Bi_{2.4}La_{3.6}O_{1.5}$, $Bi_8La_{10}O_{27}$, $Bi_{4.86}La_{1.14}O_9$, and a solid solution series $Bi_{1-x}La_xO_{1.5}$ ($0.16 \leq x \leq 0.33$) were reported.[33–38] Their space groups and lattice parameters are shown in Table 1.

Four compounds $Bi_2La_4O_9$, $Bi_{2.4}La_{3.6}O_{1.5}$, $Bi_8La_{10}O_{27}$, and solid solution series $Bi_{1-x}La_xO_{1.5}$ ($0.16 \leq x \leq 0.33$) were found by Chen and Eysel,[38] according to their study of a binary phase diagram.

Table 1. Crystallographic data of compounds for the Bi_2O_3–Fe_2O_3–La_2O_3 system.

Phase	Space group	Lattice parameters						Ref.
		a/Å	b/Å	c/Å	α/(°)	β/(°)	γ/(°)	
$Bi_2Fe_4O_9$	$Pbam$	7.965(4)	8.440(4)	5.994(4)				[16]
	$Pbam$	7.957(2)	8.423(2)	5.992(1)				this work
$Bi_3Fe_5O_{12}$	$Ia\bar{3}d$	12.6469						[17]
$BiFeO_3$	Cm	5.7900	5.6899	4.1739		91.990		[18]
	$Pnma$	5.5849	7.6597	5.3497				[18]
	$P2_1/m$	5.6148(3)	7.9725(1)	5.6467(1)			90.015(4)	[19]
	$C2/m$	17.4022	7.7024	5.4282		108.132		[20]
	$R3R$	5.459			60.36			[21]
	$R3mR$	3.9620			89.5200			[22]
	$R\bar{3}mR$	3.9520			89.6000			[23]
	$R3cH$	5.5775		13.8616				[24]
	$R3cH$	5.5799(4)		13.8736(9)				this work
$Bi_{25}FeO_{40}$	$I23$	10.1789						[25]
	$I23$	10.181(2)						this work
$Bi_{1-x}La_xO_{1.5}$ ($0.16 \leq x \leq 0.33$)	$R3mH$	4.006–4.045		27.831–27.450				[38]
$Bi_{1-x}La_xO_{1.5}$ ($0.167 \leq x \leq 0.339$)	$R3mH$	3.940–4.040		27.802–27.400				this work
$Bi_2La_4O_9$	$C2/m$	6.829	3.9887	4.0524		125.095		[33]
	$R3mH$	3.9630		9.9640				[34]
	$P\bar{1}$	3.9200	4.0230	5.6280	87.630	89.710	89.910	[35]
	$C2/m$	6.822(2)	3.983(1)	4.051(1)		125.07(2)		this work
$BiLa_2O_2$	$I4/mmm$	4.0848		13.9866				[36]
$Bi_{2.4}La_{3.6}O_9$	$R3mH$	3.96017(5)		9.9691(2)				[33]
$Bi_8La_{10}O_{27}$	$Immm$	12.083	16.340	4.0989				[33]
	$Immm$	12.047(2)	16.331(3)	4.093(1)				this work
$Bi_{4.86}La_{1.14}O_9$	$P2/c$	9.4956	3.9742	7.0425		104.700		[37]
$LaFe_3O_6$	$Cmc2$	9.4024	11.8294	5.7079				[39]
$LaFeO_3$	$Pnma$	5.5674	7.8551	5.556				[40]
	$Pm\bar{3}m$	3.9260						[41]
	$Pnma$	5.560(1)	7.844(2)	5.549(1)				this work
$LaFe_{12}O_{19}$	$P6_3/mmc$	5.8858		22.8887				[42]
	$Cmcm$	5.9025	10.1593	22.7883				[42]

1.3. Fe_2O_3–La_2O_3 system

Three compounds were reported in this system with Fe_2O_3:La_2O_3 molar ratios of 1:3 (La_3FeO_6),[39] 1:1 ($LaFeO_3$),[40,41] and 12:1 ($LaFe_{12}O_{19}$).[42] An Fe_3O_4-based solid solution $La_{0.14}Fe_3O_4$, which belongs to the cubic system with space group (SG) $Fd\bar{3}m$, was also reported in this system.[43]

1.4. Bi_2O_3–Fe_2O_3–La_2O_3 system

For this system, only one $BiFeO_3$-based solid solution $Bi_{1-x}La_xFeO_3$ was reported. $Bi_{1-x}La_xFeO_3$ belongs to a trigonal system with space group $R3cH$[24,44] or to an or-

thorhombic system with space group *Imma*[45] or *Pnma*[44] or *Pbam*.[44]

2. Experiment

Analytical grade and ultrapure grade Bi_2O_3, Fe_2O_3, and La_2O_3 (Sinopharm Chemical Reagent Co. Ltd.) were used to prepare the specimens by SSR and quenching methods in air. The powders of the raw materials with a certain chemical composition were mixed in an agate mortar to get homogeneity, and then pressed into pellets, each with a diameter of 10 mm and thickness of 1 mm–2 mm at a pressure around 10^8 Pa. The samples were sintered at different temperatures between 600 °C and 1000 °C according to different compositions and quenched in atmosphere. The sintered samples were ground into powder and identified by the X-ray powder diffraction (XRD) method. Then, the powder was again pressed into pellets and sintered at the same temperature until the powder diffraction patterns showed no change, which showed that equilibrium was achieved.

The temperature of the furnace was measured with a Pt–PtRh thermocouple and precisely controlled within ±2 °C up to 1200 °C with an intelligent controller. XRD diffraction data were collected at room temperature on a PANalytical X'Pert Pro diffractometer with Cu Kα radiation (40 kV×40 mA) using continuous mode at a rate of $2\theta = 4$ °/min.

3. Results and discussion

3.1. Binary systems

The phase relations of the three binary systems, Bi_2O_3–Fe_2O_3, Bi_2O_3–La_2O_3, and La_2O_3–Fe_2O_3, are investigated. The lattice parameters of the binary compounds are refined using the program Jade 5.0. The obtained results are listed in Table 1.

3.1.1. Bi_2O_3–Fe_2O_3 system

In the Bi_2O_3–Fe_2O_3 binary system, three compounds with the Bi_2O_3:Fe_2O_3 molar ratios of 25:1, 1:1, and 1:2 are observed in our experiments, which accords well with Maitre *et al.*'s results.[15] The samples $Bi_{25}FeO_{40}$ and $Bi_2Fe_4O_9$ are sintered at 700 °C for 72 h in a stove. The results show that $Bi_{25}FeO_{40}$ belongs to a cubic system with space group $I23$ and $Bi_2Fe_4O_9$ belongs to an orthorhombic system with S.G. *Pbam*. For the compound $BiFeO_3$, seven different phases have been reported in Refs. [18]–[24]. According to the phase diagram, $BiFeO_3$ can be obtained via SSR and it undergoes a phase transition around 825 °C.[13] We attempt to use several methods to synthesize $BiFeO_3$ (a detailed discussion is given in Subsection 3.2.3), and finally obtain single phase $BiFeO_3$ using SSR at 800 °C for 5 h by starting with ultrapure grade Bi_2O_3 and Fe_2O_3. The $BiFeO_3$ belongs to rhombohedral system with space group $R3cH$. It can keep stable after being annealed under 800 °C for 2 days.

3.1.2. Bi_2O_3–La_2O_3 system

Only two compounds ($Bi_8La_{10}O_{27}$ and $Bi_2La_4O_9$) and a solid solution are confirmed to exist in this work. This result differs from that reported in Ref. [33]. Although compound $Bi_{2.4}La_{3.6}O_9$ was found in Ref. [33], it does not exist under our experiment's conditions. XRD patterns of $Bi_{1-x}La_xO_{1.5}$ at room temperature show that they crystallize in a rhombohedral system with S.G. $R3mH$ for $0.176 \leq x \leq 0.3$. No appreciable changes in the XRD patterns of the compounds with $0.176 \leq x \leq 0.3$ are observed, except that the positions of Bragg reflections are slightly shifted, indicating the lattice parameters and unit cell volume of the compounds vary with La content x. For x values between 0.176 and 0.3, the samples each have a pure hexagonal structure. The patterns for $x = 0.1$ and $x = 0.16$ samples each consist of two phases. The $x = 0.5$ sample also consists of two phases. The dependences of lattice parameters and unit cell volume on the La content (x) are shown in Fig. 1, and the corresponding values are listed in Table 2.

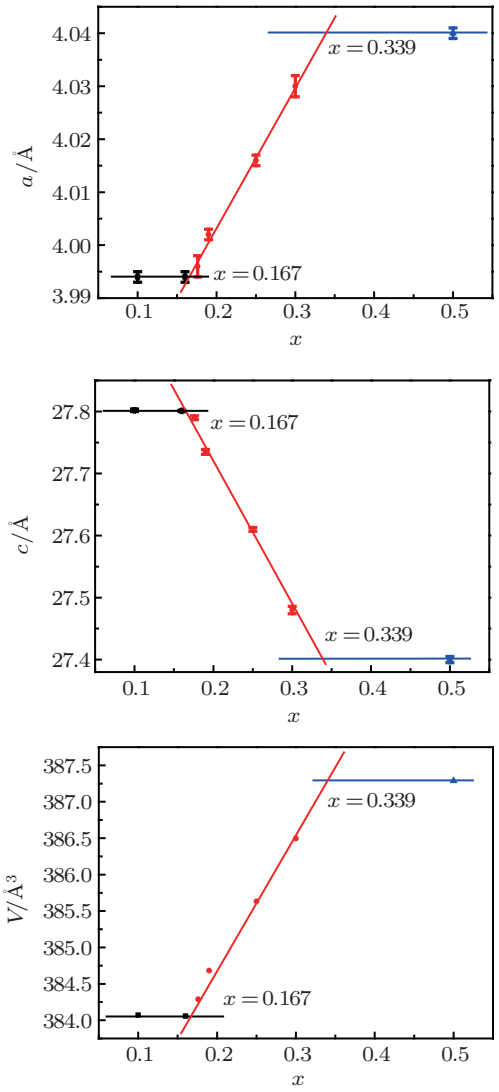


Fig. 1. (color online) Dependences of lattice parameter and unit cell volume on the La content (x) of $Bi_{1-x}La_xO_{1.5}$.

In the single-phase region, the lattice parameter a and the unit cell volume (V) increase linearly with La content (x) while the lattice parameter c decreases. In the two-phase region, the lattice parameters of each phase are unchanged, which is consistent with the phase rule for a binary system. The cell parameter a and the unit cell volume increase with the increase of La content (x) because the radius of La^{3+} is larger than that of Bi^{3+}. Nevertheless, $Bi_{1-x}La_xO_{1.5}$ is a layer-like compound, whose interlayer bond strength plays a leading role in lattice parameter c. We presume that c-lattice parameter decreases as interlayer bond strength increases with the increasing La content (x). The solid solution limit is determined based on the variations of lattice parameters with composition, and a solid solution region with $0.167 \leq x \leq 0.339$ is confirmed. This result is similar to those in Ref. [38].

3.1.3. La_2O_3–Fe_2O_3 system

In the La_2O_3–Fe_2O_3 binary system, only one 1:1 compound $LaFeO_3$ is obtained via SSR under 1000 °C for 72 h. No any other reported compounds were observed in this work. This result is in good agreement with the previous result.[46] Relative space groups and lattice parameters are shown in Table 2.

Table 2. Dependences of lattice parameter and unit cell volume on La content (x) of $Bi_{1-x}La_xO_{1.5}$.

x	a/Å	c/Å	V/Å^3
0.10	3.994 (1)	27.802(7)	384.07
0.16	3.994 (1)	27.801(5)	384.06
0.176	3.996(2)	27.790(2)	384.29
0.19	4.002(1)	27.735(8)	384.68
0.25	4.016(1)	27.610(7)	385.63
0.30	4.030(2)	27.480(6)	386.49
0.50	4.040(1)	27.400(5)	387.28

3.2. Bi_2O_3–Fe_2O_3–La_2O_3 ternary system

3.2.1. Ternary compound

No ternary compound in Bi_2O_3–Fe_2O_3–La_2O_3 system is obtained in this work.

3.2.2. Subsolidus phase relations of the system La_2O_3–Fe_2O_3–Bi_2O_3

According to the results of phase identification of 54 samples, the subsolidus phase relations of Bi_2O_3–Fe_2O_3–La_2O_3 system under our experimental condition are shown in Fig. 2. There are seven binary compounds and eight three-phase regions in this ternary system. The subsolidus phase relation of the ternary system consists of seven tie lines: $LaFeO_3$–$Bi_2Fe_4O_9$, $LaFeO_3$–$BiFeO_3$, $LaFeO_3$–$Bi_{25}FeO_{40}$, $Bi_{25}FeO_{40}$–$Bi_{1-x}La_xO_{1.5}$ ($x = 0.167$), $LaFeO_3$–$Bi_{1-x}La_xO_{1.5}$ ($0.167 \leq x \leq 0.339$), $LaFeO_3$–$Bi_8La_{10}O_{27}$, and $LaFeO_3$–$Bi_2La_4O_9$, which divides the Bi_2O_3–Fe_2O_3–La_2O_3 phase diagram into eight compatibility triangles: (i) Fe_2O_3–$LaFeO_3$–$Bi_2Fe_4O_9$, (ii) $LaFeO_3$–$Bi_2Fe_4O_9$–$BiFeO_3$, (iii) $LaFeO_3$–$BiFeO_3$–$Bi_{25}FeO_{40}$, (iv) $LaFeO_3$–$Bi_{25}FeO_{40}$–$Bi_{1-x}La_xO_{1.5}$ ($x = 0.167$), (v) $Bi_{25}FeO_{40}$–Bi_2O_3–$Bi_{1-x}La_xO_{1.5}$ ($x = 0.167$), (vi) $LaFeO_3$–$Bi_8La_{10}O_{27}$–$Bi_{1-x}La_xO_{1.5}$ ($x = 0.339$), (vii) $LaFeO_3$–$Bi_8La_{10}O_{27}$–$Bi_2La_4O_9$, and (viii) $LaFeO_3$–$Bi_2La_4O_9$–La_2O_3.

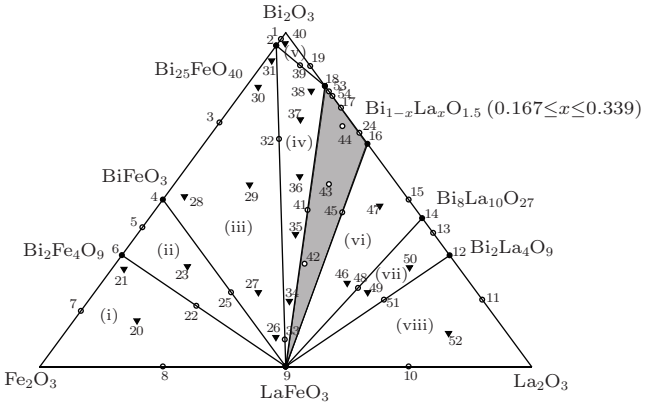


Fig. 2. Subsolidus phase relation of the system La_2O_3–Fe_2O_3–Bi_2O_3 (●: single phase, ○: two phases, ▼: three phases, and the gray region indicates pseudo-binary system $LaFeO_3$–$Bi_{1-x}La_xO_{1.5}$, $0.167 \leq x \leq 0.339$).

3.2.3. Synthesis of $BiFeO_3$

Synthesis of pure phase $BiFeO_3$ by SSR has been intensively studied, such as La-substitution sintering,[47,48] rapid liquid-phase sintering,[30,31] and traditional SSR with using ultrapure grade reactants.[32] We first tried to synthesize $BiFeO_3$ by traditional SSR with analytical grade Bi_2O_3 and Fe_2O_3. However, we could not obtain single-phase $BiFeO_3$, even by an extensive variation of sintering temperature, time, and atmosphere. Secondary phases are always found in XRD as $Bi_{25}FeO_{40}$ and $Bi_2Fe_4O_9$. However, studying the samples of two-phase region ($BiFeO_3$–$LaFeO_3$), we find that the impurity phases ($Bi_{25}FeO_{40}$ and $Bi_2Fe_4O_9$) decrease as the content of La_2O_3 (x) increases (see Fig. 3). When the content of La_2O_3 reaches 0.3, the decomposition of $BiFeO_3$ can almost be suppressed and the impurity phases disappear completely. This infers that a ternary phase $Bi_{1-x}La_xFeO_3$ perhaps exists in $BiFeO_3$–$LaFeO_3$ pseudo-binary system around $x = 0.3$, as shown in Fig. 4. However, the pure phase of $BiFeO_3$ can be obtained by rapid liquid-phase sintering in our experiment. Moreover, the impurity phase of $Bi_2Fe_4O_9$ is observed in each of the samples of $BiFeO_3$–$La_xBi_{1-x}FeO_3$ pseudo-binary system (see Fig. 3). This means that the samples are not in equilibrium, which may be caused by impurities in the starting materials.[32] To further confirm the phase-diagram, single phase $BiFeO_3$ is finally synthesized by traditional SSR using ultrapure reactants. A series of $Bi_{1-x}La_xFeO_3$ samples is prepared using ultrapure grade Bi_2O_3, Fe_2O_3, and La_2O_3 by SSR, as shown in Fig. 5. The results show that there is no intermediate compound in the $BiFeO_3$–$LaFeO_3$ system.

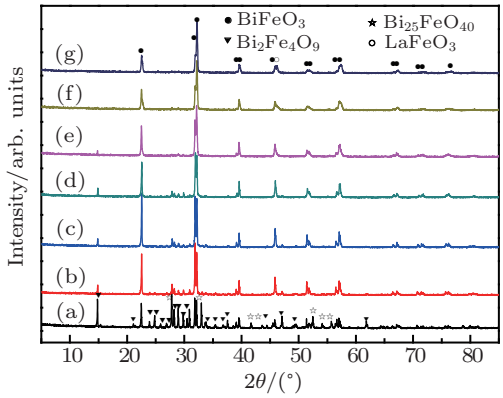


Fig. 3. (color online) X-ray diffraction patterns of $Bi_{1-x}La_xFeO_3$ (prepared using AR raw material) for different x values: (a) 0; (b) 0.02; (c) 0.04; (d) 0.1; (e) 0.2; (f) 0.3; (g) 0.4.

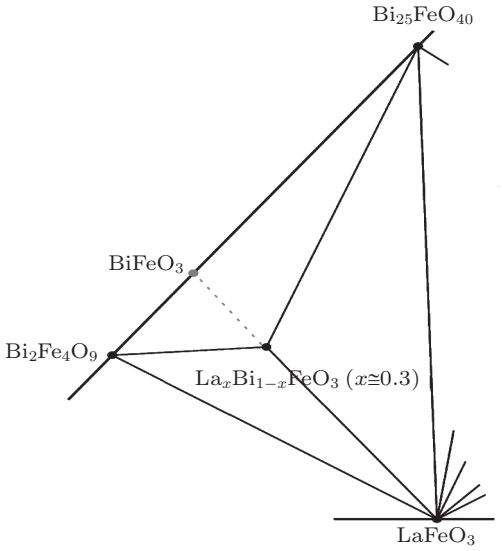


Fig. 4. Possible phase relations in the case where the ternary phase $La_xBi_{1-x}FeO_3$ exists.

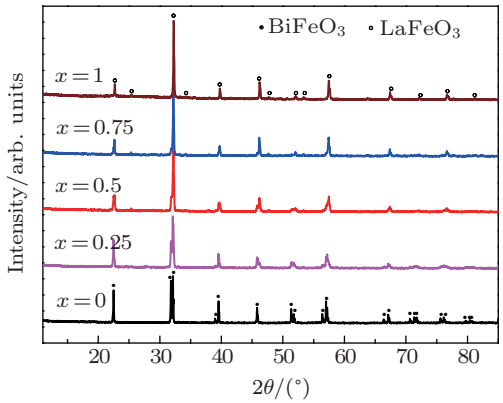


Fig. 5. (color online) X-ray diffraction patterns of $Bi_{1-x}La_xFeO_3$ prepared using ultrapure grade raw material for different x values.

4. Conclusion

The subsolidus phase relations of the Bi_2O_3–Fe_2O_3–La_2O_3 ternary system are determined. There are seven binary compounds and eight ternary-phase regions in this system. No ternary compound is found in this system. A solid solution series $Bi_{1-x}La_xO_{1.5}$ in this system is determined and its region with $0.167 \leq x \leq 0.339$ is confirmed.

References

[1] Eberl J and Kisch H 2008 *Photochemical & Photobiological Sciences* **7** 1400
[2] Kudo A, Omori K and Kato H 1999 *J. Am. Chem. Soc.* **121** 11459
[3] Harriman A, Thomas J M, Zhou W Z and Jefferson D A 1988 *J. Solid State Chem.* **72** 126
[4] Bian Z F, Zhu J, Wang S H, Cao Y, Qian X F and Li H X 2008 *J. Phys. Chem. C* **112** 6258
[5] Wang Y, Li S K, Xing X R, Huang F Z, Shen Y H, Xie A J, Wang X F and Zhang J 2011 *Chemistry A: European Journal* **17** 4802
[6] Li E J, Chen L, Zhang Q A, Li W H and Yin S F 2010 *Prog. Chem.* **22** 2282
[7] Zeng J, Zhong J B, Li J Z, Wang S H and Hu W 2011 *Adv. Mater. Res.* **239** 86
[8] Cao J Y, Kako T, Kikugawa N and Ye J H 2010 *J. Phys. D: Appl. Phys.* **43** 325101
[9] Ding J L, Lu X M, Shu H M, Xie J M and Zhang H 2010 *Mater. Sci. Eng. B* **171** 31
[10] Zhu X H, Hang Q M, Xing Z B, Yang Y, Zhu J M, Liu Z G, Ming N B, Zhou P, Song Y, Li Z S, Yu T and Zou Z G 2011 *J. Am. Ceram. Soc.* **94** 2688
[11] Wang D F, Kako T and Ye J H 2008 *J. Am. Chem. Soc.* **130** 2724
[12] Su H J, Jing L Q, Shi K Y, Yao C H and Fu H G 2010 *J. Nanoparticle Res.* **12** 967
[13] Koizumi H, Niizeki N and Ikeda T 1964 *Jpn. J. Appl. Phys.* **3** 495
[14] Speranskaya E, Skorikov V, Rode E Y and Terekhova V 1965 *Russ. Chem. Bull.* **14** 873
[15] Maitre A, Francois M and Gachon J C 2004 *Journal of Phase Equilibria and Diffusion* **25** 59
[16] Kostiner E and Shoemaker G L 1971 *J. Solid State Chem.* **3** 186
[17] Toraya H and Okuda T 1995 *J. Phys. Chem. Solids* **56** 1317
[18] Feng H J 2010 *J. Magn. Magn. Mater.* **322** 3755
[19] Haumont R, Kornev I A, Lisenkov S, Bellaiche L, Kreisel J and Dkhil B 2008 *Phys. Rev. B* **78** 134108
[20] Belik A A, Yusa H, Hirao N, Ohishi Y and Takayama-Muromachi E 2009 *Chem. Mater.* **21** 3400
[21] Feng H J and Liu F M 2008 *Phys. Lett. A* **372** 1904
[22] Tomashpol'sky Y Y, Venevtsev Y N and Zhdanov G S 1964 *Kristallografiya* **9** 846
[23] Zaslavskii A I and Tutov A G 1960 *Doklady Akademii Nauk SSSR* **135** 815
[24] Sosnowska I, Przenioslo R, Fischer P and Murashov V A 1996 *J. Magn. Magn. Mater.* **160** 384
[25] Craig D C and Stephenson N C 1975 *J. Solid State Chem.* **15** 1
[26] Radaev S F, Muradyan L A and Simonov V I 1991 *Acta Crystallographica Section B* **47** 1
[27] Li Q, Huang D H, Cao Q L and Wang F H 2013 *Chin. Phys. B* **22** 037101
[28] Zou C, Chen B, Zhu X J, Zuo Z H, Liu Y W, Chen Y F, Zhan Q F and Li R W 2011 *Chin. Phys. B* **20** 117701
[29] Ma Z Z, Li J Q, Tian Z M, Qiu Y and Yuan S L 2012 *Chin. Phys. B* **21** 107503
[30] Wang Y P, Zhou L, Zhang M F, Chen X Y and Liu J M 2004 *Appl. Phys. Lett.* **84** 1731
[31] Yuan G L, Or S W, Wang Y P, Liu Z G and Liu J M 2006 *Solid State Commun.* **138** 76
[32] Valant M, Axelsson A K and Alford N 2007 *Chem. Mater.* **19** 5431
[33] Chen X L, Eysel W and Li J Q 1996 *J. Solid State Chem.* **124** 300
[34] Wolcyrz M, Kepinski L and Horyn R 1995 *J. Solid State Chem.* **116** 72
[35] Horyn R, Wolcyrz M and Bukowski Z 1997 *J. Solid State Chem.* **131** 64
[36] Mizoguchi H and Hosono H 2011 *J. Am. Chem. Soc.* **133** 2394
[37] Obbade S, Drache M, Conflant P and Suard E 2001 *J. Solid State Chem.* **162** 10
[38] Chen X L and Eysel W 1999 *Powder Diffraction* **14** 274
[39] Roof I P, Smith M D and zur Loye H C 2010 *Solid State Sci.* **12** 1211
[40] Falcón H, Goeta A E, Punte G and Carbonio R E 1997 *J. Solid State Chem.* **133** 379
[41] Koehler W C and Wollan E O 1957 *J. Phys. Chem. Solids* **2** 100
[42] Küpferling M, Grössinger R, Pieper M W, Wiesinger G, Michor H, Ritter C and Kubel F 2006 *Phys. Rev. B* **73** 144408
[43] Vucinic-Vasic M, Antic B, Kremenovic A, Nikolic A S, Blanusa J, Rakic S, Spasojevic V and Kapor A 2007 *J. Alloys Compd.* **428** 322
[44] Troyanchuk I O, Karpinsky D V, Bushinski M V, Khomchenko V A, Kakazei G N, Araujo J P, Tovar M, Sikolenko V, Efimov V and Kholkin A L 2011 *Phys. Rev. B* **83** 054109
[45] Rusakov D A, Abakumov A M, Yamaura K, Belik A A, van Tendeloo G and Takayama-Muromachi E 2011 *Chem. Mater.* **23** 285
[46] Hrovat M, Holc J, Bernik S and Makovec D 1998 *Mater. Res. Bull.* **33** 1175
[47] Jiang Q H and Nan C W 2006 *J. Am. Ceram. Soc.* **89** 2123
[48] Cheng Z X, Li A H, Wang X L, Dou S X, Ozawa K, Kimura H, Zhang S J and Shrout T R 2008 *J. Appl. Phys.* **103** 07E507