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Composition and structure of bismuth doped dysprosium manganite

In the present work, the multiferroic material $Bi_{0.8}Dy_{0.2}MnO_3$ was synthesized by the Pechini method for its further study. As starting materials, bismuth oxide, manganese oxide, dysprosium oxide, nitric acid and urea were used.It is shown that when nitric acid and urea are used as a precipitant, single-phase powders can be obtained. The powder was sintered at various temperatures of 600 ºC, 800 ºC, 900 ºC, respectively, in order to evaluate their optimum sintering temperature based on X-ray profiles. The incorporation of Bi^{3+} ions into the perovskite crystal structure was verified by means of X-ray, SEM methods. The XRD revealed that the obtained nanocrystalline $Bi_{0.8}Dy_{0.2}MnO_3$ was cubic crystal structure of space group: Fm-3m(225) and lattice parameters were: 5.4763 Å, 5.4763 Å, 5.4763 Å, 90.000, 90.000, 90.000. The density of manganite was determined by the pycnometric method in accordance with State Standard 2211–65. Toluene served as an indifferent fluid. Satisfactory consistency of X-ray and pycnometric densities of manganite confirms the correctness of the results. The results of the electron microscope show that the atomic fractions of the elements practically coincide, which corresponds to the formula of manganite-BDMO.

Keywords: manganite of bismuth, doping, Pechini method, multiferroic, electron microscope, nanocrystal, cubic, liquid-phase process.

Introduction

Multiferroics are considered as an important class of materials which display simultaneously magnetism, ferroelectricity, and ferroelasticity in a single phase. In multiferroics, magnetic and electric orders are strongly coupled, and therefore have attracted an increasing attention in literature [1–3].A series of multiferroic materials with the compositional formula $RMnO_3$ (where R = Sm, Eu, Gd, Tb and Dy) have shown significant importance in recent years because of the fact that strongly competing magnetic interactions could play a very important role in inducing a magnetoelectric effect [4–7].The observation of colossal magnetoresistance (CMR) in (La, Ca) MnO_3 [8] has prompted a flurry of recent research on this material and related perovskite structure manganites [9]. The majority of the recent research has focused on manganites in which the large (A-site) cation was a rare earth from the left hand side of the lanthanide series.The manganites of these large rare earth ions (lanthanum manganite through dysprosium manganite) all crystallize in the cubic perovskite structure, with the same low temperature orthorhombic distortion and A-type antiferromagnetic ordering of the Mn^{3+} ions.

Experimental

Synthetic method Pechini was used for the synthesis of manganite $Bi_{0.8}Dy_{0.2}MnO_3$ (Fig. 1), which has the potential for their use in different applications.

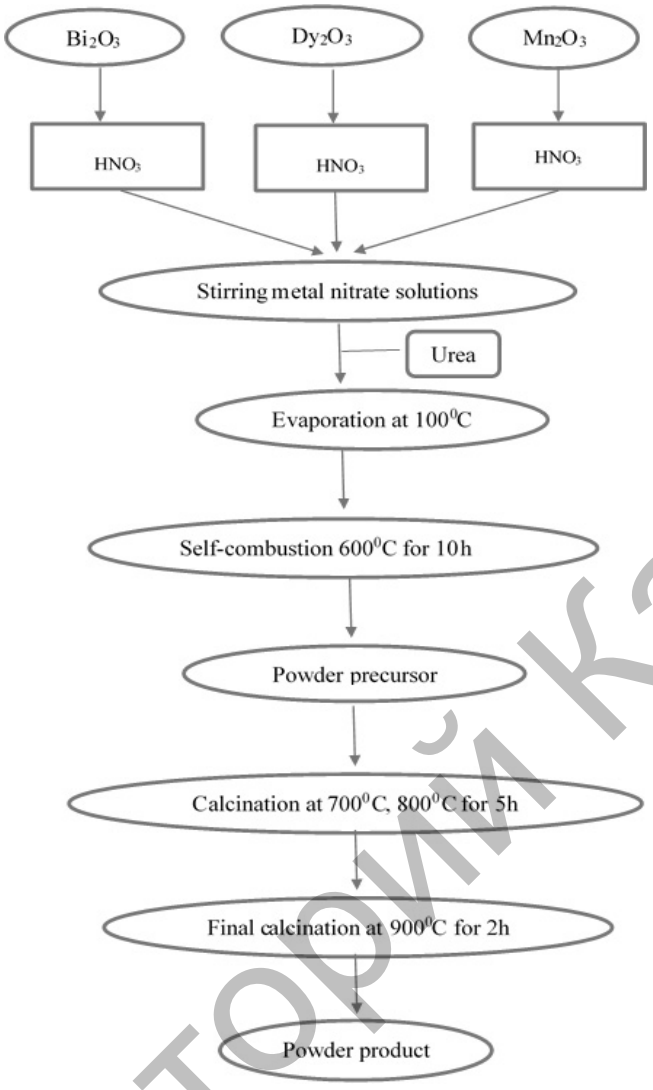

Figure 1. Flowchart for the Pechini method used to obtain the perovskite compound shown in the present work

The selection of method and composition for perovskite was based on the desired application that are described later. In the method, the standardized oxides were mixed according to the stoichiometry of the final products, namely, $Bi_{0.8}Dy_{0.2}MnO_3$ (BDMO). The starting materials were Dy_2O_3 (99.9 %) Bi_2O_3 (99.9 %) Mn_2O_3 (99.9 %) which had to be dissolved in nitric acid before the addition of the other compound (urea). A suitable amount of urea was added to the mixture as a coordinate agent. The solution was then allowed to dry to form a dried gel in an electric oven at 100 ºC. The resulting dried gel was annealed in a muffle furnace to give a black powder at 600 ºC for 10 hours. Finally, the resulting powder was heated in air at 700–900 ºC for 7 hours.

Results and Discussion

X-ray diffraction. Powder X-ray diffraction patterns (Fig. 2, 3) show that the samples show single phase and indexed (Table 1) in the cubic structure with Fm-3m(225) group space.The formation of new phases was controlled by the method of X-ray phase analysis produced by X-ray diffractometer Miniflex 600 (Rigaku) using CuKα-radiation filtered by the filter (U = 30 kV, J = 10 mA, the rotation speed of 1000 pulses per second, time constant is 5 sec., the range of angles 2θ from 5 to 900). Radiographs of the synthesized polycrystalline powders were indicated by the homology method (homologue is a distorted structure type of perovskite). The density of manganites was determined by the pycnometric method according to State Standard 2211–65 [10]. Toluene served as an indifferent liquid. The density of the manganite was measured 4–5 times and data were averaged.

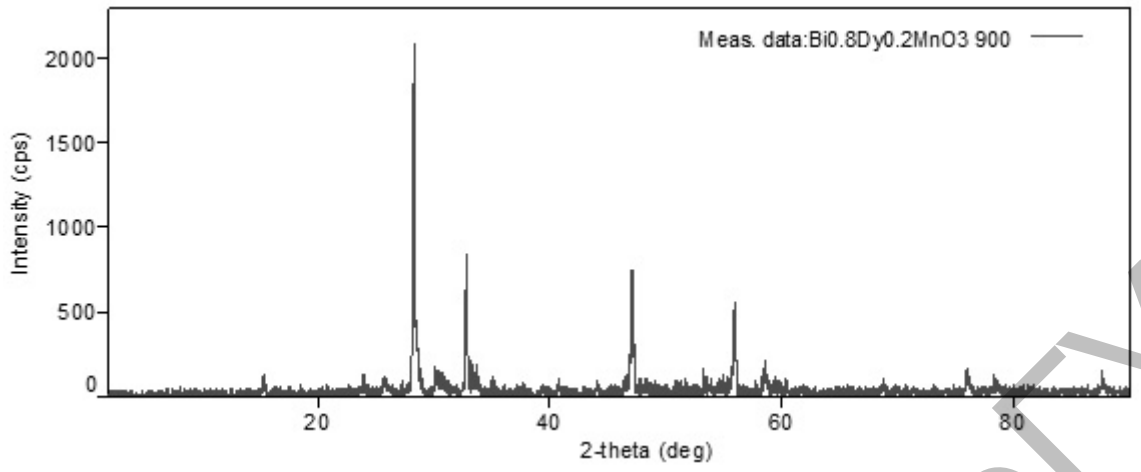

Figure 2. X-ray of BDMO powder

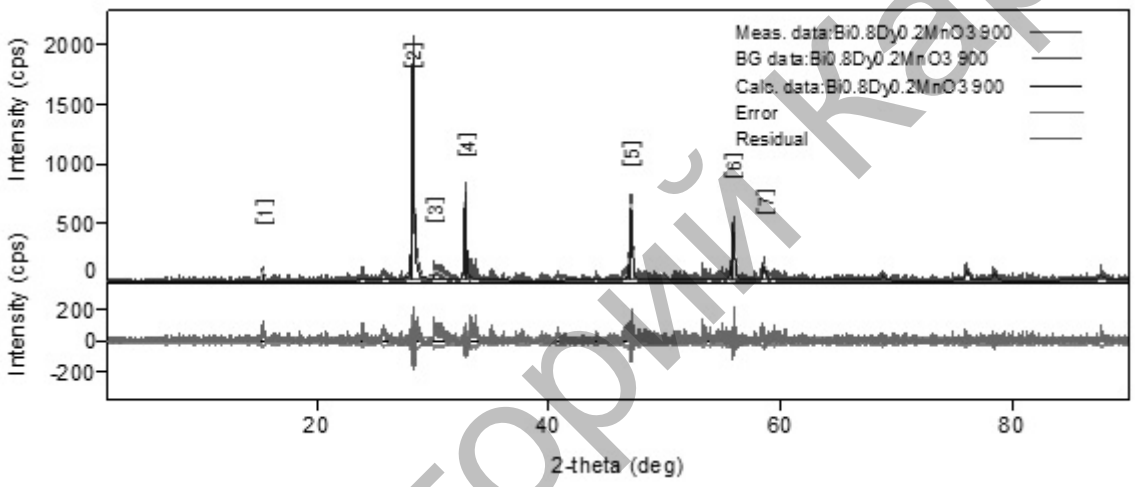

Figure 3. Observed (red symbols) and calculated (blue lines) X-ray diffraction pattern for the BDMO sample and the peaks marked with pink are the remaining after the refinement of the phase by the Rietveld method.

Table 1

The results on indexing of radiographs of manganite

No.	[2Th.]	*d*[Å]	Int. [%]	$10^4/d^2$ exp.	*hkl*	$10^4/d^2$ theory
1	28.20	3.162	100.0	1000	(1,1,1)	1000.02
2	32.68	2.738	38.5	1333.9	(2,0,0)	1333.36
3	46.89	1.936	35.2	2668.02	(2,2,0)	2667.6
4	55.62	1.651	32.4	3668.65	(3,1,1)	3669
5	58.32	1.581	8.1	4000.7	(2,2,2)	4002
6	68.48	1.369	3.8	5335.7	(4,0,0)	5336
7	75.63	1.256	9.0	6338.9	(3,3,1)	6339
8	77.96	1.225	7.6	6663.89	(4,2,0)	6664
9	87.12	1.118	5.4	8000.48	(4,2,2)	8000
10	93.92	1.054	5.2	9001.58	(5,1,1)	9002.01
11	105.44	0.968	1.4	10672.05	(4,4,0)	10671.95
12	112.64	0.926	4.6	11662.13	(5,3,1)	11661.8
13	115.12	0.913	2.7	11996.6	(6,0,0)	11997
14	125.65	0.866	1.9	13334.12	(6,2,0)	13333.7
15	134.55	0.835	1.6	14342.57	(5,3,3)	14343
16	137.83	0.826	1.6	14656.83	(6,2,2)	14659

The results of the synthesized manganite radiograph indexed by this method show that the manganite has the cubic structure with the following unit cell parameters (Table 2).

Table 2

The unit cell parameters of the manganite obtained by the Pechini method

Compound	*a*	*b*	*c*	$V_{un.cell.}$, Å^3	*Z*	$D_{X\text{-}ray.}$, g/cm^3	$D_{pyc.}$, g/cm^3
BDMO	5.4763	5.4763	5.4763	164.233	1	8.647	8.635

The reliability of the indexing results is controlled by a satisfactory coincidence of experimental and calculated values of the inverse squares of the interplanar spacings ($10^4/d^2$), and the coincidence degree of the X-ray and micrometrically densities values of the studied compounds.Thus, the double bismuth–manganite BDMO was synthesized by various methods. Using the ceramic technology, considering the Tamman's conditions, the authors determined temperature regime of the synthesis of the dual mixed manganite BDMO. The type of crystal system and unit cell parameters were determined by the radiographic method. It is established that a complex mixed manganite is crystallized in the orthorhombic crystal system, the correctness of the results of X-ray studies of the manganite is confirmed by the good concordance between the experimental and calculated values ($10^4/d^2$), concordance between the values of X-ray and picnometer densities. The comparative analysis of parameters between the lattice parameters of the source δ-Bi_2O_3 shows that the values of the parameters *a* and *b* satisfactorily coincide with the lattice parameters δ-Bi_2O_3, the parameter *c* is distorted from the value of the *a* parameter on $\sqrt{2}$.

Morphological study. Microstructure of bulk samples was studied by scanning electron microscopy (SEM) JOEL JED-2300 with approaching up to ×500 and the ability to carry out elemental analysis.Photographs of the coatings obtained are shown in Figure 4.

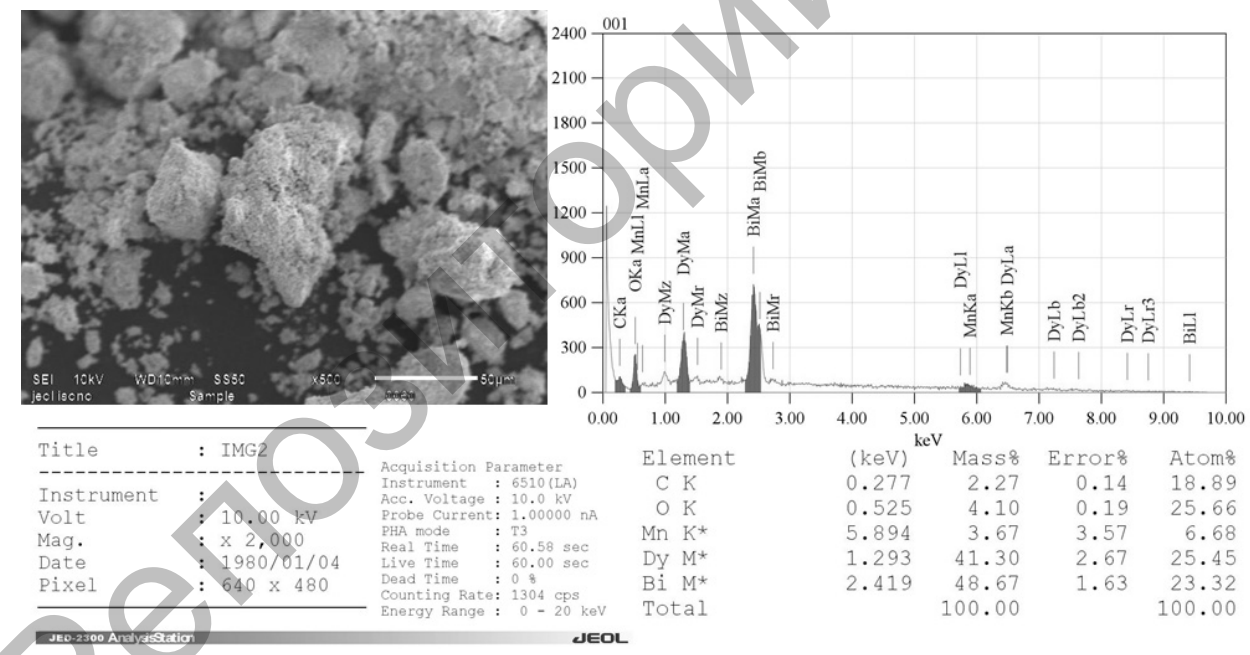

Figure 4. Results of SEM of powder BDMO obtained by the Pechini method

This increase in particle size with the level of doping is apparently due to a change in the melting point of the samples, which reduces the increase in the content of cations of alkaline earth metals. According to Harton et al. (2002), this effect leads to a liquid-phase process, which is facilitated by sintering and increasing grain growth. On the surface, it can be seen that the resulting coating has a dense structure consisting of 50 μm crystals.

The elemental analysis performed on an electron-scanning microscope (Fig. 4) shows that the atomic fractions of the elements practically coincide, which corresponds to the formula of bismuth-dysprosium manganite — BDMO. As can be seen from Figure 4, the powders obtained by this technology are practically monodisperse, which is a great advantage of the method.

Summary

The nanoparticle of the manganite BDMO was synthesized with the Pechini method, using surface-active material. Using the Pechini method, single-phase crystalline nanoparticles were obtained at lower temperatures (up to 900 ºC) as compared with the solid-phase method. Both phase and morphological understanding of the samples were made on the basis of measurements of XRD, SEM features.

Acknowledgments

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Висмутпен легирленген диспрозий манганитінің құрамы және құрылысы

Мақалада мультиферроикті $Bi_{0.8}Dy_{0.2}MnO_3$ материалы Печини әдісі арқылы ары қарай зерттеу үшін синтезделді. Бастапқы заттар ретінде висмут оксиді, марганец оксиді, диспрозий оксиді, азот қышқылы және мочевина қолданылды. Азот қышқылы мен мочевинаны тұндырушы ретінде пайдалану арқылы бір фазалы қосылысты алуға болатындығы көрсетілген. Рентген сәулесі арқылы реакцияның тиімді температурасын анықтау үшін ұнтақты әртүрлі температурада күйдірдік — 600 ºС, 800 ºС, 900 ºС. Перовскиттің кристалдық құрылысына Bi^{3+} ионының енуін рентген фазалық талдау және сканерлеуші электронды микроскоп арқылы зерттедік. Рентген нәтижесі бойынша алынған кристалды $Bi_{0.8}Dy_{0.2}MnO_3$ манганиті Fm-3m(225) кеңістік топқа және кубты кристалдық құрылысқа ие екені байқалды; және оның қарапайым ұяшық параметрлерінің мәні: 5.4763 Å, 5.4763 Å, 5.4763 Å, 90.000, 90.000, 90.000 тең болды. Манганиттің тығыздығы 2211–65 МемСТ бойынша пикнометрлік әдіспен анықталды. Индифферентті сұйықтық ретінде толуол қолданылды. Синтездеп алынған манганиттің пикнометрлік тығыздығы мен рентгендік тығыздығының сәйкес келуі тәжірибе нәтижесінің дұрыстығын дәлелдейді. Бастапқы δ-Bi_2O_3 оксидінің кристалдық ұяшық параметрлері мен манганиттің кристалдық ұяшық параметрлеріне салыстырмалы талдау жүргізілді. Зерттеу нәтижесі «a» және «b» параметрлерінің мәндері сәйкес келетінін көрсетті, «c» параметрі бастапқы мәннен $\sqrt{2}$ сығылған. Сканерлеуші электронды микроскоп нәтижесі бойынша элементтердің атомдық фракциялары толығымен висмутты-диспрозий манганитінің — BDMO берілген формуласымен толығымен сәйкес келеді.

Кілт сөздер: висмут манганиті, легирлеу, Печини әдісі, мультиферроикті, электронды микроскоп, нанокристалл, кубты, сұйық фазалы процесс.

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Состав и структура легированного висмутом манганита диспрозия

В статье мультиферроический материал $Bi_{0.8}Dy_{0.2}MnO_3$ был синтезирован методом Печини для его дальнейшего изучения. В качестве исходных материалов были использованы оксиды висмута, марганца, диспрозия, азотная кислота и мочевина. Показано, что при использовании азотной кислоты и мочевины в качестве осадителя можно получить однофазные порошки. Порошок спекали при различных температурах: 600 ºС, 800 ºС, 900 ºС, соответственно, для оценки их оптимальной температуры спекания на основе рентгеновских лучей. Включение ионов Bi^{3+} в кристаллическую структуру перовскита было проверено с помощью рентгеновского метода и СЭМ. XRD показал, что полученный нанокристаллический $Bi_{0.8}Dy_{0.2}MnO_3$ представляет собой кубическую кристаллическую структуру с пространственной группой: Fm-3m(225) и имеет следующие параметры решетки: 5.4763 Å, 5.4763 Å, 5.4763 Å, 90.000, 90.000, 90.000. Плотность манганита определялась пикнометрическим методом по ГОСТу 2211–65. Толуол служил в качестве индифферентной жидкости. Удовлетворительная согласованность величин рентгеновской и пикнометрической плотностей манганита доказывает правильность результатов эксперимента. Проведен сравнительный анализ взаимосвязи параметров кристаллической решетки с параметрами кристаллических решеток исходного оксида δ-Bi_2O_3. Анализ показывает, что значения параметров «a» и «b» удовлетворительно совпадают с параметрами кристаллической решетки δ-Bi_2O_3, параметр «c» искажен от значения параметра на $\sqrt{2}$. Результаты электронного микроскопа свидетельствуют, что атомные фракции элементов практически совпадают, что соответствует формуле манганита висмута-диспрозия — BDMO.

Ключевые слова: манганит висмута, легирование, метод Печини, мультиферроический, электронный микроскоп, нанокристалл, кубический, жидкофазный процесс.