NANOSYSTEMS: PHYSICS, CHEMISTRY, MATHEMATICS, 2013, 4 (6), P. 844–850

EFFECT OF SINTERING TEMPERATURE ON THE STRUCTURE OF COMPOSITES BASED ON SPINEL AND PEROVSKITE

M. V. Talanov[1], L. A. Shilkina[1], V. M. Talanov[2], N. P. Shabelskaya[2], L. A. Reznichenko[1]

[1]Research Institute of Physics, Southern Federal University, 344090 Rostov-on-Don, Russia

[2]South- Russian State Polytechnic University, 346428, Novocherkassk, Russia

mvtalanov@sfedu.ru

PACS 81.05.Mh, 81.05.Ni, 81.05.Pj, 81.05.Qk

Magnetoelectric composites of $0.6(Ni_{0.7}Zn_{0.3}Fe_2O_4)$ / $0.4((Na, Li, Sr)NbO_3 + MnO_2)$ are prepared by conventional ceramic technology. The effect of composite sintering temperature on their phase composition and structure is studied. It is stated that the composites obtained are two phase systems (perovskite and spinel). It is established that modulation of spinel structure is shown more accurately at low sintering temperatures (1180 ° C), while modulation of perovskite structure is shown at high temperatures (1220 ° C). The discovered modulations of perovskite and spinel structures are assumed be connected with extended defects such as crystallographic shear planes. Increasing composite sintering temperature ($T_{sint.} \geqslant 1200\,^\circ$C) was shown to lead to the disappearance of an impurity phase and the change of perovskite phase composition.

Keywords: composite, perovskite, spinel, temperature of sintering, structure modulation, crystallographic shear planes.

1. Introduction

The coexistence and interrelation of magnetic and electric subsystems in magnetoelectric materials allow us to use them to make different transducers. Towards this end, the principal possibility of controlling magnetic characteristics by variations of electric field appears and vice versa. However, at present, there are almost no materials that have magnetoelectric coefficients of the proper magnitude to make this practical.

As a result, in solid-state physics and chemistry, a new direction in scientific-research is being made — the creation and research of composites with magnetoelectric properties based on heterophase structures having ferroelectric and magnetic components (phases). The advantage of the given approach is the possibility of choosing the magnetic and ferroelectric phases separately and the method of their combination in one material (for example, layers, mixtures, etc.).

In order to create a composite with high magnetoelectric coefficients, it is necessary to satisfy a few conditions: first, magnetic and ferroelectric components of material should have high values for magnetostrictive and piezoelectric parameters; second, low conductivity values for the components and third, a developed mechanical contact between the phases. Additionally, the composite should have the optimal content of the magnetic and ferroelectric phases too.

Composites having magnetic components with spinel structures and ferroelectric components with perovskite structures satisfy these conditions. As a result, these have become widespread [1, 2], however there are poorly studied questions: mutual influence of phases which are different on structure and properties; the target optimization of compositions; and methods for producing composites with high magnetoelectric coefficients.

In this paper, the results of research aimed at finding and creating new spinel — perovskite composites with high magnetoelectric coefficients are presented. A magnetic component has been selected on the basis of a solid solution of spinel $NiFe_2O_4$ and $ZnFe_2O_4$, characterized by high resistance and magnetostrictive coefficient values. The study of composite structures $0.9BaTiO_3$-$0.1Ni_xZn_{1-x}Fe_2O_4$ and $Pb(Ti, Zr)O_3$-$Ni_xZn_{1-x}Fe_2O_4$ showed that the maximum magnetoelectric coefficient was observed at x = 0.2–0.3 [3,4]. Thus, to create a composite structure, the spinel $Ni_{0.7}Zn_{0.3}Fe_2O_4$ has been selected. The ferroelectric component was lead-free perovskite solid solutions based on $(Na, Li)NbO_3$, characterized by relatively high piezoelectric activity and Curie temperature [5].

The aim of this work is to establish the laws of formation for lead-free composites structures of $0.6(Ni_{0.7}Zn_{0.3}Fe_2O_4)$ / $0.4((Na, Li, Sr)NbO_3 + MnO_2)$ obtained using different production means.

2. Experimental

The composites studied in this work were prepared from mixtures of pre-formed spinel and perovskite. Synthesis of the spinel structure $Ni_{0.7}Zn_{0.3}Fe_2O_4$ was carried out using ceramic technology. To intensify the synthetic process for the samples, "chemically pure" potassium chloride was injected. Synthesis was performed according to [3] at 900 ° C for 5 hours. Upon completion of the synthesis, the samples were milled to grains by size less than 0.3 mm and washed with distilled water to remove KCl. Synthesis of perovskite based on $(Na, Li)NbO_3$ was made at $T_{sint.} = (850 - 870)$ ° C for 6 hours. Basic components of the composite have the following structural characteristics: $Ni_{0.7}Zn_{0.3}Fe_2O_4$ – cubic symmetry, the cell parameter a = 8.372Å, 1/8V = 73.35Å^3, $(Na, Li, Sr)NbO_3 + MnO_2$ – phase mixture: rhombic to monoclinic (M) reduced cell and rhombohedral (Rh) in approximately equal amounts. Parameters of M cell are: a = 3.912Å, b = 3.876Å, $\beta = 90.78$ ° , V = 59.32 Å^3, Rh cell parameters: a = 3.907Å, $\alpha = 89.17$ ° , V = 59.58Å^3 (at $T_{sint.} = 1200$ ° C).

The starting materials were weighed with an accuracy of 0.1 mg, homogenized in an agate mortar, placed in an alundum crucible and subjected to heat treatment at 900 ° C for 2 hours. In order to determine the optimal conditions, sintering temperatures of 1110, 1150, 1180, 1200 and 1220 ° C were selected and the samples were sintered with exposure for 2 hours.

X-ray diffraction studies were performed using a DRON 3.0 (CoK_α - radiation). The measured density ($\rho_{meas.}$) was defined by the method of hydrostatic weighing in octane. Calculation of X-ray density ($\rho_{X\text{-ray.}}$) was made by the formula: $\rho_{X\text{-ray.}}$=1,66·M/V, where is the weight of formula unit in grams, V is the volume of the perovskite cell in Å^3. Relative density ($\rho_{rel.}$) was calculated by the formula: $(\rho_{meas.}/\rho_{X\text{-ray.}})\cdot 100\%$.

3. Results and discussion

In Fig. 1, the dependence of $\rho_{meas.}$ on $T_{sint.}$ is given, testifying to the strong influence of $T_{sint.}$ upon $\rho_{meas.}$ Experimental data showed that $((\rho_{max} - \rho_{min})/\rho_{min.} \approx 12\%$, where ρ_{max} — maximum, and ρ_{min} — minimum values of $\rho_{meas.}$, achieved by changing the $T_{sint.}$).

The slowing in growth and the "saturation" of the dependence of $\rho_{meas.}$ ($T_{sint.}$) at $T_{sint.} = 1180$ ° C, may be attributed to the approach of the temperature to the melting point of the sample ($T_{sint.} = 1250$ ° C). The maximum value of $\rho_{rel.}$ (95.6 %) is reached at $T_{sint.} =$ 1200 ° C.

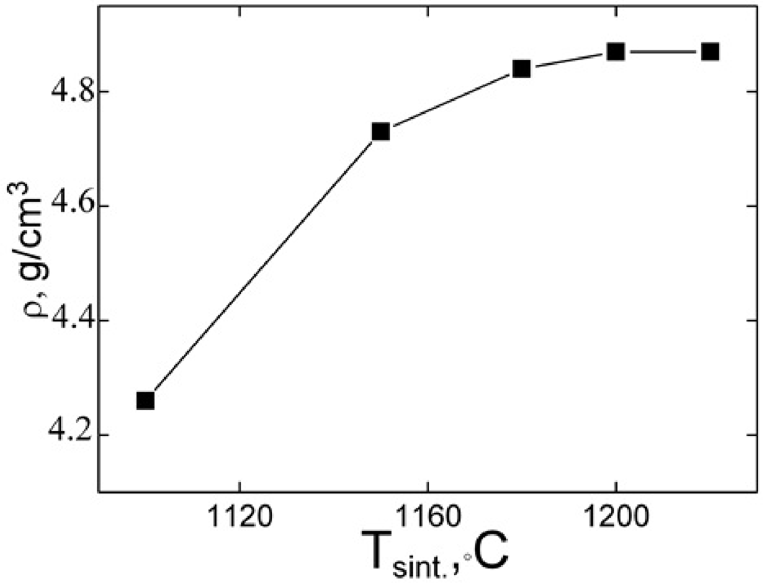

FIG. 1. The dependence of the measured density of the composite from $T_{sint.}$

Fig. 2 shows the diffraction pattern of the studied composite at $T_{sint.}$ = 1180, 1200 and 1220 °C.

In the $T_{sint.}$ = 1180 °C diffractogram, besides reflections for $Ni_{0.7}Zn_{0.3}Fe_2O_4$ and solid solutions based on the (Na, Li)NbO_3 system, few lines are present ($I/I_1 = 4$, where I — relative intensity of a strong reflex of an impurity phase, I_1 — relative intensity of the strongest line on diffractogram) for the outside phase (presumably pyrochlore). Increasing the $T_{sint.}$ to 1200 °C and 1220 °C leads to the disappearance of the lines for an impurity phase and an increase of the reflex intensity for the spinel phase. This is associated with the approach to the optimal $T_{sint.}$ For the spinel phase, at which more perfect crystal structure is formed. Thus, based on X-ray analysis and the results of ρ_{meas} measurement, the optimum $T_{sint.}$ of 1200 °C was chosen.

In Fig. 3, X-ray lines $(200)_C$ and $(220)_C$ of perovskite phase of composite are shown. In Fig. 4 X-ray lines (400) and (440) of spinel phase are given.

Fig. 3 shows that the diffraction patterns for perovskite phase is characterized by a strong diffuse scattering, which distorts the line profiles, especially the $(220)_C$. It is not possible to establish unambiguously the composition of the perovskite phase in the composite. At $T_{sint.}$ = 1180 °C, the solid solution is a mixture of orthorhombic and pseudocubic (not Rh) phases. Pseudocubic phases at $T_{sint.}$ = 1200 and 1220 °C disappear, and the presence of a small amount of Rh phase is not excluded.

Table 1 shows the unit cell parameters for the phases of the composite, and the measured, x-ray and relative densities for the ceramic samples. It is seen that the volume of cells in both cases is reduced when $T_{sint.}$ is increased to 1220 °C and the volume approaches values characteristic of the initial components.

In Fig. 3, it is seen that close to lines $(200)_C$ weak satellites are located. They testify to structure modulation (in Fig. 3, they are denoted with "c^-" and "c^+" from smaller and larger angles θ, respectively). Modulation wavelength, Λ, calculated on the position of the satellite c^- with respect to the main peak-(200), is equal to 127Å. This value equals 32.5 of the cell parameter. The calculation was performed using the formula $\Lambda = (1/d_{200}\text{-}1/d_c^-)^{-1}$ [6].

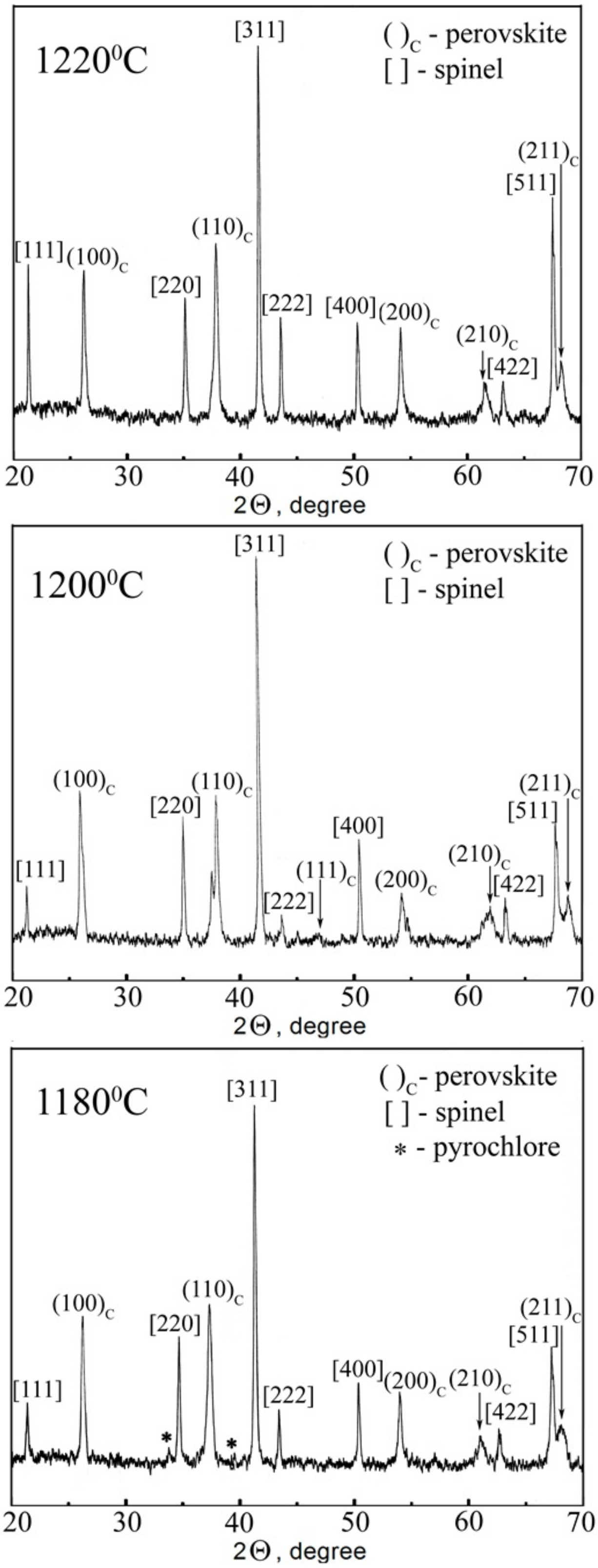

FIG. 2. The XRD pattern of the composite ($T_{\text{sint.}} = 1200\,^{\circ}$C) in the angular range $2\theta = 20$–$70\,^{\circ}$. In square brackets denote spinel lines, while parentheses denote perovskite lines

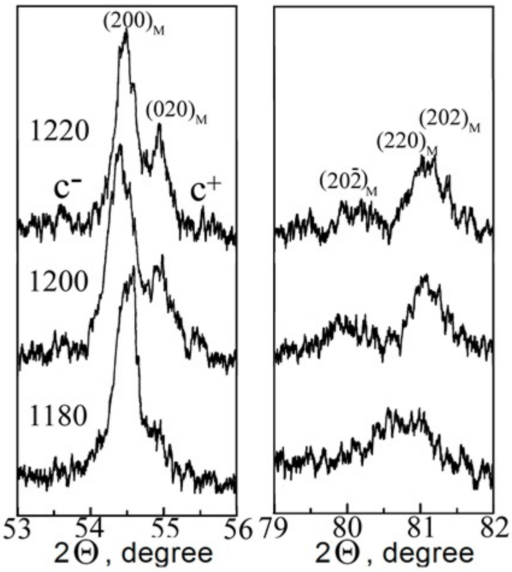

FIG. 3. Diffraction reflections $(200)_C$ and $(220)_C$ of the perovskite phase of the composite at different $T_{sint.}$

TABLE 1. Structural characterization of the composite phases, and the density of the ceramic samples: measured, x-ray and relative

T_{sint} °C	Composition, I/I_1 relative units	Symmetry	Monoclinic cell parameters of the perovskite				$\rho_{x\text{-ray}}$ of the M phase, g/cm^3	Cubic cell parameters of the spinel		$\rho_{x\text{-ray}}$ cubic phase, g/cm^3	$\rho_{x\text{-ray}}$ composite, g/cm^3	ρ_{meas} composite, g/cm^3	ρ_{rel} %
			a,Å	b,Å	β, angle degree	V,Å^3		a,Å	1/8V, Å^3,				
1180	100-spinel 38-perovskite 4-pyrochlore	Cubic+ Monoclinic+ Pseudocubic	- 3.913 3.915	3.883	90.67	59.45 60.01	4.521	8.380	73.55	5.367	5.085	4.84	95.18
1200	100-spinel 38-perovskite	Cubic+ Monoclinic	3.914	3.880	90.76	59.44 60.01	4.543	8.379	73.53	5.369	5.094	4.87	95.60
1220	100-spinel 47-perovskite	Cubic + Monoclinic	3.912	3.878	90.70	59.34	4.551	8.375	73.44	5.376	5.101	4.87	95.48

Half of the cells having wavelength modulation values for the perovskite structure means that the cause of the modulation can be ordered extended defects, such as crystallographic shear planes. In [7,8], for samples with Ti- and Nb- containing compounds, it is shown that the presence of variable valency ions in the material structure may contribute to point defects — anionic vacancies. The latter can be eliminated by shifting one part of the structure relative to the other along a particular crystallographic direction, forming extended defects — plane crystallographic shear. They can be regarded as a translational modulation of the initial structure [9].

Fig. 4 shows that the diffraction of the spinel, unlike perovskite, is characterized by sharp, narrow lines, which indicates well-formed structure.

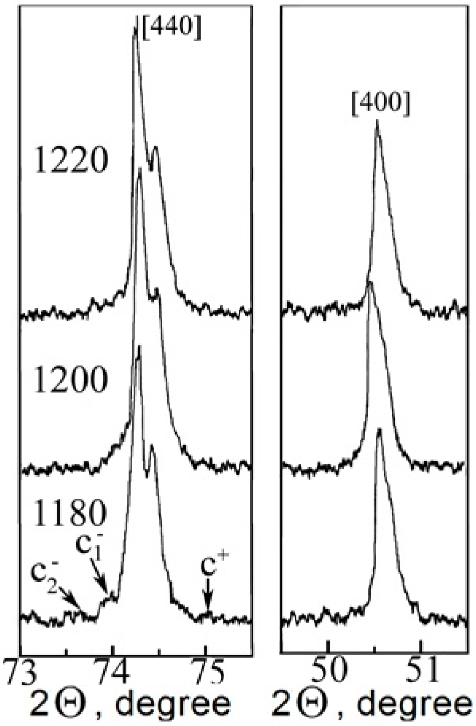

FIG. 4. Diffraction reflexes [400] and [440] of the spinel phase of the composite at different $T_{sint.}$ At $T_{sint.}$=1180 ° C diffusion maxima (satellites c_1^- and c_2^-) are accurately seen based on the [440] line from the side of smaller angles

On the pattern diffraction, obtained for $T_{sint.} = 1180$ ° C, side satellites close to the [440] line from the smaller angles θ are clearly visible. They are indicated in Fig. 4 as c_1^- and c_2^-, corresponding to the wavelength modulation $\Lambda_1 = 421$Å (35.5 cells), $\Lambda_2 = 210$Å, $\Lambda_2 = 1/2\ \Lambda_1$. Note that modulation of the spinel structure is more apparent at low sintering temperatures, while modulation of the perovskite structure – at higher $T_{sint.}$. This can be explained by the following fact; ions with more stable valency states (Ni^{2+} and Zn^{2+}) are in the spinel composition. The iron ion is supposed to be in the trivalent state. The disappearance of modulation in the spinel phase structure for increased $T_{sint.}$ may be connected with the formation of a more perfect crystal structure when approaching the optimal $T_{sint.}$

A perovskite phase contains an ion with a variable valency — Nb^{5+}. This ion is restored at increased temperatures with the formation of oxygen vacancies. These oxygen vacancies in process of their accumulation are ordered and excluded by a crystallographic shift. In [10] it was shown that in stable high-temperature modification of α-Nb_2O_5, which is the main structure-forming reagent of a perovskite phase, the density of extended defects (the planes of the crystallographic shift) increased with increased temperature.

4. Conclusion

Thus, in this paper the following results were obtained:

— the technology for the production of uncontaminated composites $0.6(Ni_{0.7}Zn_{0.3}Fe_2O_4)$ / $0.4((Na, Li, Sr)NbO_3 + MnO_2)$ is developed;

— the dependence of phase composition and structure upon $T_{\text{sint.}}$ was stated; it was shown that the optimal $T_{\text{sint.}}$ for the composite was 1200 ° C;

— it was found that by varying the $T_{\text{sint.}}$, the phase composition of perovskite changes; the disappearance of an impurity phase at increased $T_{\text{sint.}}$ ($\geqslant$ 1200 ° C) was observed; modulation of perovskite structure appeared at higher sintering temperatures ($T_{\text{sint.}} = 1220\,^{\circ}$C) and modulation of spinel structure — at lower $T_{\text{sint.}}$ ($T_{\text{sint.}} = 1180\,^{\circ}$C);

— it was supposed that the detected modulation of the structure of perovskite and spinel may be associated with ordered extended defects such as crystallographic shear planes, which condense and strengthen the composite structure.

References

[1] H. Zheng, J. Wang, S.E. Lofland, et al. Multiferroic $BaTiO_3$-$CoFe_2O_4$ Nanostructures. *Science*, **303**, P. 661–663 (2004).

[2] W. Eerenstein, N.D. Mathur, J.F. Scott. Multiferroic and magnetoelectric materials. *Nature*, **442**, P. 759–765 (2006).

[3] S.K. Upadhyay, V.R. Reddy. Study of $0.9BaTiO_3$-$0.1Ni_xZn_{1-x}Fe_2O_4$ magneto-electric composite ceramics. *J. Appl. Phys.*, **113**, P. 114107(1–5) (2013).

[4] G. Srinivasan, E.T. Rasmussen, R. Hayes. Magnetoelectric effects in ferrite-lead zirconate titanate layered composites: The influence of zinc substitution in ferrites. *Physical Review B*, **67**, P. 014418(1–10) (2003).

[5] A method for producing iron-chromium-nickel spinel, Patent 1 2257953 Russia: B 01 J 23/86, 37/04. V.M. Talanov, N.P. Shabelskaya. South-Russian State Tech. Univ. (NPI); statement 29.01.2004; Publ. 10.08.2005, Bull. N 22.

[6] A. Guinier. *Radiocristallographie.* Moscow, 604 p. (1961).

[7] L.A. Reznichenko, L.A. Shilkina, S.V. Titov, O.N. Razumovskaya. Magnéli phases in Ti-containing oxides and their solid solutions. *Crystallography Reports*, **48**(3), P. 377–383 (2003).

[8] L.A. Reznichenko, L.A. Shilkina, E.S. Gagarina, Yu.I. Yuzyuk, O.N. Razumovskaya, A.V. Kozinkin. Crystallographic shear in niobium oxides of different compositions. *Crystallography Reports*, **49**(5), P. 820–827 (2004).

[9] C.N.R. Rao, J. Gopalakrishnan. *New directions in solid state chemistry.* Cambridge University Press, Cambridge, 568 p. (1997).

[10] L.A. Reznichenko, V.V. Akhnazarova, L.A. Shilkina, O.N. Razumovskaya, S.I. Dudkina. Invar effect in n-Nb_2O_5, αht-Nb_2O_5, and L-Nb_2O_5. *Crystallography Reports*, **54**(3), P. 483–491 (2009).