Raman investigation of multiferroic $BiFeO_3$ and $Bi_{1-x}Sm_xFeO_3$ materials synthesized by the sol-gel method

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Abstract
The current work presents the investigation results of multiferroic materials ($BiFeO_3$ and $Bi_{1-x}Sm_xFeO_3$) with perovskite structure, which possesses two types of orderings: ferromagnetic and ferroelectric. Also, the obtained samples were investigated by Raman spectroscopy to provide detailed information about chemical structure, phase purity and polymorphism, crystallinity and molecular interactions. To enhance the magnetoelectric interaction of bismuth ferrite samples, Bi cations were substituted by isovalent Sm cations with the formation of systems with the general formula $Bi_{1-x}Sm_xFeO_3$, where x = 7.0; 10.0; 20.0 and 25.0. The interest was to study the features of the formation of ferromagnetic composites both in the form of powders and in the form of films on a silicon substrate, as well as to explore the effect of the formation method on their magnetoelectric properties.

Introduction
To develop new effective materials for various applications, donor and / or acceptor cationic substitutions are used to achieve the required properties. In this work, we investigated multiferroic materials ($BiFeO_3$ and $Bi_{1-x}Sm_xFeO_3$) with perovskite structure via Raman spectroscopy to provide detailed information about chemical structure, phase purity and polymorphism, crystallinity and molecular interactions.

Experimental
The synthesis of $BiFeO_3$ and $Bi_{1-x}Sm_xFeO_3$ composites was carried out by the sol-gel method. Among the available chemical methods, sol-gel synthesis is known as a universal method that allows the synthesis of nanoparticles with chemical composition and crystallography similar to particles obtained by solid-state reactions but with better morphology including $BiFeO_3$ and $Bi_{1-x}La_xFeO_3$ films and powders [1 – 4]. The synthesis of $BiFeO_3$ and $Bi_{1-x}Sm_xFeO_3$ composites was carried out using separate hydrolysis of each of the precursors (iron nitrate nanohydrate $Fe(NO_3)_3{\times}9H_2O$, 99% purity; bismuth nitrate pentahydrate $Bi(NO_3)_3{\times}5H_2O$, 99% purity, and $Sm(NO_3)_3{\times}6H_2O$ all from Merck) with their subsequent mixing. First, $Fe(NO_3)_3 \times 9H_2O$ was mixed in the diluted lemon acid ($C_6H_8O_7$) and glycerol $C_3H_8O_3$ (volume ratio 1:4) solution to form a Fe precursor solution. The solution was continuously stirred for 30 min at 50°C to completely dissolve the ferric nitrate. Bi and Sm precursor solution was obtained through a similar process. Secondly, Fe precursor solution was mixed with Bi and Sm precursor solution

(in case of formation $Bi_{1-x}Sm_xFeO_3$), followed by continuous ultrasonic stirring for 30 min at 25 °C.
$BiFeO_3$ and $Bi_{1-x}Sm_xFeO_3$ films were formed on a silicon substrate by spin coating method. Heat treatment in the air of each layer of $BiFeO_3$ or $Bi_{1-x}Sm_xFeO_3$ was carried out at a temperature of 250 °C for 5 minutes.
After that, obtained nanopowders and films were annealed in a muffle furnace for 1 hour.

Results and discussion

The dependence of the Raman spectra of samples prepared at 600 C and 650 °C temperatures on the concentration of Sm is shown in Figure 1. For the samples with lower concentration of Sm we obtained 9 Raman modes (3A+5E) which indicate the rhombohedral perovskite structures [5]. With increasing number of doping atoms, A1-1 and A1-2 modes almost merge together demonstrating the existence of the tetragonal phase with higher crystal symmetry [6]. It can be observed that for higher calcination time, the transformation from the rhombohedral to tetragonal structure takes place with a higher concentration of doping atoms. The positions of Raman modes for the samples are presented in table 1.

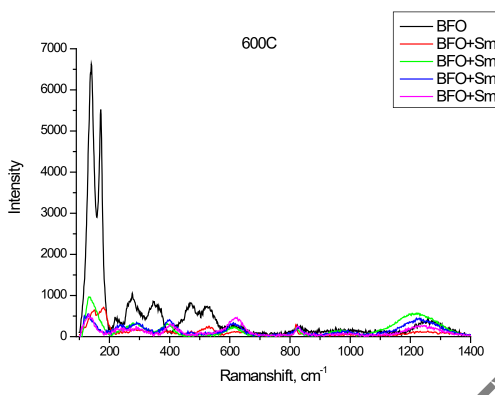

Fig. 1a. Raman spectra of BFO with different concentration of Sm (600 °C)

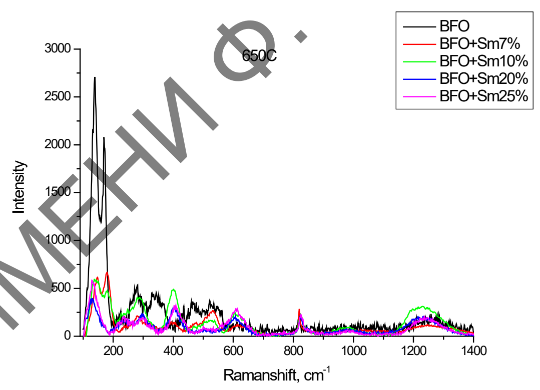

Fig. 1b. Raman spectra of BFO with different concentration of Sm (650 °C)

Table 1. Positions of Raman modes for the samples

Raman mode (cm^{-1})	600C					650C				
	BFO	BFO +Sm 7%	BFO+ Sm 10%	BFO+ Sm 20%	BFO +Sm 25%	BFO	BFO +Sm 7%	BFO+ Sm 10%	BFO+ Sm 20%	BFO+ Sm25 %
A1-1	140	148	133	130	133	139	147	137	132	130
A1-2	171	179	-	-	-	170	180	181	-	-
A1-3	220	230	-	-	-	225	236	240	238	235
E	276	290	291	290	289	276	281	288	295	296
A1-4	346	399	394	398	402	344	400	401	404	403
E	470	472	-	-	-	469	478	474	-	-
E	525	530	-	-	-	524	530	527	-	-
E	614	615	616	617	619	612	613	611	612	613

Conclusion

Multiferroic materials ($BiFeO_3$ and $Bi_{1-x}Sm_xFeO_3$) with the perovskite structure (600 °C and 650 °C annealing temperature) with different Sm content from 7% to 25% were synthesized by sol-gel method and were investigated by Raman spectroscopy. It was established that with the increasing number of doping atoms, A1-1 and A1-2 modes almost merge demonstrating the existence of the tetragonal phase with higher crystal symmetry.

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References

[1] Shirsath S. E., Mane M. L., Yasukawa Y., Liu X., Morisako A. J Nanopart Res. 2013;15:1976. DOI 10.1007/s11051-013-1976-8.
[2] Brinker C. J., Scherer G. W. Sol-gel science: The physics and Chemistry of Sol-Gel Processing, Academ. Press, San Diego, 1990.
[3] Semchenko A. V., Sidsky V. V., Bdikin I., Gaishun V. E., Kopyl S., Kovalenko D. L., Pakhomov O., Khakhomov S. A., Kholkin A. L. Materials. 1 (2021) 1694.
[4] A. V. Semchenko, S. A. Khakhomov, V. V. Sidsky, V. E. Gaishun, D. L. Kovalenko, et al. International Conference on Global Research and Education, 9/4 ,(2019) :113 – 118.
[5] Rodrigues, H. O., et al. Physica B: Condensed Matter 406.13 (2011): 2532 – 2539.
[6] Zhang, Cheng, et al. Journal of Advanced Dielectrics 5.03 (2015): 1550025.