Volume 509 (2017) ISSN: 0015-0193

FERROELECTRICS

The international journal devoted to the theoretical, experimental, and applied aspects of ferroelectrics and related materials.

PROCEEDINGS OF

SECOND INTERNATIONAL WORKSHOP MODERN NANOTECHNOLOGY (IWMN-2016)

PART II OF II

Ekaterinburg, Russia August 27–29, 2016

GUEST EDITOR Vladimir Shur

Taylor & Francis Taylor & Francis Group

Ferroelectrics

ISSN: 0015-0193 (Print) 1563-5112 (Online) Journal homepage: https://www.tandfonline.com/loi/gfer20

Low-temperature features of Raman spectra below magnetic transitions in multiferroic $Ho_{1-x}Nd_xFe_3(BO_3)_4$ and $Sm_{1-y}La_yFe_3(BO_3)_4$ single crystals

A. Krylov, E. Moshkina, S. Sofronova, I. Gudim, V. Temerov & A. Vtyurin

To cite this article: A. Krylov, E. Moshkina, S. Sofronova, I. Gudim, V. Temerov & A. Vtyurin (2017) Low-temperature features of Raman spectra below magnetic transitions in multiferroic $Ho_{1-x}Nd_xFe_3(BO_3)_4$ and $Sm_{1-y}La_yFe_3(BO_3)_4$ single crystals, Ferroelectrics, 509:1, 92-96, DOI: 10.1080/00150193.2017.1294040

To link to this article: https://doi.org/10.1080/00150193.2017.1294040

Published online: 10 May 2017.

FERROELECTRICS
2017, VOL. 509, 92–96
http://dx.doi.org/10.1080/00150193.2017.1294040

Taylor & Francis
Taylor & Francis Group

Low-temperature features of Raman spectra below magnetic transitions in multiferroic $Ho_{1-x}Nd_xFe_3(BO_3)_4$ and $Sm_{1-y}La_yFe_3(BO_3)_4$ single crystals

A. Krylov, E. Moshkina, S. Sofronova, I. Gudim, V. Temerov, and A. Vtyurin

Kirensky Institute of Physics, Federal Research Center KSC SB RAS, Krasnoyarsk, Russia

ABSTRACT

Raman spectra changes in multiferroic $Ho_{1-x}Nd_xFe_3(BO_3)_4$ (x = 0, 0.25, 0.5, 0.75) and $Sm_{1-y}La_yFe_3(BO_3)_4$ (y = 0, 0.75) single crystals at low temperatures have been analyzed. The anomalies corresponding to the phase transition of the second order have been detected at the temperatures of magnetic phase transitions, being consistent with previously reported results of the magnetization study. A number of anomalies in the temperature dependences of the spectral lines associated with the occurrence of magnetic order. A mode corresponding to two-magnon scattering was revealed. Comparison of the features of low-temperature low-frequency spectra of solid solutions Ho-Nd and Sm-La has been carried out.

ARTICLE HISTORY
Received 29 August 2016
Accepted 21 November 2016

KEYWORDS
Raman spectra; magnetic ordering; huntite; rare-earth ferroborates

1. Introduction

Multiferroic materials demonstrating the coexistence of at least two ferroic orders ((anti)ferroelectric, (anti)ferromagnetic, and (anti)ferroelastic) are expected to find applications in many devices. Among these materials, the ones with the coexistence of ferroelectricity and ferromagnetism are the most promising. In this case, a strong coupling between the two ferroic orders is of utmost importance, as in multiferroic materials the coupling between different order parameters can produce additional functionalities. The application of multiferroics will make it possible to enlarge significantly the functional possibilities of spintronics.

Crystals of the $RFe_3(BO_3)_4$ family (R is a rare earth ion) were reported to possess multiferroic features, demonstrating both structural and magnetic phase transitions [1–4], where transition points may vary by rare earth composition. The high-temperature phase of crystals with a huntite structure has trigonal symmetry with space group R32. Depending on the radii ratio of the rare-earth and metal ions, the structural phase transition to the phase with P3121 space symmetry can be realized in huntites. This phase transition does not take place in $Sm_{1-x}La_xFe_3(BO_3)_4$ (x = 0, 0.75). At low temperatures, these crystals possess trigonal symmetry with space group R32. The magnetic moments of the Fe ions in $Sm_{1-x}La_xFe_3(BO_3)_4$ (x = 0, 0.75) are ordered antiferromagnetically at T_N = 32 K (x = 0) and T_N = 31 K (x = 0.75) and are located in the basal plane ab. The magnetic moments of samarium ions,

CONTACT S. Sofronova shusy@iph.krasn.ru
Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gfer.

biased by the exchange field of the Fe subsystem, are also located in the basal plane. Under substitution of the Sm ions by the nonmagnetic lanthanum ions, the antiferromagnetic interactions between the iron and rare-earth subsystems become weaker. This fact is confirmed by the total magnetic moment increasing [5].

In this work, we used Raman spectroscopy to study $Ho_{1-x}Nd_xFe_3(BO_3)_4$ (x = 0, 0.25, 0.5, 0.75) and $Sm_{1-x}La_xFe_3(BO_3)_4$ (y = 0, 0.75) single crystals. The aim of this study is to investigate possible existence of a soft mode and effects of magnetic transitions on Raman spectra.

2. Experiment

Temperature measurements were performed in the temperature range 10–75 K. Raman spectra of the single crystals were recorded with a Horiba Jobin Yvon T64000 triple spectrometer equipped with a liquid nitrogen cooled charge coupled device detection system in subtractive dispersion mode using backscattering geometry. Ar+ ion laser Spectra-Physics Stabilite 2017 with $\lambda = 514.5$ nm and 7 mW power on a sample was used as an excitation light source. Temperature measurements were carried out with closed cycle ARS CS204-X1. SS helium cryostat controlled by LakeShore 340 temperature controller. The temperature was monitored by LakeShore DT-6SD1.4L silicon diode. Indium foil was used as a thermal interface. Measurements were taken inside the cryostat under pressure of 10^{-6} mBar. The spectra were studied with a temperature step 0.5 K. This measurement protocol was the same as that described in Refs. [6, 7].

3. Results and discussion

Raman spectra of Sm-La system have no changes associated with structural phase transition in the entire temperature range. Raman spectra change at low temperatures T = 10–75 K, including the region of the magnetic phase transition, has been analyzed. The anomalies corresponding to the phase transition of the second order have been detected at temperatures $T_N = 32$ K (x = 0) and $T_N = 31$ K (x = 0.75) in the spectra of the studied compounds. These temperatures correspond to those of magnetic phase transitions and are consistent with previously reported results of the magnetization study. It was found, that one of the major changes in the spectrum occurred in the low-frequency range (below 100 cm^{-1}). A mode corresponding to two-magnon scattering is observed there (Fig. 1). Detailed studies have shown that this mode has internal structure due to a number of unstable modes (40–80 cm^{-1}). Nevertheless, the nature of the changes relevant to the phase transition for crystals with different quantity Sm and La is different. It can be seen in the offset lines below the temperature of the magnetic phase transition similar to those previously observed in $TbFe(BO_3)_4$ [8], as well as in the emergence of new lines below the temperature of the magnetic phase transition in the solid solutions $Nd_{1-x}Ho_xFe_3(BO_3)_4$.

In Nd-doped crystals, significant modification of Raman scattering was induced by magnetic ordering below the Neel temperature (about 40 K), that include both magnon scattering and strong intensity redistribution of lattice modes [7]. This is caused by appearance of the low wavenumber mode due to magnetoelastic scattering in the crystal, which is strongly temperature-dependent below the Neel temperature. Detailed study of this magnon revealed the presence of an internal structure consisting of a number of unstable vibrations

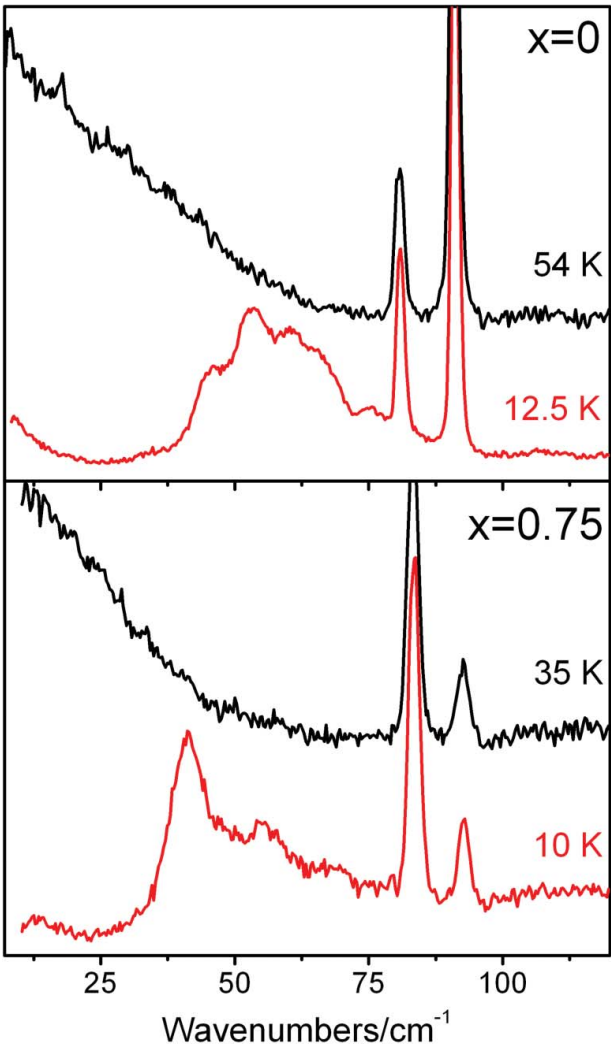

Figure 1. The low wavenumber part of Raman spectra of the single crystals $Sm_{1-x}La_xFe_3(BO_3)_4$ (x = 0; 0.75).

(40–80 cm^{-1} at x = 0 and 30–75 cm^{-1} at x = 0.75) (Fig. 2). This result is consistent with the Raman spectroscopy study of other compounds of the rare-earth ferroborates family (R = Nd, Gd, Y, Tb). Indeed, with the appearance of long-range magnetic order in the iron subsystem, the Raman spectra demonstrate the growth of a broad-structured scattering band ascribed to two-magnon Raman scattering, followed by the creation of the magnon pair. The center position of this broad magnetic scattering band in the spectrum of studied huntites $Sm_{1-x}La_xFe_3(BO_3)_4$ (x = 0, 0.75) depends on the radius of the rare-earth ion. What confirms an earlier assumption about the direct proportional dependence of the center position shift on the ionic radii (R(Nd) = 0.983 Å, R(Sm) = 0.958 Å, R(La) = 1.032 Å) [2]. Another typical feature of the low-wavenumber Raman spectra of magnetically-ordered phase ferroborates is the low-frequency peak corresponding to spin-flip scattering on single rare-earth ion moments [2, 10]. Here, the

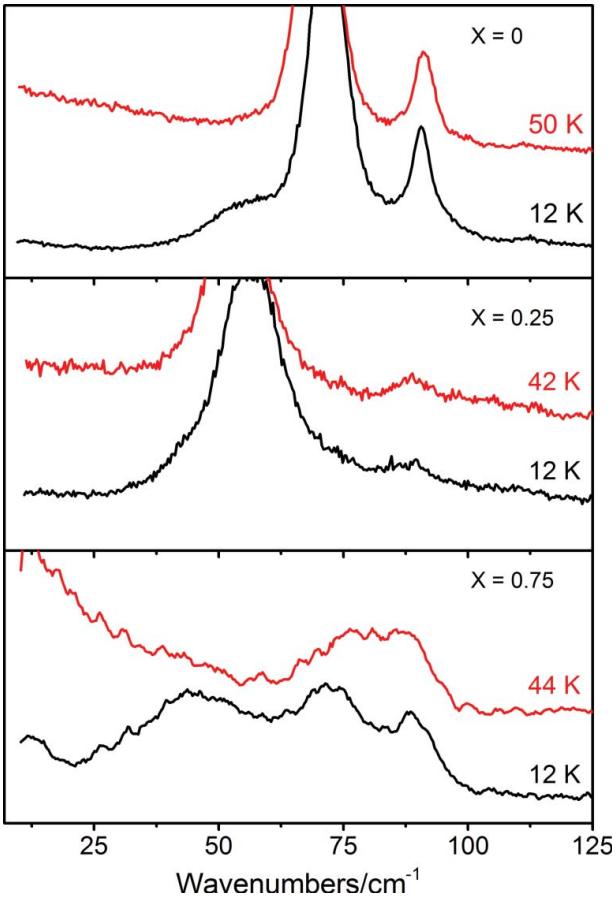

Figure 2. The low wavenumber part of Raman spectra of the single crystals $Nd_{1-x}Ho_xFe_3(BO_3)_4$ (x = 0; 0.25; 0.75).

low-frequency peak was not found. This result is also consistent with the data on the magnetization measurements of $Sm_{1-x}La_xFe_3(BO_3)_4$ (x = 0, 0.75), where spin-flip transitions are absent [5].

Below Neel temperature [11, 12], the crystals $Ho_{1-x}Nd_xFe_3(BO_3)_4$ are observed to recover the soft modes, earlier this was explained by magnon scattering [2]. Close temperatures of magnetic transitions and the recovery patterns of magnon soft modes in pure and mixed crystals indicate that their magnetic ordering is not related to the rare-earth subsystem and is determined by exchange interactions in Fe–O–Fe chains [4].

4. Conclusion

The presence of low-frequency modes emerging from the elastic line after magnetic ordering is possible to note when we compare the features of low-temperature low-frequency spectra of solid solutions Ho-Nd and Sm-La. The interesting feature of low-temperature Raman spectra is the internal structure of this mode in Sm-La solid solution. We link of the internal structure with the splitting of the electron levels of the magnetic ion samarium.

Acknowledgments

This work was partly supported by Russian Foundation for Basic Research (Grant No. 16-02-00102). Authors thank Dr. Svetlana Krylova for discussion and perform results.

References

1. A. K. Zvezdin, S. S. Krotov, A. M. Kadomtseva, G. P. Vorob'ev, P. opov. YuF, A. P. Pyatakov, L. N. Bezmaternykh, E. A. Popova, Magnetoelectric effects in gadolinium iron borate $GdFe_3(BO_3)_4$. *JETP Lett.* **81**, 272–276 (2005).
2. D. Fausti, A. A. Nugroho, P. H. M. van Loosddrecht, S. A. Klimin, M. N. Popova, L. N. Bezmaternykh, Raman scattering from phonons and magnons in $RFe_3(BO_3)_4$. *Phys Rev B.* **74**, 024403 (2006).
3. A. M. Kuzmenko, A. A. Mukhinn, I. vanov. VYu, A. M. Kadomtseva, L. N. Bezmaternykh, Effects of the interaction between R and Fe modes of the magnetic resonance in $RFe_3(BO_3)_4$ rare-earth iron borates. *JETP Lett.* **94**, 294–300 (2011).
4. A. S. Krylov, S. N. Sofronova, I. A. Gudim, A. N. Vtyurin, Magnetoelastic interactions in Raman spectra of $Ho_{1-x}Nd_xFe_3(BO_3)_4$ crystals. *Solid State Commun.* **174**, 26–29 (2013).
5. E. V. Eremin, N. V. Volkov, V. L. Temerov, I. A. Gudim, A. F. Bovina, Specific features of magnetic properties of rare-earth ferroborates $Sm_{1-x}La_xFe_3(BO_3)_4$. *Phys Solid State.* **57**, 569–575 (2015).
6. A. S. Krylov, E. M. Kolesnikova, L. I. Isaenko, S. N. Krylova, A. N. Vtyurin, Measurement of Raman-scattering spectra of $Rb_2KMoO_3F_3$ crystal: evidence for controllable disorder in the lattice structure. *Cryst Growth Des.* **14**, 923–927 (2014).
7. A. S. Krylov, S. N. Sofronova, E. M. Kolesnikova, I. vanov. YuN, A. A. Sukhovsky, S. V. Goryainov, A. A. Ivanenko, N. P. Shestakov, A. G. Kocharova, A. N. Vtyurin, Experimental and theoretical methods to study structural phase transition mechanisms in $K_3WO_3F_3$ oxyfluoride. *J Solid State Chem.* **218**, 32–37 (2014).
8. A. V. Peschanskii, A. V. Yeremenko, V. I. Fomin, L. N. Bezmaternykh, I. A. Gudim, Raman scattering under structural and magnetic phase transitions in terbium ferroborate. *Low Temp Phys.* **40**, 171–178 (2014).
9. V. I. Zinenko, M. S. Pavlovskii, A. S. Krylov, I. A. Gudim, E. V. Eremin, Vibrational spectra and elastic, piezoelectric, and magnetoelectric properties of $HoFe_3(BO_3)_4$ and $HoAl_3(BO_3)_4$ crystals. *J Exp Theor Phys.* **117**, 1032–1041 (2013).
10. A. V. Peschanskii, V. I. Fomin, I. A. Gudim, Raman scattering in multiferroic $SmFe_3(BO_3)_4$. *Low Temp Phys.* **42**, 475–483 (2016).
11. T. Stanislavchuk, E. Chukalina, M. Popova, L. N. Bezmaternikh, I. A. Gudim, Investigation of the iron borates $DyFe_3(BO_3)_4$ and $HoFe_3(BO_3)_4$ by the method of Er^{3+} spectroscopic probe. *Phys Lett A.* **368**, 408–411 (2007).
12. P. Fischer, V. Pomjakushin, D. Septyakov, L. Keller, M. Janoschek, B. Roessli, J. Schefer, G. Petrakovskii, L. N. Bezmaternikh, V. Temerov, D. Velikanov, Simultaneous antiferromagnetic Fe^{3+} and Nd^{3+} ordering in $NdFe_3(^{11}BO_3)_4$. *J Phys Condens Mat.* **18**, 7975–7989 (2006).