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SHORT COMMUNICATION

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Temperature-dependent absorption lines observation in Raman spectra of $SmFe_3(BO_3)_4$ ferroborate

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Abstract

The paper demonstrates possibilities of observation and thermal dependency study of the absorption lines as a co-product of Raman spectroscopy study in $SmFe_3(BO_3)_4$ ferroborate. Raman spectra of the ferroborate were studied in a wide temperature range ($T = 10 \div 300$ K). Temperature-dependent absorption lines sensitive to the magnetic phase transition have been observed in Raman spectra at two spectral ranges.

KEYWORDS

absorption, ferroborates, huntite, level splitting, magnetic phase transitions

1 | INTRODUCTION

Rare-earth ferroborates attract much attention of the research groups as magnetic, optic, and magnetoelectric materials.[1–6] Due to the large variety of the interesting anomalous effects and the potential applications, to date, the physical properties of many compounds of this family have been studied in detail.[1–6] Among the set of the excellent works, there are those devoted to Raman spectroscopy study, involving temperature and pressure evolution of the spectral lines, high-quality spectra analysis.[5–8]

The present paper is a continuation of the Raman spectroscopy study of $SmFe_3(BO_3)_4$.[9] The previous part of the research is devoted to crystal growth conditions, thermal evolution of the Raman lines, and the investigation of the magnetic phase transition via the changing of the Raman spectra. The observation of the magnetic phase transition at the absence of the external magnetic field was possible due to the presence of the intrinsic "exchange field" due to the establishment of the magnetic order in the sample. It was shown that $SmFe_3(BO_3)_4$ ferroborate undergoes a magnetic phase transition at the temperature $T_N = 32$ K; no additional structure or magnetic phase transitions have been observed in $T = 10 \div 300$ K temperature range as expected.[9] The main changes of Raman spectra at the temperature of found magnetic phase transition have been observed in the low-wavenumber region (up to 100 cm^{-1}) where the mode ascribed to magnon scattering appears. We have shown in detail that this mode has internal structure, meaning that the set of spectral lines ascribed to two-magnon scattering appears (40–80 cm^{-1}). Along with the low-wavenumber anomalies, the sensitivity to the magnetic phase transition of positions, linewidths, and relative intensities of some spectra lines of lattice vibration range has been found. Peschanskii et al.[10] considered that these changes had a non-phonon origin and related to the splitting of the ground multiplet $^6H_{5/2}$ of a Sm^{3+} ion. The hypothesis has been confirmed by the comparison of the Raman spectra and the optical absorption spectra.[11] So Peschanskii et al.[10] showed that using Raman technique, it is possible to study the low-wavenumber electronic transitions.

Along with the features of the spectra mentioned above and studied in previous studies[7,9,10] in detail, one more feature of the spectra related to the electronic transition has been found using Raman spectroscopy study. Moreover, we would like to devote the present paper to this peculiarity.

2 | EXPERIMENT

A single crystal of $SmFe_3(BO_3)_4$ has been synthesized from the flux based on the bismuth trimolibdate $Bi_2Mo_3O_{12}$.[9] The studied sample size was about $2 \times 2 \times 1$ mm^3, without any visible defects.

Raman spectra in the backscattering geometry 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. Ar + ion laser Spectra-Physics Stabilite 2017 with $\lambda = 514.5$ nm and $\lambda = 488$ nm and 7 mW power on a sample was used as an excitation light source.

The temperature experiments were carried out in the dynamic regime by varying the sample temperature. The rate of temperature variation was 0.5 K/min. Overall time for a single spectrum accumulation was within 30 s. The spectra were acquired with a temperature step 0.5 K. The measurement protocol in detail is described by Moshkina et al.[9]

3 | RESULTS

Raman spectrum of $SmFe_3(BO_3)_4$ single crystal obtained at the temperature $T = 12.5$ K and spectral range up to 1,700 cm^{-1} using $\lambda = 514.5$ nm excitation is shown in Figure 1. The interesting feature of this spectrum is the presence of the lines with the low "negative" intensity in comparison with the background level in the spectral ranges 520–550 cm^{-1} and 1,630–1,660 cm^{-1}. These spectral lines are considered as absorption lines of the optical spectrum. The appearance of these lines in the Raman spectra could be related to the weak luminescence typical for the crystals of rare-earth huntites or to the re-emission from the indium foil substrate.

To prove the accuracy of the obtained data, the Raman spectrum of $SmFe_3(BO_3)_4$ was registered using different wavelengths of the excitation radiation. So for proving this hypothesis, the same experiment has been carried out using $\lambda = 488$ nm excitation wavelength. In Figure 2, two spectra—obtained at $T = 12.5$ K using two excitation wavelengths $\lambda = 514.5$ nm and $\lambda = 488$ nm—are presented. It is clear that the changing of the wavelength does not change the positions of the found lines—the wavelength dependence of the positions means the non-phonon origin of these spectral "absorption" lines. Using absolute scale, the detected lines correspond to the spectral ranges 17,780–17,800 cm^{-1} (Figure 2) and 18,880–18,915 cm^{-1} (Figure 2). In the scale of the absolute cm^{-1}, the obtained values of the wavenumbers of the absorption lines have matched in the spectral range 18,880–18,915 cm^{-1}. In addition, due to the experiment with the $\lambda = 488$ nm excitation wavelength, one more range with the absorption lines have been found (19,960–19,990 cm^{-1}).

Optical transmission spectra of $SmFe_3(BO_3)_4$ ferroborate were studied by Popova et al.[11] In agreement with this work, found absorption lines correspond to $^6H_{5/2} \rightarrow {}^4F_{5/2}$ and $^6H_{5/2} \rightarrow {}^4F_{3/2}$ transitions. The line positions are in good agreement with the values of the energy levels of the Sm^{3+} ion in paramagnetic phase.

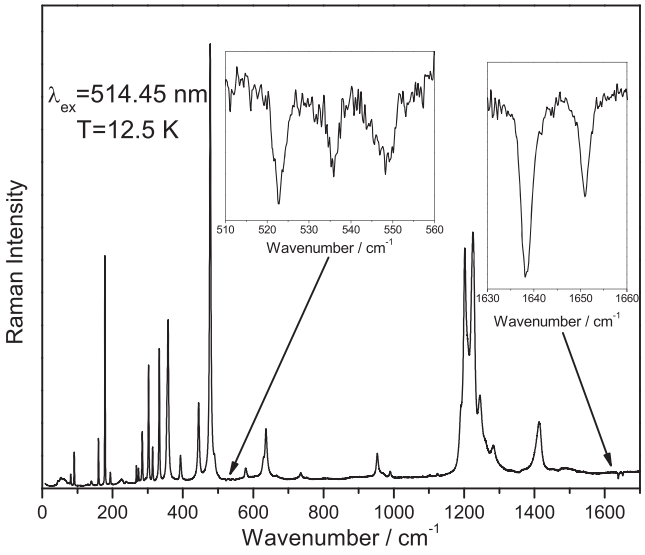

FIGURE 1 Raman spectrum of $SmFe_3(BO_3)_4$ single crystal obtained at $T = 12.5$ K

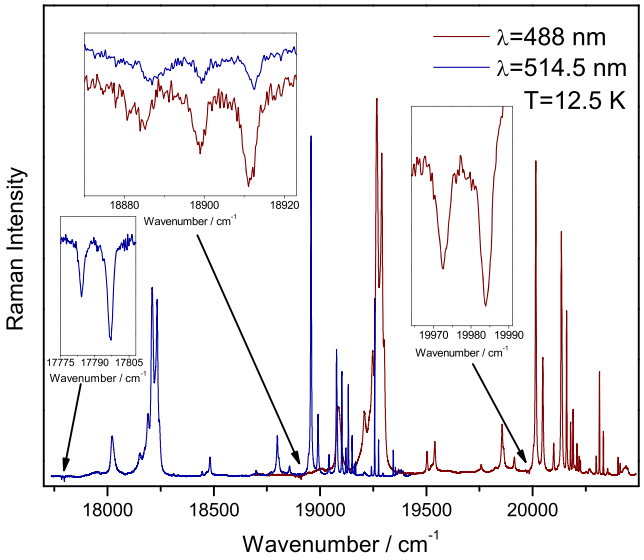

FIGURE 2 Raman spectra of $SmFe_3(BO_3)_4$ single crystal obtained at $T = 12.5$ K using two excitation wavelengths $\lambda = 514.5$ nm and $\lambda = 488$ nm (using absolute scale). Evidence of the non-phonon origin of the observed "absorption" lines [Colour figure can be viewed at wileyonlinelibrary.com]

The temperature dependencies of the absorption lines have been studied using dynamical regime of the temperature driving. The dependencies of the line positions on the temperature are shown in Figures 3 and 4. As it is seen, there is a splitting of absorption lines in both spectral ranges below the temperature about $T_N = 32$ K, which corresponds to the temperature of magnetic phase transition. This splitting is caused by the double Kramers degeneracy removal of the energy levels by exchange interactions of the samarium and iron ions, which magnetic moments orient in planes $\perp c$.[11,12]

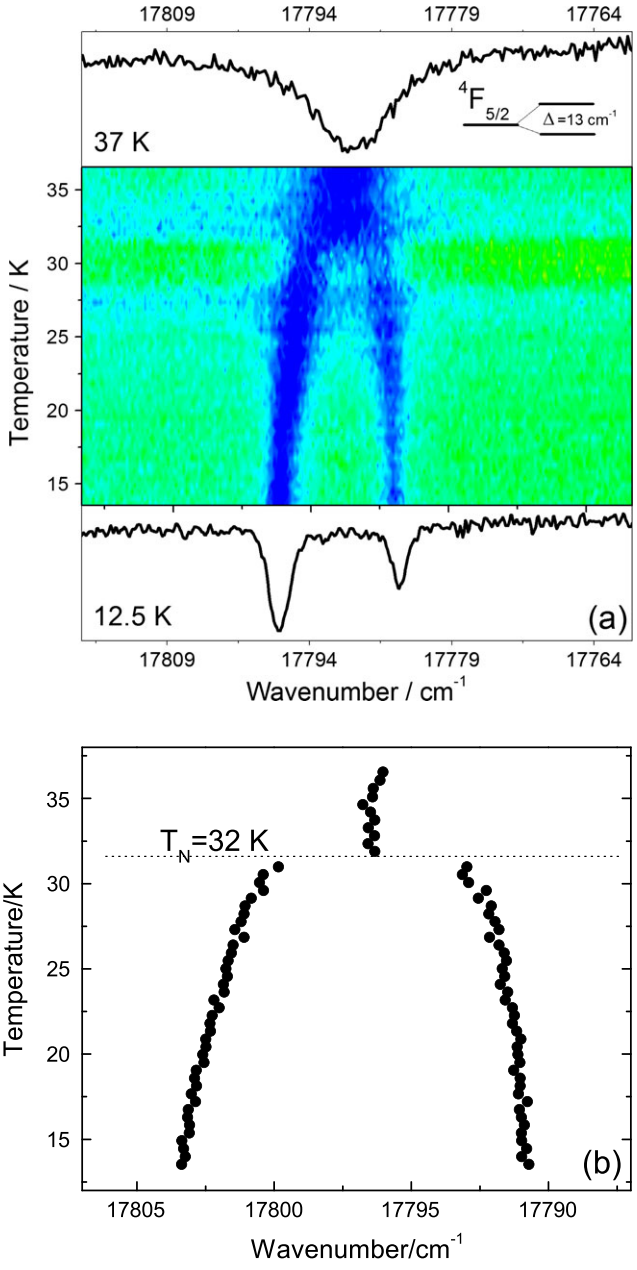

FIGURE 3 Temperature dependence of absorption lines observed in the Raman spectra (Raman signal map [a] and fitting results [b])[9] of $SmFe_3$ $(BO_3)_4$ in the range 17,780–17,800 cm^{-1} [Colour figure can be viewed at wileyonlinelibrary.com]

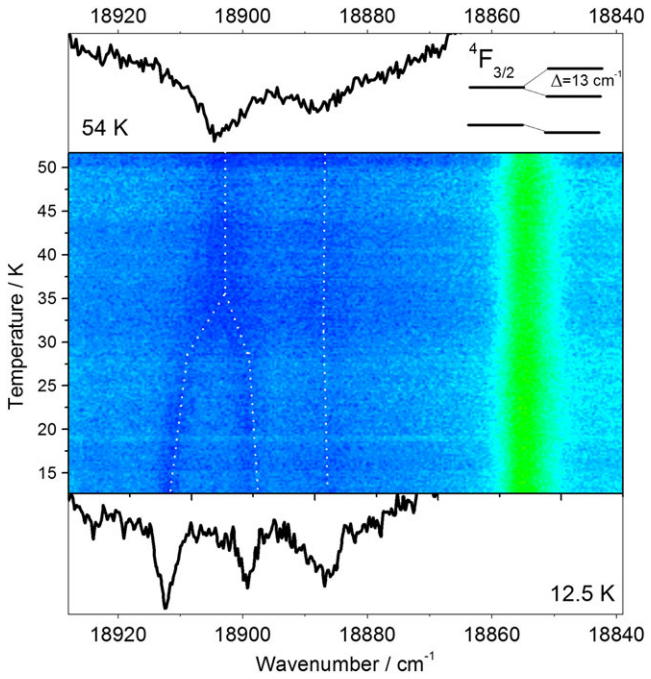

FIGURE 4 Temperature dependence of absorption lines observed in the Raman spectra of $SmFe_3$ $(BO_3)_4$ in the range 18,880–18,915 cm^{-1} [Colour figure can be viewed at wileyonlinelibrary.com]

The present results show that the Raman technique due to the high sensitivity and the high spectral lines resolution could be applied not only to the vibration transitions study of the rare-earth ferroborates but also to the study of separate ranges of its optical spectra. Moreover, the dynamical technique of the temperature lowering used in this work allows registering the smallest peculiarities of the temperature behavior of the optical spectra of crystals that makes possible to measure the value of the exchange splitting of Kramers doublets with a high accuracy.

4 | CONCLUSIONS

The temperature-dependent absorption lines were detected in the two spectral ranges in the Raman spectra of $SmFe_3$ $(BO_3)_4$ ferroborate. The magnetic phase transition affects the temperature behavior of these lines that results in the splitting of the detected lines below the phase transition temperature. These line positions agree with the known optical studies.[11]

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