

Vibrational spectra of NdF₃ crystal

A.S. Oreshonkov, A.S. Krylov, N.P. Shestakov, V. N. Voronov, A.A. Ershov, E.A. Strikina & A.N. Vtyurin

To cite this article: A.S. Oreshonkov, A.S. Krylov, N.P. Shestakov, V. N. Voronov, A.A. Ershov, E.A. Strikina & A.N. Vtyurin (2016) Vibrational spectra of NdF₃ crystal, *Ferroelectrics*, 501:1, 15-19, DOI: [10.1080/00150193.2016.1198201](https://doi.org/10.1080/00150193.2016.1198201)

To link to this article: <https://doi.org/10.1080/00150193.2016.1198201>



Published online: 17 Oct 2016.



Submit your article to this journal [↗](#)



Article views: 102



View related articles [↗](#)



View Crossmark data [↗](#)



Citing articles: 4 View citing articles [↗](#)

Vibrational spectra of NdF₃ crystal

A.S. Oreshonkov^{a,b}, A.S. Krylov^{a,b}, N.P. Shestakov^{a,b}, V. N. Voronov^a, A.A. Ershov^a,
E.A. Strikina^a, and A.N. Vtyurin^{a,b}

^aKirensky Institute of Physics, SB RAS, Krasnoyarsk, Russia; ^bSiberian Federal University, Krasnoyarsk, Russia

ABSTRACT

The vibrational spectroscopy investigation of phase transitions in NdF₃ crystal is reported. Spectra were obtained in temperature range from 300 to 10 K. It has been shown that, down to 10 K, the trigonal tysonite structure of NdF₃ trifluoride remains stable.

ARTICLE HISTORY

Received 13 September 2015
Accepted 23 January 2016

KEYWORDS

Trifluorides; tysonite structure; Raman spectroscopy; infrared spectroscopy

Introduction

The NdF₃ crystal belong to the rare-earth trifluoride crystals with the tysonite structure ReF_3 ($Re = La, Ce, Pr, Nd$, space group $P-3c1$, $Z = 6$), which are extensively studied due to their wide applications in fiberoptics, as an active medium of solid-state lasers, sensors and scintillators [1–5]. The unit cell structure of NdF₃ crystal [6] is shown in Fig. 1. According to [7, 8], ReF_3 crystals with tysonite structure undergoes a structural phase transition to high-pressure phase $Cmma$ near 20 GPa. On the other hand, the quantum mechanical simulations [9] and in situ X-ray diffraction [10] show less distorted $I4/mmm$ structure for high-pressure phase of the LaF₃ crystal. The crystal structure of La, Ce, Pr and Nd trifluorides is stable until melting [10]. The melting point of NdF₃ crystal is 1410 K.

The aim of this work was to investigate vibrational spectra of NdF₃ crystal in a wide temperature range looking for some features of structural phase transitions.

Experimental

Single crystals of NdF₃ were grown by Bridgeman-Stockbarger method at the hot zone temperature 1400°C. The starting material was NdF₃ of spectral purity grade. The growth was performed in evacuated and sealed platinum ampoule. Temperature gradient inside the heater was 30 K/cm, and the pulling rate was 0.8 mm/hour. As-grown single crystal samples were of several millimeter size and had several growth facets of rather high optical quality, the latter being varying for different facets. No strange reflections were observed with X-ray. Before measurement, as-grown crystals were polished to produce surfaces with perfect optical quality.

CONTACT A.A. Ershov  ershov@iph.krasn.ru

Color versions of one or more of the figures in this article can be found online at www.tandfonline.com/gfer.

© 2016 Taylor & Francis Group, LLC

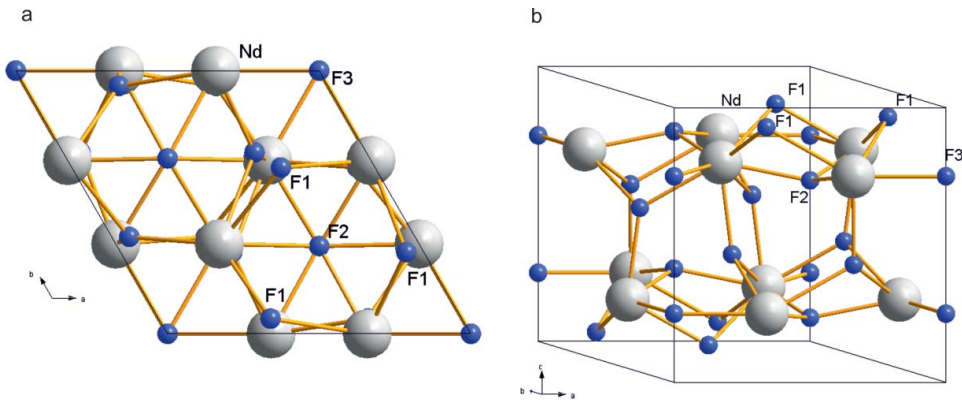


Figure 1. Structure of NdF_3 crystal: a) projection on the ab plane, b) perspective view.

Raman spectra were collected using the polarized radiation of a 488 nm Ar+ laser (Spectra-Physics Stabilite 2017) in the wavenumber region between 10 and 800 cm^{-1} . The spectra were recorded on a Horiba Jobin Yvon T64000 spectrometer. The temperature studies were performed using an ARS CS204–X1.SS closed cycle helium cryostat in the temperature range of 13 – 300K. The accuracy of temperature stabilization during spectra measurement was $<0.2\text{ K}$. The samples for the far IR range was prepared by mixing of melted NdF_3 powder and polyethylene, pellet was made using pellet press. The spectra in the mid-IR range were collected from potassium bromide (KBr) pellet samples, KBr was used instead of polyethylene. The spectra were obtained with Vertex 80V IR spectrometer (Bruker). The temperature studies were performed using an Optistat TM AC-V cryostat in the temperature range of 10 – 286 K.

Results and discussion

A mechanical representation of the $P\text{-}3c1$ trigonal phase at Brillouin zone centre of NdF_3 crystal is:

$$\begin{aligned} \Gamma_{\text{Mech}} &= 5A_{1g} + 5A_{1u} + 7A_{2g} + 7A_{2u} + 12E_u + 12E_g, \\ \text{acoustic and optic modes: } \Gamma_{\text{acoustic}} &= A_{2u} + E_u, \quad \Gamma_{\text{optic}} = 5A_{1g} + 5A_{1u} + 7A_{2g} + 6A_{2u} + 11E_u + 12E_g, \\ \text{Infrared and Raman active modes } \Gamma_{\text{Raman}} &= 5A_{1g} + 12E_g, \quad \Gamma_{\text{Infrared}} = 6A_{2u} + 11E_u. \end{aligned}$$

The Raman spectra and mid-infrared spectra of the NdF_3 crystal recorded at ambient condition are shown in Fig. 2 and the frequencies observed are listed in Table 1.

To calculate the NdF_3 vibrational spectrum we used simulation package LADY [11]. Complete spectra of the NdF_3 crystal obtained within the framework of simplified version of the Born-Karman model [12].

Within this model, only the pair-wise interactions and bond-stretching force constants $A = \frac{\partial^2 E}{\partial R^2}$ (E is the energy, R is the bond length) are considered. Simplified version of the Born-Karman model implies that A depends on R and the $A(R)$ dependences are the same for all atom pairs:

$$A = \lambda \exp(-r_{ij}/\rho),$$

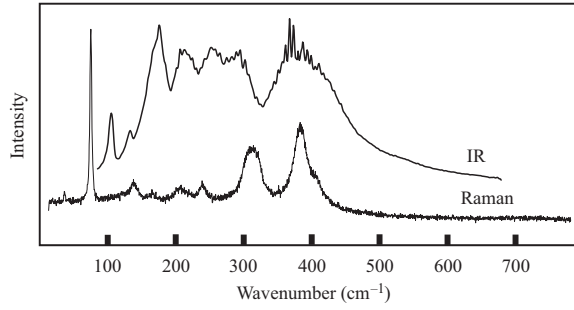


Figure 2. The Raman spectra and mid-infrared spectra of the NdF₃ crystal.

Table 1. Experimental and calculated Raman and Infrared frequencies for NdF₃ crystal.

Raman exp 13K (cm ⁻¹)	Raman exp 300K (cm ⁻¹)	Raman calc. 300K (cm ⁻¹)	IR exp 300K (cm ⁻¹)	IR Calc 300K (cm ⁻¹)
37	36	36		38
45		53	105	41
78	75	81	132	58
123	120	84		75
140	138	129	163	116
146		141	176	121
151		164	212	137
169	165	176		140
209	207	181	253	165
219		199		181
245	240	248	294	217
308	306	295		238
316		296	345	252
327	319	322	367	295
382		372	311	
388	384	398	432	336
412	407	401		381

where r_{ij} is the interatomic distance, and λ and ρ are the parameters characterizing selected pair interaction. To find the parameters of the model the special optimization program was written and tested for several compounds [13–15]. The crystal lattice stability conditions were taken into account. The parameters obtained for NdF₃ crystal are shown in Table 2.

A temperature transformation of Raman spectra is shown in Fig. 3. A crystal cooling leads to reduction of line widths and to the appearance of the line about 45 cm⁻¹. According to calculations of the NdF₃ lattice dynamics, three Raman active modes should appear in the region below

Table 2. Parameters of the interatomic interaction potential.

Interactions	λ , aJ/Å ²	ρ , Å
Nd – F1	544.6	0.340
Nd – F2	321.6	0.286
Nd – F3	400.6	0.363
F1 – F1	345.3	0.379
F1 – F2	242.8	0.330
F1 – F3	196.8	0.323

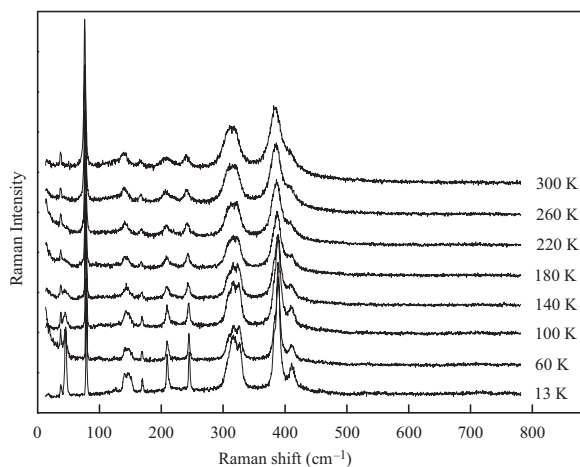


Figure 3. Temperature transformation of Raman spectra of the NdF_3 crystal.

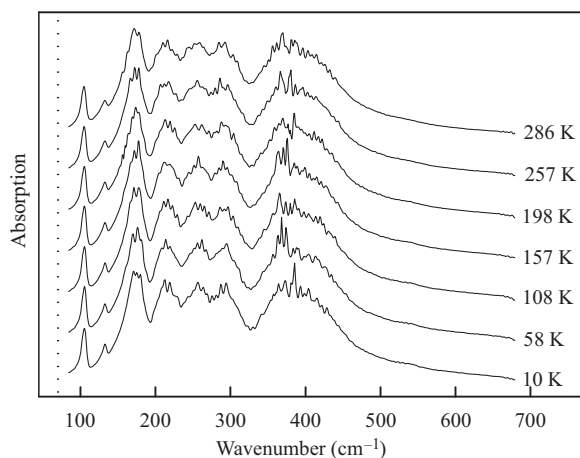


Figure 4. IR spectra of the NdF_3 crystal at different temperatures.

100 cm^{-1} . Two of them are clearly seen in Fig. 3 at 36 and 75 cm^{-1} at room temperature. The third line should exist near 50 cm^{-1} . Thus, it can be assumed that the appearing of the line near 50 cm^{-1} is related to its intensity increasing. No any significant changes in Raman spectra associated with the structural phase transitions are observed. The IR spectra of the NdF_3 compound at different temperatures are shown in Fig. 4. It is seen that, down to 10 K , the infrared spectra do not exhibit noticeable changes that could be attributed to structural phase transitions too. Thus, the crystal structure is argued to be stable from 300 to 10 K .

Conclusion

As a result of these investigations, we can conclude that NdF_3 crystal do not undergo the structural phase transitions in the temperature range 300 – 10 K . No any significant changes in vibrational spectra associated with the structural phase transitions are observed. The number of active spectral lines is an agreement with the selection rules and the lattice dynamics calculation.

Funding

The reported study was funded by RFBR according to the research project No. 16-32-00351 mol_a. It was partially supported by the Ministry of Education and Science of the Russian Federation and the “Krasnoyarsky regional fund of scientific support and scientific-technical activity.”

References

1. A. Kaminskii, *Laser Crystals* (Springer, Berlin, 1990).
2. S. Krause, W. Moritz, and I. Grohmann, Improved long-term stability for an LaF₃ based oxygen sensor. *Sens. Actuators B*. **18**, 148–154 (1994).
3. S. Ye, B. Zhu, J. Luo, J. X. Chen, G. Lakshminarayana, and J. R. Qui, Enhanced cooperative quantum cutting in Tm³⁺-Yb³⁺ codoped glass ceramics containing LaF₃ nanocrystal. *Opt. Express*. **16**, 8989–8994 (2008).
4. A. A. Kalinkin, A. A. Kalachev, and V. V. Samartsev, Polarization Properties of Pure and Triggering Superradiance in a LaF₃:Pr³⁺ crystal. *Laser Physics*. **13**, 1313–1318 (2003).
5. F. Wang and X. G. Liu, Recent advances in the chemistry of lanthanide-doped upconversion nanocrystal. *Chem. Soc. Rev*. **38**, 976–989 (2009).
6. E. M. Diniz and C.W.A. Paschoal, Structural phase transition under pressure the rare earth triuorides compounds with tysonite structure. *Solid State Communications*. **136**, 538–542 (2005).
7. T. I. Dyuzheva, L. M. Lityagina, G. B. Demishev, and N. A. Dendeliani, Phase transition and compressibility of LaF₃ under pressure up to 40 GPa. *Journal of Alloys and Compounds* **335**, 59–61 (2002).
8. T. I. Dyuzheva, L. M. Lityagina, G. B. Demishev, and N. A. Dendeliani, High-pressure phase transition of LaF₃ and CeF₃. *Inorganic Materials*. **39**, 1198–1202 (2003).
9. B. Winkler, K. Knorr, and V. Milman, Prediction of the structure of LaF₃ at high pressure. *J. Alloys Compd*. **349**, 111–113 (2003).
10. A. Wilson P. Crichton B. Bouvier Winkler, and A. Grzechnik, The structural behaviour of LaF₃ at high pressure. *Dalton Trans*. **39**, 4302–4311 (2010).
11. M. B. Smirnov and V. Yu. Kazimirov, *JINR communications E* (Dubna, 2001).
12. M. Smirnov, and R. Baddour-Hadjean, Li intercalation in TiO₂ anatase: Raman spectroscopy and lattice dynamic studies. *J. Chem. Phys*. **121**, 2348–2355 (2004).
13. A. S. Krylov, A. N. Vtyurin, A. S. Oreshonkov, V. N. Voronov, and S. N. Krylova, Structural transformations in single crystal Rb₂NaYF₆: Raman scattering study. *J. Raman Spectr*. **44**, 763–769 (2013).
14. Y. V. Gerasimova, A. S. Oreshonkov, A. N. Vtyurin, A. A. Ivanenko, L. I. Isaenko, A. A. Ershov, and E. I. Pogoreltsev, Infrared absorption investigation of the role of octahedral groups upon the phase transition in the Rb₂KMoO₃F₃ crystal. *Phys. Solid State*. **55**, 2331–2334 (2013).
15. M. S. Zhiguo Xia, A. S. Molochev, V. V. Oreshonkov Ru-Shi Liu, Atuchin, and Dong, Cheng, Crystal and local structure refinement in Ca₂Al₃O₆F explored by X-ray diffraction and Raman spectroscopy. *Phys. Chem. Chem. Phys*. **16**, 5952–5957 (2014).