

ENERGY BAND STRUCTURE OF $\text{LaF}_3:\text{Sm}$ AND $\text{LaF}_3:\text{Pm}$ CRYSTALS

V. O. Karнаushenko¹, Ya. M. Chornodolsky¹, V. V. Vistovsky¹,
S. V. Syrotyuk², A. S. Voloshinovskii¹

¹*Ivan Franko National University of Lviv, 8, Kyrylo & Mefodiy St., Lviv, UA-79005, Ukraine,*

²*Lviv Polytechnic National University, 12, S. Bandera St., Lviv, UA-79013, Ukraine*

(Received 09 September 2020; accepted 11 November 2020; published online 14 December 2020)

The papers presents the results of the theoretical calculations of the partial and total density of states of $\text{LaF}_3:\text{Sm}$ and $\text{LaF}_3:\text{Pm}$ crystals. We analyze the positions of $4f$ and $5d$ energy states of activator ions in the energy structure of the host material. We calculated and described electronic energy band structures of the above mentioned crystals. We made a quantitative and qualitative comparison between the energy structure of $\text{LaF}_3:\text{Sm}$ and $\text{LaF}_3:\text{Pm}$ crystals.

Key words: energy band structure, partial density of states, total density of states, scintillators, lanthanides.

DOI: <https://doi.org/10.30970/jps.24.4703>

I. INTRODUCTION

Heavy inorganic scintillating crystals based on fluoride compounds with lanthanides elements as activators become more popular among researchers due to high temperature stability and high luminescence intensity [1]. In particular, an important advantage of these compounds, compared to similar oxide compounds, is the low phonons energy, which makes the light yield efficiency much higher [2]. A large amount of experimental studies of $\text{LaF}_3:\text{Sm}$ [3] and $\text{LaF}_3:\text{Pm}$ [4] crystal optical properties have been reported in recent years, but there is almost no theoretical information about their energy structure, which is very important for their effective use in lasers and radiation detectors.

At present, the most complete information about the energy positions of $4f$ and $5d$ ion levels of lanthanides elements in the structure of LaF_3 is collected in the article [5]. The above mentioned work complements essentially the results of the fundamental work [6], in which lanthanide energy levels positions were analyzed for the first time.

In the current work, the results of the theoretical calculations of the partial and total density of states of $\text{LaF}_3:\text{Sm}$ and $\text{LaF}_3:\text{Pm}$ crystals have been reported. The energy positions of $4f$ and $5d$ states of activator ions in the energy structure of the host material have been analyzed. Electronic band structures of the crystals have been calculated and the energies of the most probable optical transitions have been analyzed. Quantitative and qualitative comparison between the energy structures of $\text{LaF}_3:\text{Sm}$ and $\text{LaF}_3:\text{Pm}$ crystals have been made.

The energy levels of Sm^{3+} and Pm^{3+} ions occupy equivalent positions and differ only in the splitting energy value and the presence of additional levels near the conduction band bottom for Sm^{3+} . The energy levels of Pm^{3+} are similar to Pr^{3+} in their laser properties [4], but since all its isotopes are radioactive, and the element is extremely rare, our study of this element is rather of academic interest than a practical one. Sm^{3+} is widely used in optoelectronics as well as lasers. Numerous studies on $4f$ Sm^{3+} levels splitting have been reported on the basis of the Judd–Ofelt (J–O) theoretical model [2].

There is enough information in the literature about the main optical properties of divalent and trivalent samarium hosted in the LaF_3 matrix, but theoretical information about the energy positions of $4f$ and $5d$ levels, relative to the valence band top, is absent.

II. MODELLING AND CALCULATIONS

The model of the LaF_3 primitive lattice cell [7], which was used for the calculations, is presented in Fig. 1 and corresponds to the case when one of the La^{3+} ions is replaced by the Pm^{3+} or Sm^{3+} , respectively. The spatial group of this structure is $P3c1$, and the cell parameters are as follows: $a = b = 7.247 \text{ \AA}$; $c = 7.391 \text{ \AA}$.

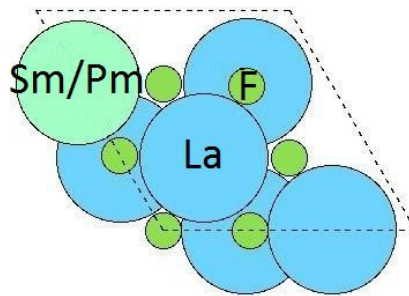


Fig. 1. Unit lattice model for $\text{LaF}_3:\text{Ln}$ ($\text{Ln} = \text{Sm}, \text{Pm}$)

To take into account the spin-orbit interaction, which causes additional splitting of levels, the spin value of $2.5\hbar$ for promethium and $3\hbar$ for samarium were taken for calculations. The occupation of energy levels has been considered according to the Fermi–Dirac distribution.

The calculation of the crystals electron-energy structure in this work is carried out using the projected augmented waves (PAW) method within the density function theory framework. The Hubbard correction (DFT+U) is used to consider the peculiarities of strongly localized states of lanthanides. In the general case, the exchange-correlation interaction energy between electrons has been determined from the PBE potential. All of the above approaches are implemented in the

Abinit software [8], distributed with GPL open license.

The use of the Hubbard corrections allows us to include strong correlations of Ln levels with limited computational resources. Similar experiments, using the hybrid exchange-correlation potential PBE0 with different mixing parameters α (from 0.05 to 0.95), allows us to obtain good positions of $4f$ Ln³⁺ levels or correct the splitting of $5d$ Ln³⁺ levels, but not both qualities simultaneously, using a cutting energy of 30 Ha, and a k-grid 8x8x8. The calculations in this work were based on the modified Hubbard potential reported in [9]. In this way, it was found that changes in the correlation potential of $5d$ La states result in a significant change of the band gap energy and strongly affect the $4f$ splitting of Ln³⁺ levels. Instead, a change in this parameter for $4f$ Ln³⁺ levels affects the position of these levels relative to the top of the valence band.

III. RESULTS AND DISCUSSIONS

The obtained partial and total densities of states for LaF₃:Pm are presented in Fig. 2 and Fig. 3, respectively. As can be seen from the graphs, the width of the $2p$ F states is 2.7 eV, the width of the $5d$ La levels is 3.2 eV. The $5d$ Pm levels undergo a strong splitting with the total width of 1.6 eV and the centroid position at 8.6 eV. Peaks of the $4f$ Pm levels are characterized by strong intensity and relatively small width, what is typical of them. The position of these peaks is determined by the energy of 0.4 eV, 2.9 eV, 5 eV and 5.5 eV, what corresponds to the results of the experimental data analysis presented in [5]. The main difference from the experimental predictions is the value of the level splitting, which is smaller for the obtained results and may be caused by the low correlation energy.

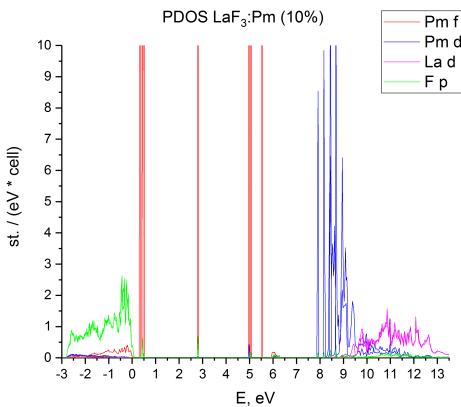


Fig. 2. Partial density of states of LaF₃:Pm

Similar results for LaF₃:Sm are shown in Fig. 3 and Fig. 4. Comparing these graphs with the data for LaF₃:Pm, we can see almost identical values of the width of $2p$ F and $5d$ La levels. Although $5d$ Sm levels are characterized by a similar width and position of the centroid, they have a less expressed splitting, with some smearing of peaks at the energy higher than 8.5 eV.

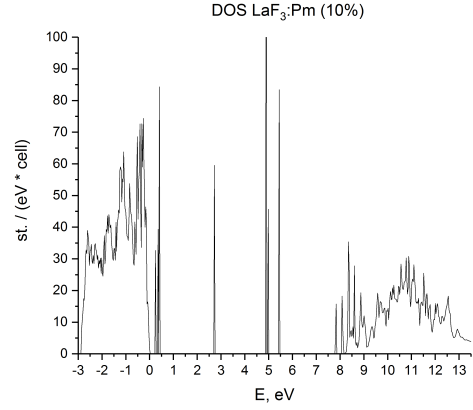


Fig. 3. Total density of states of LaF₃:Pm

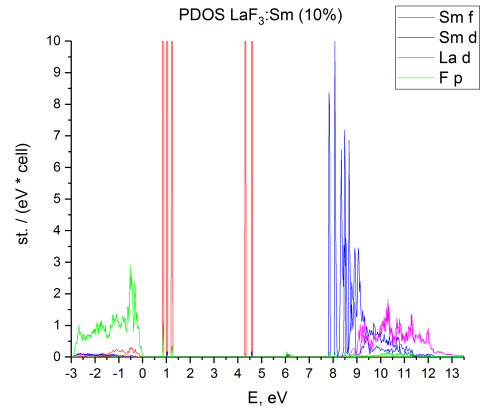


Fig. 4. Partial density of states of LaF₃:Sm

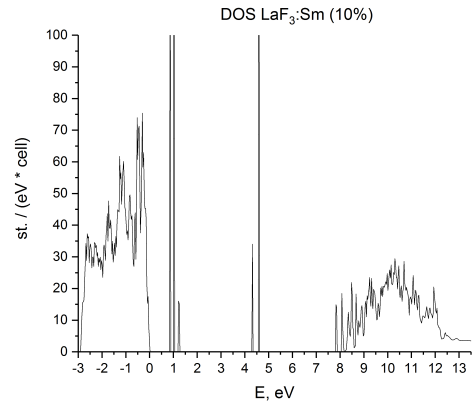


Fig. 5. Total density of states of LaF₃:Sm

The $4f$ Sm levels have the same properties as in the case of Pm and have the following energy positions: 0.9 eV, 1 eV, 1.2 eV, 4.4 eV, and 4.6 eV. It is important to note that despite the insufficient splitting of these levels, their positions correlate with the positions shown in [5], except for the absence of the third group of $4f$ levels, which is located just below the $5d$ levels of Sm. The

aforementioned disadvantage of the obtained results, as well as the relative small smearing of $5d$ levels, is associated with a small Hubbard correction value for $5d$ La levels.

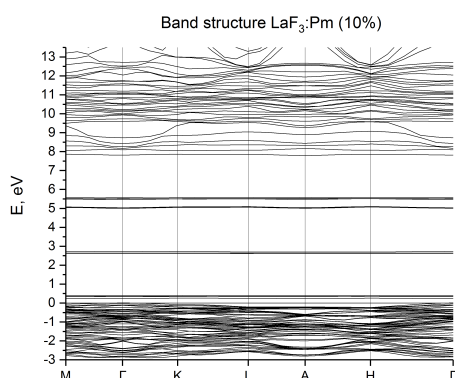


Fig. 6. Electron energy band structure of $\text{LaF}_3\text{:Pm}$

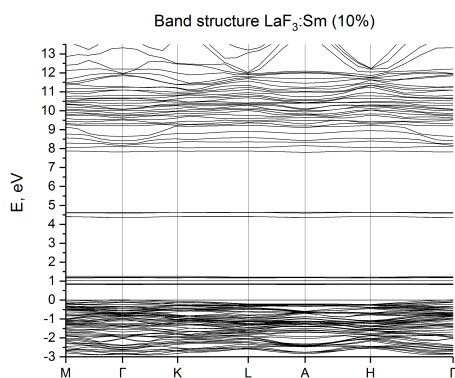


Fig. 7. Electron energy band structure of $\text{LaF}_3\text{:Sm}$

The band energy structures for the investigated crystals are shown in Fig. 6 and Fig. 7. The results are calculated along the line of high symmetry points $M - \Gamma - K - L - A - H - \Gamma$. The valence band bottom of the crystals, in both cases, is formed by $2p$ F levels, and the top of the conduction band — by $5d$ La levels.

Activator levels are located in the forbidden zone and are characterized by low dispersion with respect to the wave vector \mathbf{k} . Also, from the calculated energy band scheme, a stronger tightening of the $5d$ La levels in the region of $5d$ activator levels can also be seen in the case of Sm. The calculated band gap is 9.6 eV in the case of $\text{LaF}_3\text{:Pm}$ and 9.4 eV in case of $\text{LaF}_3\text{:Sm}$. The fact of the smaller $\text{LaF}_3\text{:Sm}$ band gap confirms the above-mentioned inaccuracy of the Hubbard correction for samarium levels once again.

IV. CONCLUSIONS

1. Simulations with different methods of the electron energy structure calculations for strongly correlated materials such as $\text{LaF}_3\text{:Sm}(10\%)$ and $\text{LaF}_3\text{:Pm}(10\%)$ have been performed and the effectiveness of the DFT+U approach in comparison with the hybrid exchange-correlation PBE0 usage, in the case of limited computational resources, has been shown.
2. Changes in the Hubbard correction for $5d$ levels were shown to affect the splitting $4f$ and $5d$ levels, as well as the energy band gap width.
3. The obtained results are in a good agreement with the experiment based predictions of Sm and Pm levels positions environment.
4. The valence band top of $\text{LaF}_3\text{:Sm}$ and $\text{LaF}_3\text{:Pm}$ is shown to be formed by $2p$ F levels and the conduction band bottom by $5d$ La levels.
5. $5d$ $\text{Sm}^{3+}/\text{Pm}^{3+}$ levels are split and located just before the conduction band bottom.
6. The $4f$ $\text{Sm}^{3+}/\text{Pm}^{3+}$ levels are shown to be placed in the forbidden band and characterized by a small width, high intensity and similar energy levels positions for both crystals.

-
- [1] R. Kumar Sharma, A.-V. Mudring, P. Ghosh, J. Lumin. **189**, 44 (2017); <https://doi.org/10.1016/j.jlumin.2017.03.062>.
 - [2] Hoang Manh Ha, Tran Thi Quynh Hoa, Le Van Vu, Nguyen Ngoc Long, J. Mater. Sci.: Mater. Electron. **28**, 884 (2017); <https://doi.org/10.1007/s10854-016-5603-1>.
 - [3] R. M. Macfarlane, R. M. Shelby, Phys. Lett. A **116**, 299 (1986); [https://doi.org/10.1016/0375-9601\(86\)90599-2](https://doi.org/10.1016/0375-9601(86)90599-2).
 - [4] M. D. Shinn *et al.*, IEEE J. Quantum Electron. **24**, 1100 (1988); <https://doi.org/10.1109/3.232>.
 - [5] P. Dorenbos, J. Lumin. **135**, 93 (2013); <https://doi.org/10.1016/j.jlumin.2012.09.034>.
 - [6] G. H. Dieke, H. M. Crosswhite, Appl. Opt. **2**, 675 (1963); <https://doi.org/10.1364/AO.2.000675>.
 - [7] K. Persson, <https://materialsproject.org/materials/mp-905/> (2014); <https://doi.org/10.17188/1272758>.
 - [8] X. Gonze, Comp. Phys. Commun. **248**, 107042 (2020); <https://doi.org/10.1016/j.cpc.2019.107042>.
 - [9] M. Topsakal, R. M. Wentzcovitch, Comput. Mater. Sci. **95**, 263 (2014); <https://doi.org/10.1016/j.commatsci.2014.07.030>.

ЗОННА ЕНЕРГЕТИЧНА СТРУКТУРА КРИСТАЛІВ $\text{LaF}_3:\text{Pm}$ ТА $\text{LaF}_3:\text{Sm}$

В. О. Карнаушенко¹, Я. М. Чорнодольський¹, В. В. Вістовський¹, С. В. Сиротюк², А. С. Волошиновський¹

¹Львівський національний університет імені Івана Франка,
вул. Кирила і Мефодія 8, Львів, 79005, Україна,

²Національний університет "Львівська політехніка",
вул. С. Бандери 12, Львів, 79013, Україна

На сьогодні велику увагу світових науковців зосереджено на експериментальних дослідженнях люмінесцентних властивостей кристалів $\text{LaF}_3:\text{Sm}$ та $\text{LaF}_3:\text{Pm}$, проте майже відсутня інформація про теоретичні підходи для визначення енергетичних положень $4f$ та $5d$ рівнів лантанідів у цих сполуках.

У роботі проведено теоретичні розрахунки електронної енергетичної структури кристалів $\text{LaF}_3:\text{Sm}$ та $\text{LaF}_3:\text{Pm}$ з використанням методу приєднаних проєкційних хвиль та поправок Габбарда для врахування сильно локалізованих станів лантанідів. Зроблено кількісне та якісне порівняння парціальної та загальної густини станів цих кристалів. Отримано значення ширини забороненої зони 9.4 еВ для кристала $\text{LaF}_3:\text{Sm}$ та 9.6 еВ для $\text{LaF}_3:\text{Pm}$. В обох сполуках ширина валентної зони, утвореної $2p$ -станами F, становить 2.7 еВ, нижню частину зони провідності, шириною 3.2 еВ, утворюють $5d$ -стани La. $5d$ -рівні Pm зазнають сильного розщеплення близько 1.6 еВ і займають положення в зоні 8.6 еВ щодо вершини валентної зони. Піки густини електронних станів $4f$ -рівнів Pm, що розміщені всередині забороненої зони, характеризуються високою інтенсивністю та відносно малою шириною. Положення цих піків відповідають значенням енергій 0.4 еВ, 2.9 еВ, 5 еВ і 5.5 еВ. Подібні результати отримано для кристала $\text{LaF}_3:\text{Sm}$. $4f$ -рівні Sm займають енергетичні позиції: 0.9 еВ, 1 еВ, 1.2 еВ, 4.4 еВ і 4.6 еВ. Розраховані значення енергетичних параметрів кристалів $\text{LaF}_3:\text{Sm}$ та $\text{LaF}_3:\text{Pm}$ добре узгоджуються з експериментальними даними. Відмінністю від експериментальних значень є менша величина розщеплення енергетичних рівнів, пов'язана з низькою кореляційною енергією.

Ключові слова: зонна енергетична структура, парціальна густина станів, загальна густина станів, сцинтилятори, лантаніди.