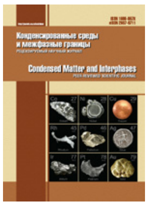

ISSN 1606-867X (Print)
ISSN 2687-0711 (Online)
Condensed Matter and Interphases
Kondensirovannye Sredy i Mezhfaznye Granitsy
https://journals.vsu.ru/kcmf/

**Original articles**

Research article
https://doi.org/10.17308/kcmf.2026.28/13561

# Semi-empirical description of the regularity of change in thermal conductivity of single crystals based on the example of a concentration series of $Ba_{1-x}La_xF_{2+x}$ solid solutions

**P. A. Popov**[1], **A. V. Shchelokov**[1], **N. V. Mitroshenkov**[1], **A. A. Kushnereva**[1], **V. A. Konyushkin**[2], **A. N. Nakladov**[1], **P. P. Fedorov**[2], **S. V. Kuznetsov**[2]✉

[1]*Petrovsky Bryansk State University*
*14, Bezhitskaya st., 241036 Bryansk, Russian Federation*

[2]*Prokhorov General Physics Institute of the Russian Academy of Sciences*
*38, Vavilov st., 119991 Moscow, Russian Federation*

## Abstract

*Purpose:* To study the thermal conductivity of single crystals of a $Ba_{1-x}La_xF_{2+x}$ solid solution and a semi-empirical description of changes in thermal conductivity depending on the lanthanum content.

*Experimental:* In the temperature range of 50–300 K, the thermal conductivity of single crystal $Ba_{1-x}La_xF_{2+x}$ samples with lanthanum content from $x = 0.001$ to $x = 0.300$ was determined by the experimental method of long heat flow.

*Conclusions:* A monotonic concentration dependence of thermal conductivity has been revealed. A semi-empirical expression has been proposed to approximate the experimental values of thermal conductivity.

**Keywords:** Barium difluoride, Lanthanum, Solid solution, Defect clusters, Thermal conductivity, Semi-empirical model

***For citation:*** Popov P. A., Shchelokov A. V., Mitroshenkov N. V., Kushnereva A. A., Konyushkin V. A., Nakladov A. N., Fedorov P. P., Kuznetsov S. V. Semi-empirical description of the regularity of change in thermal conductivity of single crystals based on the example of a concentration series of $Ba_{1-x}La_xF_{2+x}$ solid solutions. *Condensed Matter and Interphases*. 2026;28(1): 92–102. https://doi.org/10.17308/kcmf.2026.28/13561

***Для цитирования:*** Попов П. А., Щелоков А. В., Митрошенков Н. В., Кушнерёва А. А., Конюшкин В. А., Накладов А. Н., Федоров П. П., Кузнецов С. В. Полуэмпирическое описание закономерности изменения теплопроводности монокристаллов на примере концентрационной серии твердых растворов $Ba_{1-x}La_xF_{2+x}$ *Конденсированные среды и межфазные границы*. 2026;28(1): 92–102. https://doi.org/10.17308/kcmf.2026.28/13561

---

✉ Sergey V. Kuznetsov e-mail: kouznetzovsv@gmail.com

## 1. Introduction

Bulk crystalline materials based on calcium, strontium, and barium fluorides doped with rare earth elements are widely used as functional elements of photonics, scintillators [1–5], and elements of passive and active optics [6–10], both in the form of single crystals [11] and optical ceramics [12]. Besides its use in photonics, these solid solutions are used as ionic conductors [13–22], ion batteries [13–24], and catalysts [25]. The thermal conductivity of good-quality optical ceramics is no different from that of single crystals, allowing a comparison of their characteristics [26].

For various applications, one of the key characteristics is thermal conductivity, as it determines the material’s ability to dissipate heat under various intense types of pumping. Solid solutions based on calcium, strontium, and barium fluorides, doped with rare earth elements, tend to form clusters of the $R_6F_{36}$ type [27–31], which leads to a complex dependence of thermal conductivity on temperature. This is expressed by the fact that with an increase in the content of rare earth elements and with an increase in temperature from 50 to 300 K, a change in the nature of the temperature dependence is observed. At low rare earth element concentrations and low temperatures, the temperature dependence is typical of a crystalline material. As the rare earth content increases at low temperatures, the temperature dependence becomes more glass-like. Such complex behavior of the temperature dependence is extremely difficult to describe because the indicated patterns are observed for samples of the same solid solution with the same crystal structure. The best approximation based on a semi-empirical algorithm for describing the behavior of this type of materials was proposed in [32–33].

The processes of partial reduction of some trivalent ions to the divalent state (Sm, Eu, Dy, Yb, Tm) are often observed upon doping calcium, strontium, and barium fluorides with active rare earth ions [34–37]. To prevent this effect it was previously proposed to increase the complexity of the original matrix by adding optically inactive yttrium to the crystal composition. As a result, a new matrix for optical materials such as yttrofluorite ($CaF_2$:Y) was developed [38]. In addition to yttrium, various studies have proposed the use of lanthanum [39], which is a more effective ion for preventing the reduction of triply charged ions and preventing cluster formation. To reduce multiphonon relaxation processes, it is desirable to use matrices with lower phonon energy, therefore a barium fluoride matrix was chosen in preference to calcium and strontium fluorides.

The aim of the study was to investigate the patterns and mathematical description of the change in thermal conductivity in the temperature range of 50–300 K for the $Ba_{1-x}La_xF_{2+x}$ solid solution with a rare earth element content from 0.1 to 30.0 mol %.

To approximate the experimental values of thermal conductivity in the temperature range, we tested a simple semi-phenomenological model, which is significantly simpler than existing ones. The approximation does not have a strict physical justification, but it makes it possible to reliably describe the dependence of thermal conductivity on temperature and is useful for improving the theoretical understanding of heat transfer processes in media with a complex structure.

## 2. Experimental

Single crystals of $Ba_{1-x}La_xF_{2+x}$ solid solutions ($0.001 \leqslant x \leqslant 0.300$) were grown by the Bridgman technique in a vacuum growth oven using an Ar and $CF_4$ atmosphere in multi-cell graphite crucibles, allowing the growth of a concentration series of samples in one growth cycle. Barium fluoride (99.99 %, LANHIT) and lanthanum fluoride (99.99 %, LANHIT) were used as initial reagents.

The thermal expansion coefficient in the temperature range from 78 K to room temperature for samples containing 4, 10, and 20 mol % La was estimated based on the determination of the lattice parameters of the powders by the Debye-Scherrer method on a DRON-7.0 X-ray diffractometer (Burevestnik JSC, St. Petersburg, Russia) using an X-ray cryostat [40] in Cu-$K\alpha$ radiation with a wavelength of 1.54184 Å. Reflections from the {355} crystallographic plane were registered around diffraction angles of 146, 147, and 149°, respectively. The error in determining the lattice parameter over the entire temperature range studied did not exceed $\pm 1 \cdot 10^{-4}$ Å.

Thermal conductivity in the temperature range of 50–300 K was measured using the absolute stationary longitudinal heat flux method. The equipment and measurement technique are described in [41]. The samples were cylindrical with 9.6 mm in diameter and 22–26 mm in length. The thermal conductivity measurement error was within ±5 %.

## 3. Results

Prior to the study of the thermal and physical characteristics of $Ba_{1-x}La_xF_{2+x}$ solid solutions, the dependences of the lattice parameter and thermal expansion coefficient in the temperature range of thermal conductivity measurements were studied. The experimental points of the lattice parameter $a(T)$ for samples with a lanthanum content of 4, 10, and 20 mol. % are shown in Fig. 1. The behavior of $a(T)$ was typical for crystalline materials without anomalies, which indicates the high quality of the samples. The values of the lattice parameter $a$ at $T$ = 300 K were 6.1864, 6.1661, and 6.1360 Å for 4, 10, and 20 mol %, respectively. Data agree with the concentration dependence of $a(x)$ proposed in [42]. From the $a(T)$ data, the values of the thermal expansion coefficient (TEC) were calculated in accordance with the expression $\alpha = \frac{\Delta a}{\Delta T}\cdot\frac{1}{a}$. Fig. 1 shows the calculation results in comparison with previously obtained TEC data for the $Ba_{0.70}La_{0.30}F_{2.30}$ composition [43] and the $BaF_2$ matrix [44]. The analysis of the results demonstrated that a significant effect of lanthanum addition on the TEC is observed only in the low temperature range.

The thermal conductivity of $Ba_{1-x}La_xF_{2+x}$ samples with $x$ = 0.008, 0.120 in the low temperature region and $x$ = 0.045, 0.330, 0.460 with an increase in temperature to room temperature were studied [45–46]. Previously conducted studies [46–48] demonstrated that the thermal conductivity of the $LaF_3$ crystal is significantly lower than that of $BaF_2$.

The magnitude and temperature behavior of thermal conductivity are directly affected by heat capacity. Calorimetric studies of the $Ba_{1-x}La_xF_{2+x}$ solid solution in the range $T \leqslant 1$ K were summarized in [45]. The heat capacity of the $Ba_{0.70}La_{0.30}F_{2.30}$ crystal in the range of 63–313 K was investigated in [49]. The heat capacity of a $Ba_{0.51}La_{0.49}F_{2.49}$ sample in the range of 500–1000 K

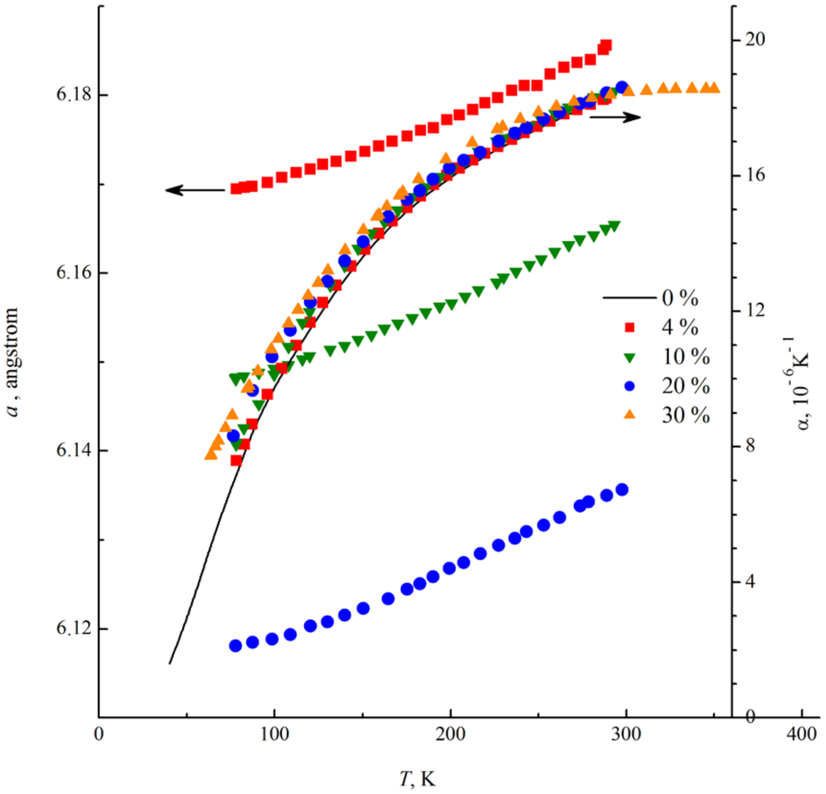

**Fig 1.** Temperature dependence of the lattice parameter and TEC of crystals of a $Ba_{1-x}La_xF_{2+x}$ solid solution

was measured [50]. In the temperature range from liquid nitrogen to room temperature, the effect of the LaF$_3$ doping has a character close to additive.

The thermal conductivity of the Ba$_{1-x}$La$_x$F$_{2+x}$ solid solution are presented graphically in Fig. 2 and in numerical form in Table 1. Fig. 2 includes data of $k(T)$ for previously studied samples using the experimental equipment and methods used in this study: BaF$_2$ corresponding to the composition $x = 0$ [48], and samples with $x = 0.25$ and $x = 0.30$ [51]. The markers in Fig. 2 show the experimental points $k(T)$ while lines show the results of calculations using Formula 1 (see below). A comparison of our $k(T)$ data with those presented graphically in [46] showed their close agreement.

An analysis of the results (Fig. 2) shows that the thermal conductivity value decreases sharply with an increase in the lanthanum content and the decreasing temperature dependence $k(T)$ weakens and turns into a weakly increasing one. A similar effect of trivalent rare earth elements introduced into crystals with a fluorite structure has been discovered for many heterovalent solid solutions of the type M$_{1-x}$R$_x$F$_{2+x}$, where M = Ca, Sr, Ba, Cd, R = REE [52–57]. This phenomenon was explained by the formation of large clusters of R$_6$F$_{36}$ defects, which are highly efficient phonon scattering centers. The thermal conductivity of highly concentrated samples is lower than that of quartz glass ($k = 1.36$ W·m$^{-1}$·K$^{-1}$) at $T = 300$ K [58]). Crystals of the Ba$_{1-x}$La$_x$F$_{2+x}$ solid solution are characterized by high fluorine-ion conductivity, which increases with an increasing concentration of $x$ [59–68]. The anticorrelation between the thermal conductivity and anionic conductivity of heterovalent solid solutions of fluorides with a fluorite structure, established in [69], is associated with the inelastic interaction of phonons and mobile fluorine ions. In accordance with the ion transport model proposed in [70], F$^-$ ions occupy interstitial positions in Ba$_{1-x}$La$_x$F$_{2+x}$ crystal structure. A sharp decrease in thermal conductivity with a decrease in temperature to $T = 50$ K, as was noted for solid solutions of Ca$_{1-x}$Y$_x$F$_{2+x}$ [56, 71] and Ba$_{0.50}$Ce$_{0.50}$F$_{2.50}$ [51], was not observed for Ba$_{1-x}$La$_x$F$_{2+x}$ crystals. Monotonic increasing dependence $k(T)$ occurs only for one composition with the maximum lanthanum

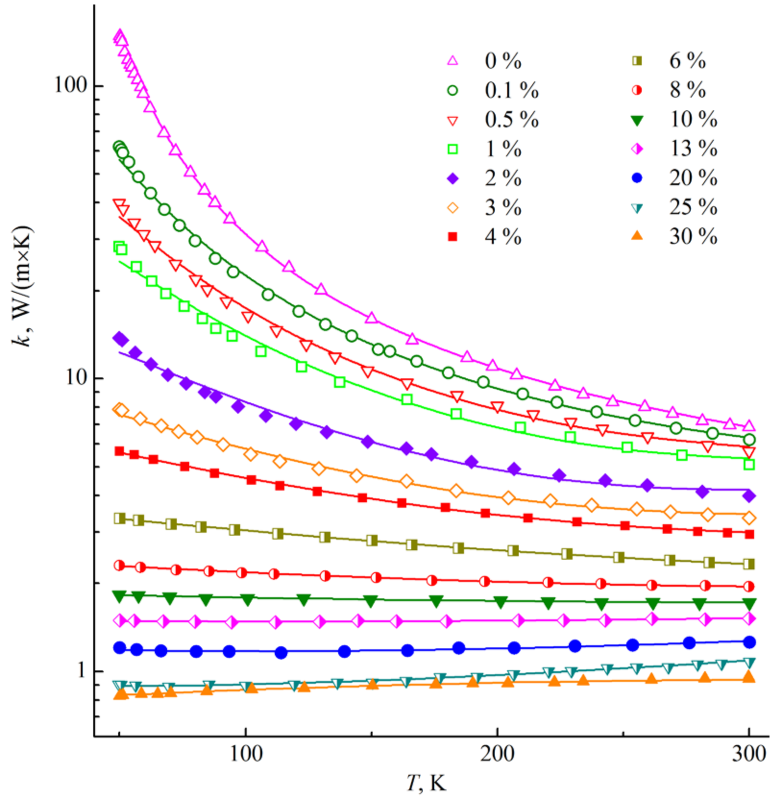

**Fig. 2.** Temperature dependence of thermal conductivity of single crystals of a Ba$_{1-x}$La$_x$F$_{2+x}$ solid solution (in the legend the La content is in mol %)

**Table 1.** Thermal conductivity values (W/(m·K) at different temperatures

| Lanthanum content $x$ mol. fraction | Temperature, K | | | | | |
|---|---|---|---|---|---|---|
| | 50 | 100 | 150 | 200 | 250 | 300 |
| 0.001 | 62.1 | 21.8 | 13.1 | 9.42 | 7.36 | 6.20 |
| 0.005 | 39.9 | 16.6 | 10.6 | 8.11 | 6.56 | 5.66 |
| 0.01 | 28.3 | 13.3 | 9.08 | 7.03 | 5.87 | 5.10 |
| 0.02 | 13.8 | 7.91 | 6.06 | 5.01 | 4.42 | 3.98 |
| 0.03 | 7.86 | 5.62 | 4.61 | 4.00 | 3.63 | 3.35 |
| 0.04 | 5.67 | 4.56 | 3.86 | 3.44 | 3.17 | 2.95 |
| 0.06 | 3.34 | 3.03 | 2.79 | 2.59 | 2.44 | 2.33 |
| 0.08 | 2.30 | 2.18 | 2.09 | 2.03 | 1.98 | 1.95 |
| 0.10 | 1.83 | 1.79 | 1.76 | 1.74 | 1.73 | 1.72 |
| 0.13 | 1.50 | 1.48 | 1.49 | 1.49 | 1.50 | 1.52 |
| 0.20 | 1.21 | 1.16 | 1.18 | 1.20 | 1.23 | 1.26 |
| 0.25 | 0.904 | 0.898 | 0.936 | 0.976 | 1.03 | 1.08 |
| 0.30 | 0.828 | 0.865 | 0.893 | 0.914 | 0.929 | 0.939 |

content of $x$ = 0.30. Obviously, a sharp decrease in the thermal conductivity of the crystals of this solid solution will occur with a more significant decrease in temperature. For three highly concentrated compositions ($x$ = 0.25, $x$ = 0.20, $x$ = 0.13), the $k(T)$ curves have weakly defined minima, while for all other samples the $k(T)$ dependence is monotonously decreasing.

The concentration dependences of the thermal conductivity of the $Ba_{1-x}La_xF_{2+x}$ solid solution for temperatures ($T$ = 50 K and $T$ = 300 K) were shown in Fig. 3. Data analysis demonstrated that the $k(x)$ dependences are monotonic, allowing one to fairly confidently estimate the values of the thermal conductivity coefficient for intermediate (not studied) compositions.

Comparison between the concentration dependences of thermal conductivity $k(x)$ for the $Ba_{1-x}La_xF_{2+x}$ solid solution and the previously studied close analogue $Ba_{1-x}Yb_xF_{2+x}$ with an ytterbium content of up to $x$ = 0.06 (Fig. 4) [48] was carried out. The thermal conductivity of $Ba_{1-x}La_xF_{2+x}$ crystals significantly exceeds that of the corresponding $Ba_{1-x}Yb_xF_{2+x}$ compositions due to size and weight factors. The radius of the barium cation is larger than that of lanthanum and ytterbium while the size of the lanthanum cation is larger than that of ytterbium [72]. Furthermore, the atomic masses of Ba and La are close and significantly smaller than the mass of Yb. As a result, the intensity of phonon-defect scattering in the case of the $Ba_{1-x}Yb_xF_{2+x}$ solid solution will be higher, and, consequently, the thermal conductivity will be lower than in the case of the $Ba_{1-x}La_xF_{2+x}$ solid solution with more homogeneous in cationic characteristics.

The experimental values of thermal conductivity $k(T)$ for studied $Ba_{1-x}La_xF_{2+x}$ crystals was described by expression (1) [33] based on the specific thermal resistance $w = 1/k$ of heterovalent solid solutions. It allows one to satisfactorily approximate the experimental values of $k(T)$ for $Ca_{1-x}Y_xF_{2+x}$ [71], $Ca_{1-x}Yb_xF_{2+x}$ [33], and $Ca_{1-x-y}Sr_xNd_yF_{2+y}$ solid solutions [73]. The expression has the form:

$$\frac{1}{k}=\frac{(1-A)}{\beta\sqrt{\frac{k_0}{d}}\cdot\arctan\left(\frac{\sqrt{k_0 d}}{\beta}\right)}+\frac{A}{D+BT+CT^2}. \qquad (1)$$

Here $A$ is the contribution of thermal resistance associated with the introduction of trivalent rare earth ions and the formation of defect clusters (“amorphous component”); β is a parameter depending on the type of rare earth impurity; $k_0$ is the thermal conductivity coefficient of the undoped crystal; $d$ is the concentration of the rare earth impurity (in the case of a two-component solid solution $Ba_{1-x}La_xF_{2+x}$ it is equal to the mole fraction $x$); $T$ is the temperature in K. Parameters $D$, $B$, and $C$ are coefficients of the polynomial describing the “amorphous component” of the thermal conductivity coefficient and have no explicit physical meaning. The phonon heat

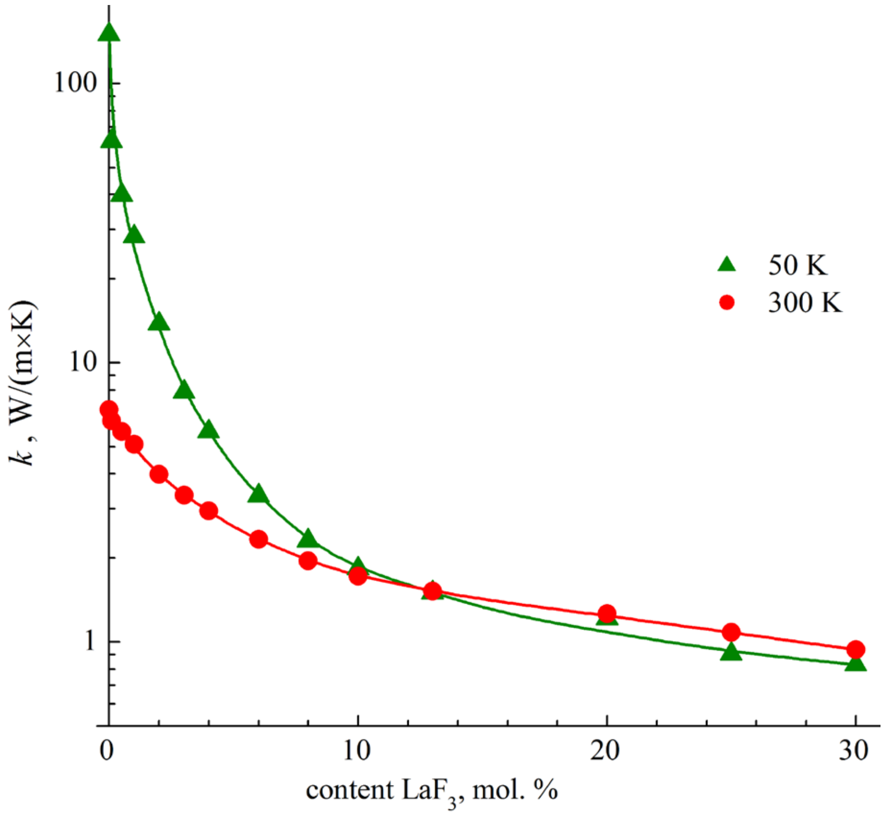

**Fig. 3.** Concentration dependence of thermal conductivity of a $Ba_{1-x}La_xF_{2+x}$ solid solution for different temperatures

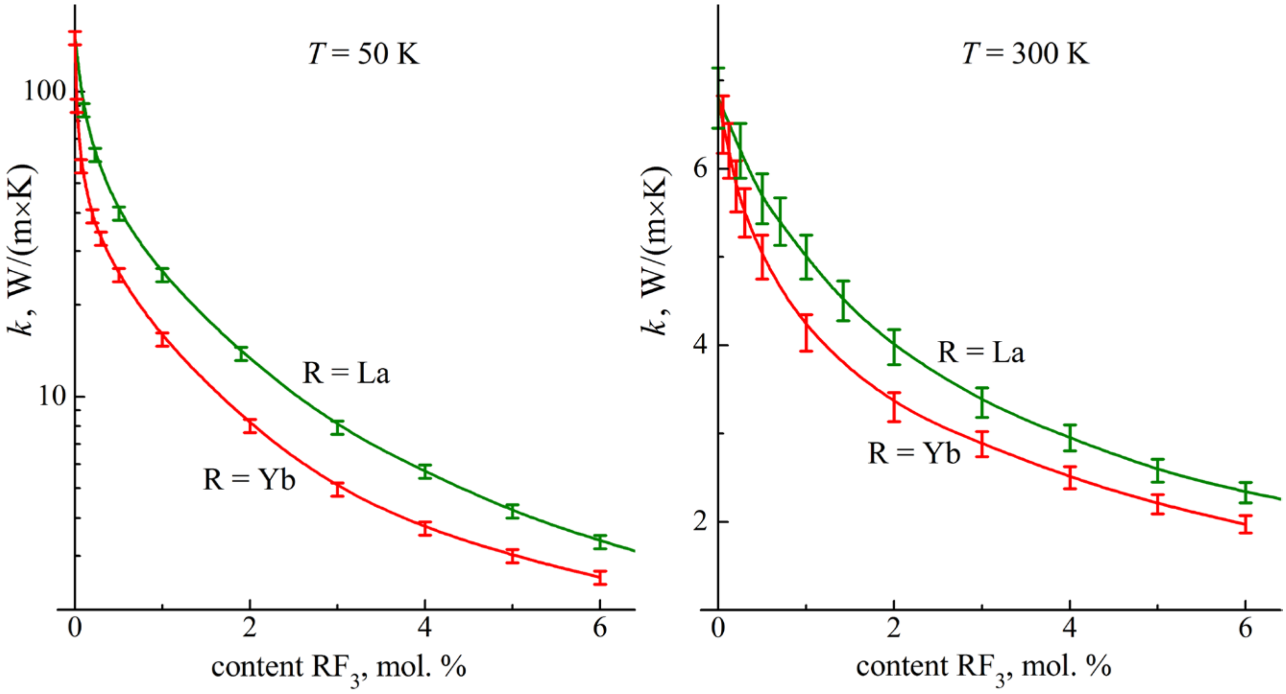

**Fig. 4.** Comparison of concentration dependences of thermal conductivity of $Ba_{1-x}La_xF_{2+x}$ and $Ba_{1-x}Yb_xF_{2+x}$ solid solutions (vertical frames correspond to the measurement error of thermal conductivity ± 5 %)

transfer model developed for single crystals is also conditionally applicable to amorphous media. In these media, the mean free path of phonons reaches its minimum value.

An approximation of the experimental data made it possible to achieve agreement with the corresponding calculated values of $k(T)$ at $\beta = 1$. As the coefficient $k_0$ for a nominally pure $BaF_2$ crystal, an approximating expression of the form was used:

$$k_0 = 1.49 + 1184\exp\left(\frac{91.6}{T}\right)T^{-1} \qquad (2).$$

The values of parameters $A$, $B$, $C$, and $D$ for different compositions are given in Table 2. Their concentration dependences are summarized in Fig. 5. It is evident that the main changes in the values of these parameters occur within the concentration range $0 < x < 10$ mol %. At lanthanum concentrations greater than 10 mol %,

**Table 2.** The values of parameters *A*, *B*, *C* and *D* included in expression 1

| $LaF_3$ content, mol % | $A$ | $C$, $W·m^{-1}·K^{-3}$ | $B$, $W·m^{-1}·K^{-2}$ | $D$, $W·m^{-1}·K^{-1}$ |
|---|---|---|---|---|
| 0.1 | 0.10 | $1.099·10^{-4}$ | $-5.841·10^{-2}$ | 11.33 |
| 0.5 | 0.15 | $1.137·10^{-4}$ | $-5.503·10^{-2}$ | 9.599 |
| 1 | 0.22 | $1.030·10^{-4}$ | $-5.068·10^{-2}$ | 9.056 |
| 2 | 0.33 | $5.769·10^{-5}$ | $-2.848·10^{-2}$ | 5.762 |
| 3 | 0.40 | $2.823·10^{-5}$ | $-1.452·10^{-2}$ | 3.849 |
| 4 | 0.45 | $1.510·10^{-5}$ | $-8.498·10^{-3}$ | 3.013 |
| 5 | 0.51 | $2.453·10^{-6}$ | $-1.978·10^{-3}$ | 1.835 |
| 8 | 0.56 | $1.732·10^{-6}$ | $-7.156·10^{-4}$ | 1.338 |
| 10 | 0.60 | $5.520·10^{-7}$ | $6.453·10^{-5}$ | 1.105 |
| 13 | 0.63 | $6.887·10^{-7}$ | $2.401·10^{-4}$ | 0.9337 |
| 20 | 0.70 | $1.993·10^{-6}$ | $-1.892·10^{-4}$ | 0.8403 |
| 25 | 0.73 | $2.161·10^{-6}$ | $1.266·10^{-5}$ | 0.6490 |
| 30 | 0.76 | $-1.088·10^{-6}$ | $8.417·10^{-4}$ | 0.5947 |

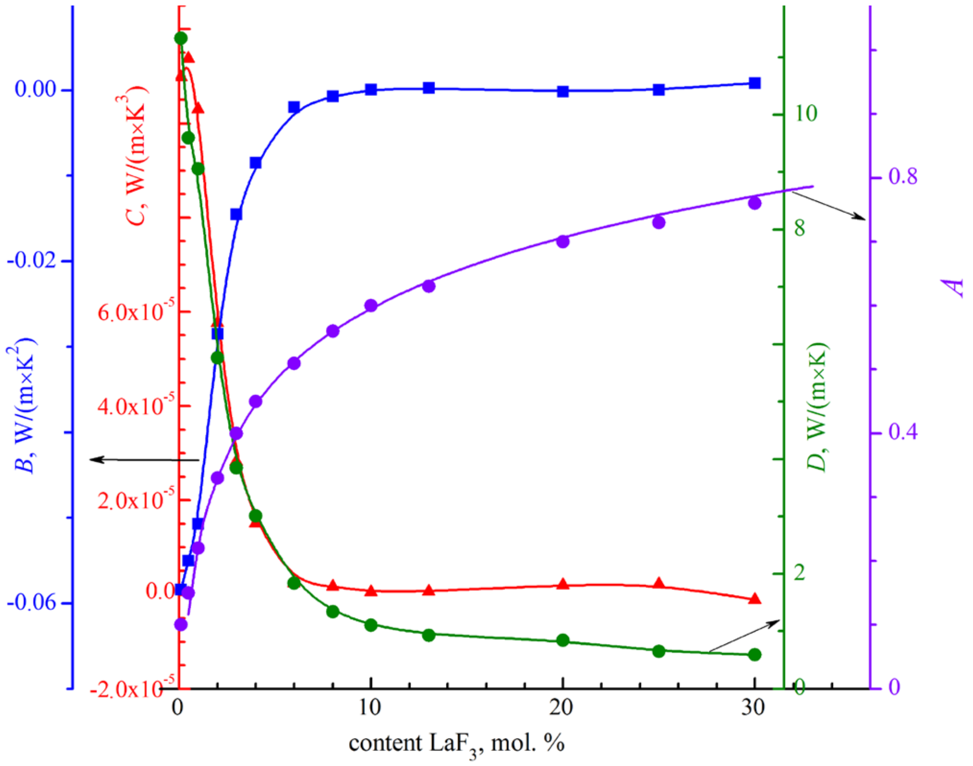

**Fig. 5.** Concentration dependences of the coefficients of the polynomial A, B, C, and D describing the “amorphous component”

the temperature dependences of the thermal conductivity of $Ba_{1-x}La_xF_{2+x}$ crystals practically disappear. To approximate the parameter $A(d)$, the formula $A = 1 + 0.16 \cdot \ln(0.8d)$ was used. Its largest value is obviously lower than $A_{max} = 1$, which corresponds to the intended relative meaning of this parameter.

## 4. Conclusion

For the first time, the thermal conductivity of single-crystal samples of the heterovalent solid solution $Ba_{1-x}La_xF_{2+x}$ ($0 \leqslant x \leqslant 0.30$) was experimentally studied in the temperature range of 50–300 K. It was noted that with increasing La content, the thermal conductivity decreases monotonically, and its temperature dependence changes from a strong decrease to a weak increase. Samples with high lanthanum content demonstrated thermal conductivity values close to those of optical glasses. The experimental results were accurately described by a semi-empirical expression that takes into account the contribution of the crystalline and amorphous components to the thermal resistance of the heterovalent solid solution. The values of the thermal expansion coefficient of $Ba_{1-x}La_xF_{2+x}$ crystals, experimentally determined in the temperature range (from liquid nitrogen to room temperature), have noticeable differences from the thermal expansion coefficient for the $BaF_2$ matrix only at low temperatures.

## Author contributions

The authors contributed equally to this article.

## Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

## References

1. Schotanus P., Dorenbos P., van Eijk C. W. E., Lamfers H. J. Suppression of the slow scintillation light output of $BaF_2$ crystals by $La^{3+}$ doping. *Nuclear Instruments and Methods in Physics Research. A*. 1989;281(1): 162–166. https://doi.org/10.1016/0168-9002(89)91229-1

2. Herweg K., Nadig V., Schulz V., Gundacker S. On the prospects of $BaF_2$ as a fast scintillator for Time-of-Flight positron emission tomography systems. *IEEE Transactions on Radiation and Plasma Medical Sciences*. 2023;7(3): 241–252. https://doi.org/10.1109/TRPMS.2023.3237254

3. Belov M. V., Zavertyaev M. V., Kozlov V. A., Tskhay V. S. Scintillation properties of electromagnetic calorimeter modules based on $BaF_2$ crystals. *Bulletin of the Lebedev Physics Institute*. 2024;51(8): 273–277. https://doi.org/10.3103/S1068335624600475

4. Wojtowicz J., Glodoay J., Wisniewski D., Lempicki A. Scintillation mechanism in RE-activated fluorides. *Journal of Luminescence*. 1997;72–74: 731–733. https://doi.org/10.1016/S0022-2313(97)80790-9

5. Vladimirov S. V., Kaftanov V. S., Nilov A. F. … Skvortsov V. N . Characteristics of BaF2 scintillation crystals. *Atomic Energy*.2001;90: 55–62. https://doi.org/10.1023/A:1011391923801

6. Shendrik R., Radzhabov E., Myasnikova A., … Pankratov V. Ultrafast core-to-core luminescence in $BaF_2$ – $LaF_3$ single crystals. *Scientific Reports*. 2025;15: 26558. https://doi.org/10.1038/s41598-025-11505-w

7. Nepomnyashchikh A. I., Radzhabov E. A., Egranov A. V., Ivashechkin V. F. Luminescence of $BaF_2$–$LaF_3$. *Radiation Measurements*. 2001;33: 759–762. https://doi.org/10.1016/S1350-4487(01)00101-9

8. Radzhabov E. A., Shalaev A., Nepomnyashikh, A. I. Exciton luminescence suppression in $BaF_2$–$LaF_3$ solid solutions. *Radiation Measurements*. 1998;29(3-4): 307–309. https://doi.org/10.1016/S1350-4487(98)00048-1

9. Madirov E. I., Kuznetsov S. V., Konyushkin V. A., Busko D., Richards B. S., Turshatov A. Pushing the limits: down-converting $Er^{3+}$-doped $BaF_2$ single crystals with photoluminescence quantum yield surpassing 100%. *Advanced Optical Materials*. 2024;12(16): 2303094. https://doi.org/10.1002/adom.202303094

10. Kaminskii A. A. *Laser cystals, their physics and properties*. In: Springer Series in Optical Sciences. Berlin: Springer; 1990, vol. 14, 2nd ed. https://doi.org/10.1007/978-3-540-70749-3

11. Lu Z., Zhang Z., Jiang D., … Su L. Thermo-mechanical properties and laser-induced damage behaviors in NYCF and NYSF crystals with different orientations. *Optics Express*. 2025;33(16): 33153–33168. https://doi.org/10.1364/OE.566275

12. Kuznetsov S. V., Aleksandrov A. A., Fedorov P. P. Optical fluoride nanoceramics. *Inorganic Materials*. 2021;57(6): 555–578. https://doi.org/10.1134/S0020168521060078

13. Sorokin N. I., Breiter M. W. Anionic conductivity and thermal stability of single crystals of solid solutions based on barium fluoride. *Solid State Ionics*. 1997;99(3-4): 241–250. https://doi.org/10.1016/S0167-2738(97)00190-2

14. Ivanov-Shits A. K., Sorokin N. I., Fedorov P. P., Sobolev B. P. Specific features of ion transport in nonstoichiometric fluorite-type $Ba_{1-x}R_xF_{2+x}$ (R=La–Lu phases). *Solid State Ionics*. 1989;31(4): 269–280. https://doi.org/10.1016/0167-2738(89)90466-9

15. Preishuber-Pflűgl F., Bottke P., Pregartner V., Bitschnauc B., Wilkening M. Correlated fluorine diffusion and ionic conduction in the nanocrystalline $F^-$ solid electrolyte $Ba_{0.6}La_{0.4}F_{2.4}$–$^{19}F$ $T_{1(\rho)}$ NMR relaxation vs. conductivity measurements. *Physical Chemistry Chemical Physics*. 2014;16(20): 9580–9590. https://doi.org/10.1039/C4CP00422A

16. Rammutla K. E., Comins J. D. High temperature raman scattering studies of $Ba_{1-x}La_xF_{2+x}$. *Radiation Effects and*

*Defects in Solids*. 1999;150(1–4): 347–353. https://doi.org/10.1080/10420159908226255

17. Den Hartog H. W., Langevoort J. C. Ionic thermal current of concentrated cubic solid solutions of $SrF_2$: $LaF_3$ and $BaF_2$: $LaF_3$. *Physical Review B*. 1981;24(6): 3547–3554. https://doi.org/10.1103/PhysRevB.24.3547

18. Den Hartog H. W., Pen K. F., Meuldijk J. Defect structure and charge transport in solid solutions $Ba_{1-x}La_xF_{2+x}$. *Physical Review B*. 1983;28(10): 6031–6040. https://doi.org/10.1103/PhysRevB.28.6031

19. Laredo E., Suarez N., Bello A., Puma M., Figueroa D., Schoonman J. Dislocation polarization and space-charge relaxation in solid solutions $Ba_{1-x}La_xF_{2+x}$. *Physical Review B*. 1985;32(12): 8325–8331. https://doi.org/10.1103/PhysRevB.32.8325

20. Wapenaar K. E. D., Koesveld J. L., Schoonmam J. Conductivity enhancement in fluorite-structured $Ba_{1-x}La_xF_{2+x}$ solid solutions. *Solid State Ionics*. 1981;2(3): 145–154. https://doi.org/10.1016/0167-2738(81)90172-7

21. Ivanov-Shits A. K., Sorokin N. I., Fedorov P. P., Sobolev B. P. Specific features of ion transport in nonstoichiometric $Sr_{1-x}R_xF_{2+x}$ phases (R=La-Lu, Y) with the fluorite-type structure. *Solid State Ionics*. 1989;31(4): 253–268. https://doi.org/10.1016/0167-2738(89)90465-7

22. Trnovcova V., Sorokin N. I., Fedorov P. P., Krivandina E. A., Šramkova T., Sobolev B. P. Electrical properties of heavily doped fluorite-structured $BaF_2$:$RF_3$ (R=rare earth element, Y, Sc) single crystals. *Ionics*. 2000;6(5): 351–358. https://doi.org/10.1007/BF02374152

23. Munnangi R., Mohammad I., Fichtner M. Room temperature fluoride ion batteries. *ECS Meeting Abstracts, Vol. MA2019-01, A02-Lithium Ion Batteries and Beyond*. 346. https://doi.org/10.1149/MA2019-01/2/346

24. Rongeat C., Munnangi A. R., Witter R., Fichtner M. Nanostructured fluorite-type fluorides as electrolytes for fluoride ion batteries. *The Journal of Physical Chemistry C*. 2013;117(10): 4943–4950. https://doi.org/10.1021/jp3117825

25. Astruc A., Celerier S., Pavon E., Mamede A.-S., Delevoye L., Brunet S. Mixed $Ba_{1-x}La_xF_{2+x}$ fluoride materials as catalyst for the gas phase fluorination of 2-chloropyridine by HF. *Applied Catalysis B: Environmental*. 2017;204: 107–118. https://doi.org/10.1016/j.apcatb.2016.11.019

26. Akchurin M. Sh., Gainutdinov R. V., Smolyanskii P. L., Fedorov P. P. Anomalously high fracture toughness of polycrystalline optical fluorite from the Suran deposit (South Urals). *Doklady Physics*. 2006;51(1): 10–12. https://doi.org/10.1134/S1028335806010034

27. Aminov L. K., Kurkin I. N., Kurzin S. P., Gromov I. A., Mamin G. V. Identification of the $La_6F_{37}$ cubooctahedral clusters in mixed crystals $(BaF_2)_{1-x}(LaF_3)_x$ by the electron paramagnetic resonance method. *Physics of the Solid State*. 2007;49 (11): 2086–2090. https://doi.org/10.1134/S1063783407110121

28. Aminov L. K., Abdulsabirov R. Y., Korableva S. L., Kurkin I. N., Kurzin S. P. EPR of rare-earth ion clusters in mixed crystals $Ba_{1-x}La_xF_{2+x}$ doped with $Yb^{3+}$ Ion. *Applied Magnetic Resonance*. 2005;29(4): 561–568. https://doi.org/10.1007/BF03166332

29. Fedorov P. P. Association of point defects in non-stoichiometric $M_{1-x}R_xF_{2+x}$ fluorite-type solid solutions. *Butlletí de les Societats Catalanes de Física, Química, Matemàtiques i Tecnologia*. 1991;12(2): 349–381. Режим доступа: https://raco.cat/index.php/ButlletiSCFQMT/article/view/221696

30. Moore D. S., Wright J. C. Laser spectroscopy of defect chemistry in $CaF_2$:Er. *The Journal of Chemical Physics*. 1981;74: 1626–1636. https://doi.org/10.1063/1.441303

31. Kazanskii S. A., Ryskin A. I., Nikiforov A. E., Zaharov A. Y., Ougrumov M. Y., Shakurov G. S. EPR spectra and crystal field of hexamer rare-earth clusters in fluorites. *Physical Review B*. 2005;72(1): 014127. https://doi.org/10.1103/PhysRevB.72.014127

32. Liu K., Bian G., Zhang Z., Ma F., Su L. Modelling and analyzing the glass-like heat transfer behavior of rare-earth doped alkaline earth fluoridecrystals. *CrystEngComm*. 2022;24(37): 6468–6476. https://doi.org/10.1039/D2CE00698G

33. Popov P. A., Shchelokov A. V., Fedorov P. P. Numerical model of temperature-dependent thermal conductivity in $M_{1-x}R_xF_{2+x}$ heterovalent solid Solution nanocomposites, where M stands for alkaline-earth metals and R for rare-earth Metals. *Nanosystems: Physics, Chemistry, Mathematics*. 2024;15(2): 255–259. https://doi.org/10.17586/2220-8054-2024-15-2-255-259

34. Kaczmarek S. M., Tsuboi T., Ito M., Boulon G., Leniec G. Optical study of Yb $^{3+}$/$Yb^{2+}$ conversion in $CaF_2$ crystals. *Journal of Physics: Condensed Matter*. 2005;17(25): 3771–3786. https://doi.org/10.1088/0953-8984/17/25/005

35. Angervaks A. E., Shcheulin A. S., Ryskin A. I., … Fedorov P. P. Di- and trivalent ytterbium distributions along a melt-grown $CaF_2$ crystal. *Inorganic Materials*. 2014;50(7): 733–737. https://doi.org/10.1134/S0020168514070024

36. Savchuk R. N., Omelchuk A. A., Kompanichenko N. M., Nagorny P. G. Reduction of rare earth element fluorides with zirconium. *Russian Journal of Inorganic Chemistry*. 2003;48(10): 1454–1458. Available at: https://elibrary.ru/item.asp?id=27970487

37. Azarov V. V., Skorobogatov B. S. Reduction of rare-earth ions in $LaF_3$ single crystals. *Izvestiya Akademii Nauk SSSR. Neorganicheskiye Materialy* (Inorganic Materials) 1968;4(10): 1748–1749.

38. Kaminskii A. A., Osico V. V., Prokhorov A. M., Voronko Yu. K. Spectral investigation of the stimulated radiation of $Nd^{3+}$ in $CaF_2$–$YF_3$. *Physics Letters*. 1966;22(4): 419–421. https://doi.org/10.1016/0031-9163(66)91208-X

39. Kitajima S., Yamakado K., Shirakawa A., Ueda K., Ezura Y., Ishizawa H. $Yb^{3+}$-doped $CaF_2$–$LaF_3$ ceramics laser. *Optics Letters*. 2017;42(9): 1724–1727. https://doi.org/10.1364/OL.42.001724

40. Novikov V. V., Matovnikov A. V., Avdashchenko D. V., … Shevelkov A. V. Low-temperature structure and lattice Dynamics of the thermoelectric clathrate $Sn_{24}P_{19.3}I_8$. *Journal of Alloys and Compounds*. 2012;520: 174–179. https://doi.org/10.1016/j.jallcom.2011.12.171

41. Popov P. A., Sidorov A. A., Kul'chenkov E. A., … Fedorov P. P. Thermal conductivity and expansion of $PbF_2$ single crystal. *Ionics*. 2017;23(1): 233–239. https://doi.org/10.1007/s11581-016-1802-2

42. Sobolev B. P., Tkachenko N. L. Phase diagrams of $BaF_2$-(Y, Ln)$F_3$ systems. *Journal of the Less Common Metals*. 1982;85: 155–170. https://doi.org/10.1016/0022-5088(82)90067-4

43. Sidorov A. A., Popov P. A., Aksenov S. V., Begunov A. I., Fedorov P. P. Thermal expansion of solid solutions based on

calcium and barium fluorides. *Inorganic Materials*. 2013;49(5): 525–527. https://doi.org/10.1134/S0020168513040146

44. White G. K. Thermal eExpansion at low temperatures of the alkaline earth fluorides and $PbF_2$. *Journal of Physics C: Solid State Physics*.1980;13(26): 4905–4913. https://doi.org/10.1088/0022-3719/13/26/012

45. Cahill D. G., Pohl R. O. Low-energy excitations in the mixed crystal $Ba_{1-x}La_xF_{2+x}$. *Physical Review B*. 1989;39: 10477–10480. https://doi.org/10.1103/PhysRevB.39.10477

46. Cahill D. G., Watson S. K., Pohl R. O. Lower limit to the thermal conductivity of disordered crystals. *Physical Review B*, 1992;46(10): 6131–6140. https://doi.org/10.1103/PhysRevB.46.6131

47. Popov P A., Moiseev N. V., Filimonova A. V., ... Mironov I. Thermal conductivity of $LaF_3$-based single crystals and ceramics. *Inorganic Materials*. 2015;48(3): 304–308. https://doi.org/10.1134/S0020168512030120

48. Popov P. A., Fedorov P. P., Kuznetsov S. V., Konyushkin V. A., Osiko V. V., Basiev T. T. Thermal conductivity of single crystals of $Ba_{1-x}Yb_xF_{2+x}$ solid solution. *Doklady Physics*. 2008;53(7): 353–355. https://doi.org/10.1134/S1028335808070045

49. Moiseev N. V., Popov P. A., Reiterov V.M., Fedorov P. P. Heat Capacity and Thermodynamic Functions of $Ba_{0.70}La_{0.30}F_{2.30}$ heterovalent solid solution. *Condensed Matter and Interphases*. 2010;12(3): 243–246. Available at: https://journals.vsu.ru/kcmf/article/view/1121

50. Andeen N. H., Clausen K. N., Kjems J. K., Schoonman J. A Study of the Disorder in Heavy Doped $Ba_{1-x}La_xF_{2+x}$ by Neutron Scattering. *Journal of Physics C: Solid State Physics*. 1986;19(14): 2377–2389. https://doi.org/10.1088/0022-3719/19/14/004

51. Popov P. A., Fedorov P. P., Konyushkin V. A. Thermal conductivity of single crystals of $Ba_{1-x}R_xF_{2+x}$ (R=La, Ce, Nd, Gd) solid solutions. *Crystallography Reports*. 2017;62(2): 283–287. https://doi.org/10.1134/S1063774517020225

52. Popov P. A., Fedorov P. P., Konyushkin V. A., Nakladov A. N., Kuznetsov S. V., Osiko V. V., Basiev T. T. Thermal conductivity of single crystals of $Sr_{1-x}Yb_xF_{2+x}$ solid solution. *Doklady Physics*. 2008;53(8): 413–415. https://doi.org/10.1134/S1028335808080016

53. Popov P. A., Fedorov P. P., Kuznetsov S. V., Konyushkin V. A., Osiko V. V., Basiev T. T. Thermal conductivity of single crystals of $Ca_{1-x}Yb_xF_{2+x}$ solid solutions. *Doklady Physics*. 2008;53(4): P. 198-200. https://doi.org/10.1134/S102833580804006X

54. Popov P. A., Fedorov P. P., Osiko V. V., Reiterov V. M., Garibin E. A., Demidenko A. A., Mironov I. A. Thermal conductivity of single crystals of $Ca_{1-x}Er_xF_{2+x}$ and $Ca_{1-x}Tm_xF_{2+x}$ solid solutions. *Doklady Physics*. 2012;57(3): 97–99. https://doi.org/10.1134/S1028335812030111

55. Popov P. A., Fedorov P. P., Garibin E. A., Smirnov A. N., Gusev P. E., Krutov M. A. Thermal conductivity of $Ca_{1-x}Ho_xF_{2+x}$ optical ceramics. *Inorganic Materials*. 2012;48(8): 857–860. https://doi.org/10.1134/S002016851207014X

56. Popov P. A., Fedorov P. P., Osiko V. V. Thermal conductivity of single crystals of the $Ca_{1-x}Y_xF_{2+x}$ solid solution. *Doklady Physics*. 2014;59(5): 199–202. https://doi.org/10.1134/S1028335814050036

57. Popov P. A., Fedorov P. P., Konyushkin V. A. Heat conductivity of $Ca_{1-x}R_xF_{2+x}$ (R = La, Ce, Pr, $0 \leqslant x \leqslant 0.25$) heterovalent solid solutions. *Crystallography Reports*. 2015;60(5): 744–748. https://doi.org/10.1134/S1063774515050107

58. Sergeev O. A., Shashkov A. G., Umanskii A. S. Thermophysical properties of quartz glass. *Journal of Engineering Physics*. 1982;43(6): 1375–1383. https://doi.org/10.1007/BF00824797

59. Wapenaar K. E. D., Van Koesveld J. L., Schoonman J. Conductivity enhancement in fluorite-structured $Ba_{1-x}La_xF_{2+x}$ solid solutions. *Solid State Ionics*. 1981;2(3): 145–154. https://doi.org/10.1016/0167-2738(81)90172-7

60. Trnovcova V., Garashina L. S., Skubla A., ... Sobolev B. P. Structural aspects of fast ionic conductivity of rare earth fluorides. *Solid State Ionics*. 2003;157(1-4): 195–201. https://doi.org/10.1016/S0167-2738(02)00209-6

61. Hull S. Superionics: crystal structures and conduction. *Reports on Progress in Physics*. 2004;67(7): 1233–1314. https://doi.org/10.1088/0034-4885/67/7/R05

62. Düvel A., Bednarcik J., Šepelák V., Heitjans P. Mechanosynthesis of the fast fluoride ion conductor $Ba_{1-x}La_xF_{2+x}$: from the fluorite to the tysonite structure. *The Journal of Physical Chemistry* C. 2014;118(13): 7117–7129. https://doi.org/10.1021/jp410018t

63. Sobolev B. P., Sorokin N. I., Bolotina N. B. Nonstoichiometric single crystals $M_{1-x}R_xF_{2+x}$ and $R_{1-y}M_yF_{3-y}$ (M = Ca, Sr, Ba: R = rare earth elements) as fluorine-ionic conductive solid electrolytes. In: *Photonic & Electronic Properties of Fluoride Materials.* Tressaud A., Poeppelmeier K. (ed.). Elsevier; 2016. pp. 465–491. https://doi.org/10.1016/B978-0-12-801639-8.00021-0

64. Gschwind F., Rodrigues-Garsia G., ... Hörmann N. Fluoride ion batteries: theoretical performance, safety, toxicity, and a combinatorial screening of new electrodes. *Journal of Fluorine Chemistry*. 2016;182: 76–90. https://doi.org/10.1016/j.jfluchem.2015.12.002

65. Cheng X., Wang S., Lin X. Preparation and electrochemical properties of $Ba_{1-x}La_xF_{2+x}$ fluoride electrolyte. *IOP Conference Series: Materials Science and Engineering*. 2019;678: 012148. https://doi.org/10.1088/1757-899X/678/1/012148

66. Nikolaichik V. I., Sobolev B. P., Sorokin N. I., Avilov A. S. Electron diffraction study and ionic conductivity of fluorite $Ba_{1-x}La_xF_{2+x}$ and tysonite $La_{1-y}Ba_yF_{3-y}$ phases in the $BaF_2$-$LaF_3$ system. *Solid State Ionics*. 2022;386: 116052. https://doi.org/10.1016/j.ssi.2022.116052

67. Sorokin N. I. Concentration and mobility of charge carriers in the superionic conductor $Ba_{1-x}La_xF_{2+x}$ ($0.05 \leqslant x \leqslant 0.5$). *Physics of the Solid State*. 2024;66(1): 53–58https://doi.org/10.61011/PSS.2024.01.57854.253 Available at: https://journals.ioffe.ru/articles/viewPDF/57854

68. Andersen N. H., Clausen K. N., Kjems J. K., Schoonman J. A study of the disorder in heavily doped $Ba_{1-x}La_xF_{2+x}$ by neutron scattering, ionic conductivity and specific heat measurements. *Journal of Physics C: Solid State Physics*. 1986;19(14): 2377–2389. https://doi.org/10.1088/0022-3719/19/14/004

69. Fedorov P. P., Sorokin N. I., Popov P. A. Inverse correlation between the ionic and thermal conductivities of single crystals of $M_{1-x}R_xF_{2+x}$ (M = Ca, Ba; R–rare-earth element) fluorite solid solutions. *Inorganic Materials*. 2017;53(6): 626–632. https://doi.org/10.1134/S0020168517060036

70. Sorokin N. I., Karimov D. N. Crystallophysical model of ion transport in single crystals of $Ba_{1-x}La_xF_{2+x}$ and $Ca_{1-x}Y_xF_{2+x}$ superionics conductors. *Physics of the Solid State*. 2021;63(12): 1821–1832. https://doi.org/10.1134/S106378342110036X

71. Popov P. A., Shchelokov A. V., Konyushkin V. A., Nakladov A. N., Fedorov P. P. Application of the numerical model of temperature-dependent thermal conductivity in $Ca_{1-x}Y_xF_{2+x}$ heterovalent solid solution nanocomposites. *Nanosystems: Physics, Chemistry, Mathematics*. 2024;16(1): 67–73. https://doi.org/10.17586/2220-8054-2025-16-1-67-73

72. Shannon R. D. Revised effective ionic radii and systematic studies of interaction distance in halides and chalcogenides. *Acta Crystallographica Section A*. 1976;32(5): 751–767. https://doi.org/10.1107/S0567739476001551

73. Popov P. A., Shchelokov A. V., Zentsova A. A., Fedorov P. P. Thermal conductivity of single crystals of $Ca_{1-x-y}Sr_xNd_yF_{2+y}$ solid solution. *Inorganic Materials*. 2024;60(5): 590–600. https://doi.org/10.31857/S0002337X24050082

## Information about the authors

*Pavel A. Popov*, Dr. Sci. (Phys.-Math.), Professor at the Department of Experimental and Theoretical Physics, Bryansk State Academician I. G. Petrovski University (Bryansk, Russian Federation).

https://orcid.org/0000-0001-7555-1390
tfbgubry@mail.ru

*Alexander V. Shchelokov*, graduate student at the Department of Experimental and Theoretical Physics, Bryansk State Academician I. G. Petrovski University (Bryansk, Russian Federation).

https://orcid.org/0009-0001-4090-2506
alexandershchelokov@mail.ru

*Nikolay V. Mitroshenkov*, Cand. Sci. (Phys.-Math.), Head of the Department of Experimental and Theoretical Physics, Bryansk State Academician I. G. Petrovski University (Bryansk, Russian Federation).

https://orcid.org/0000-0002-4418-9613
weerm@yandex.ru

*Alena A. Kushnereva,* master's student at the Department of Experimental and Theoretical Physics, Bryansk State Academician I. G. Petrovski University (Bryansk, Russian Federation).

https://orcid.org/0000-0002-9793-7099
alenazen01@mail.ru

*Vasily A. Konyushkin*, Senior Researcher, Prokhorov General Physics Institute of the Russian Academy of Sciences (Moscow, Russian Federation).

https://orcid.org/0000-0002-6028-8937
vasil@lst.gpi.ru

*Andrey N. Nakladov*, Junior Researcher, Prokhorov General Physics Institute of the Russian Academy of Sciences (Moscow, Russian Federation).

https://orcid.org/0000-0002-4060-8091
andy-nak@yandex.ru

*Pavel P. Fedorov*, Dr. Sci. (Chem.), Chief Researcher, Prokhorov General Physics Institute of the Russian Academy of Sciences (Moscow, Russian Federation).

https://orcid.org/0000-0002-2918-3926
ppfedorov@yandex.ru

*Sergey V. Kuznetsov*, Cand. Sci. (Chem.), Leading Researcher, Prokhorov General Physics Institute of the Russian Academy of Sciences (Moscow, Russian Federation).

https://orcid.org/0000-0002-7669-1106
kouznetzovsv@gmail.com

*Received September 18, 2025; accepted after reviewing October 13, 2025; accepted for publication November 15, 2025; published online April 01, 2026.*