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Original article

Numerical model of temperature-dependent thermal conductivity in $M_{1-x}R_x\mathrm{F}_{2+x}$ heterovalent solid solution nanocomposites where M stands for alkaline-earth metals and R for rare-earth metals

Pavel A. Popov[1], Alexander V. Shchelokov[1], Pavel P. Fedorov[2]

[1]Petrovsky Bryansk State University, Bryansk, Russia
[2]Prokhorov General Physics Institute of the Russian Academy of Sciences, Moscow, Russia

Corresponding author: Pavel P. Fedorov, ppfedorov@yandex.ru

ABSTRACT We propose a mathematical model to fit the temperature-dependent thermal conductivity of $M_{1-x}R_x\mathrm{F}_{2+x}$ heterovalent solid solutions where M stands for alkaline-earth metals and R for rare-earth metals. These solid solutions experience composition-driven transition from the crystal-like to glass-like behavior of thermal conductivity. When tested on $\mathrm{Ca}_{1-x}\mathrm{Yb}_x\mathrm{F}_{2+x}$ solid solutions, the model showed a potential for use with an option for further improvements.

KEYWORDS thermal conductivity, thermal resistance, temperature dependence, solid solution, mathematical model

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1. Introduction

Heat transfer in solids is related to many diverse factors, including the crystal structure, structure perfection and symmetry, chemical composition, temperature, and some others. Accordingly, extant theoretical models used to fit the behavior of the thermal conductivity coefficient are intricate and ineffective (see, e.g., [1–6]). These models are frequently far from providing good fits even for structurally simple and perfect single crystals. Especially serious problems arise in the mathematical description of thermal conductivity in solid solutions with heterovalent ion substitutions.

Rare-earth (R) fluoride solid solutions in fluorite matrices, $M_{1-x}\mathrm{R}_x\mathrm{F}_{2+x}$ (where M = Ca, Sr, Ba, Cd, or Pb), are some types of nanocomposites [7]. Association of oppositely charged point defects generates nanosized defect clusters in these solid solutions; as the rare-earth doping level (x) increases, percolation of defect areas occurs. What we call an "*anti-glass*" is thus formed, that is, a material where the short-range order is destroyed while the long-range order intrinsic to the fluorite structure is preserved [7]. The $R_6\mathrm{F}_{36}$ associates are typical clusters of defects embedded in the fluorite lattice with the replacement of the corresponding fragments $M_6\mathrm{F}_{32}$ of the crystal lattice. The size of these associates is about 1.5 nm. Each cluster is surrounded by a deformation zone. This evolution of the defect structure brings about a radical change in physical properties of crystals. A solid solution has its thermal conductivity decreasing dramatically in response to increasing rare-earth concentration; ultimately, the material becomes a heat insulator. The thermal conductivity coefficient $k(T)$ changes its temperature-dependent trend from that typical of crystals with a low-temperature peak to a glass-like monotone curve with k ascending as temperature rises.

There is now a significant amount of experimental thermal conductivity data for $M_{1-x}R_x\mathrm{F}_{2+x}$ fluoride solid solutions where M stands for Ca, Sr, or Ba and R for rare-earth elements (see, e.g., [8–12]). When M = Ca, the transition from single crystals to anti-glass nanocomposites is particularly clear-cut because of the greatest difference in weight between calcium ions and substituent ions R^{3+}.

Liu et al. [13, 14] proposed a numerical model to fit the temperature-dependent thermal conductivity in $M_{1-x}R_x\mathrm{F}_{2+x}$ solid solutions. This is a synthetic model combining Gaumé et al.'s model for the prediction of thermal conductivity in pure and doped insulating crystals [6] and a simple third-order polynomial for the thermal conductivity coefficient of an amorphous material. The correlation relation of Liu et al.'s model [13] is

$$k = A\beta\sqrt{\frac{k_0}{d}} \cdot \arctan\left(\frac{\sqrt{k_0 d}}{\beta}\right) + (1-A)\left(BT + CT^3\right), \tag{1}$$

where A is a parameter related to the crystal-like heat transfer behavior, β is a dopant-dependent parameter related to the non-crystalline heat transfer behavior, k_0 is the thermal conductivity coefficient of an undoped crystal, d is the dopant concentration, and B and C are the factors of the polynomial for the thermal conductivity coefficient of an amorphous material.

It is evidently an interesting and promising idea to sum-up the terms relating to crystalline and amorphous states. However, the summing-up of thermal conductivity coefficients may have physical meaning only when the heat flow passes in the sample *along parallel* dislike layers that have differing properties. The presence of diverse phonon scattering centers in solid solutions makes it more appropriate to consider the sequential passage of heat flow *through* areas with different thermal resistances. The Matthiessen rule [15] of the additivity of specific resistances in the approximation of independence of scattering centers is fulfilled both for the electric current and for the heat flow [16].

Figure 1 illustrates the results we obtained when applying equation (1) to some $Ca_{1-x}Yb_xF_{2+x}$ solid solution samples [8]. We set $k_0 = 3193T^{-1}$, as Liu et al. did [13]. Liu et al. [13] obtained this simple expression as a fit to the $k(T)$ data set for the $Ca_{1-x}Yb_xF_{2+x}$ sample that had the least dopant level ($x = 0.01$ mol %) taken from our data [8]. The fitted curves and datapoints show an appreciable divergence in the dopant concentration range from 0.7 to 9 mol %. The measured $k(T)$ values exhibit like trends for the 0.7, 1, 1.5, and 3 % rare-earth samples, with temperature-diffuse $k(T)$ peaks typical of appreciably disordered crystal structures. However, not only do the fitted curves deviate strongly from the datapoints, but their runs are also different: for the 0.7, 1, and 1.5 % rare-earth samples, the fitted $k(T)$ curves decline throughout the range of temperatures studied (50 – 300 K), while for the 3 % sample the curve is typical of an amorphous material.

Liu et al.'s model [13] gave a satisfactory fit of temperature-dependent thermal conductivity coefficient $k(T)$ data for $Ca_{1-x}Yb_xF_{2+x}$ solid solution crystals [8] only when equation (1) was used in "three stages". For low dopant concentration levels, Liu et al. [13] confined the model to the first term of the expression, which relates to crystalline thermal conductivity. For moderate dopant concentrations, the entire temperature range was divided into a pair of areas. In the

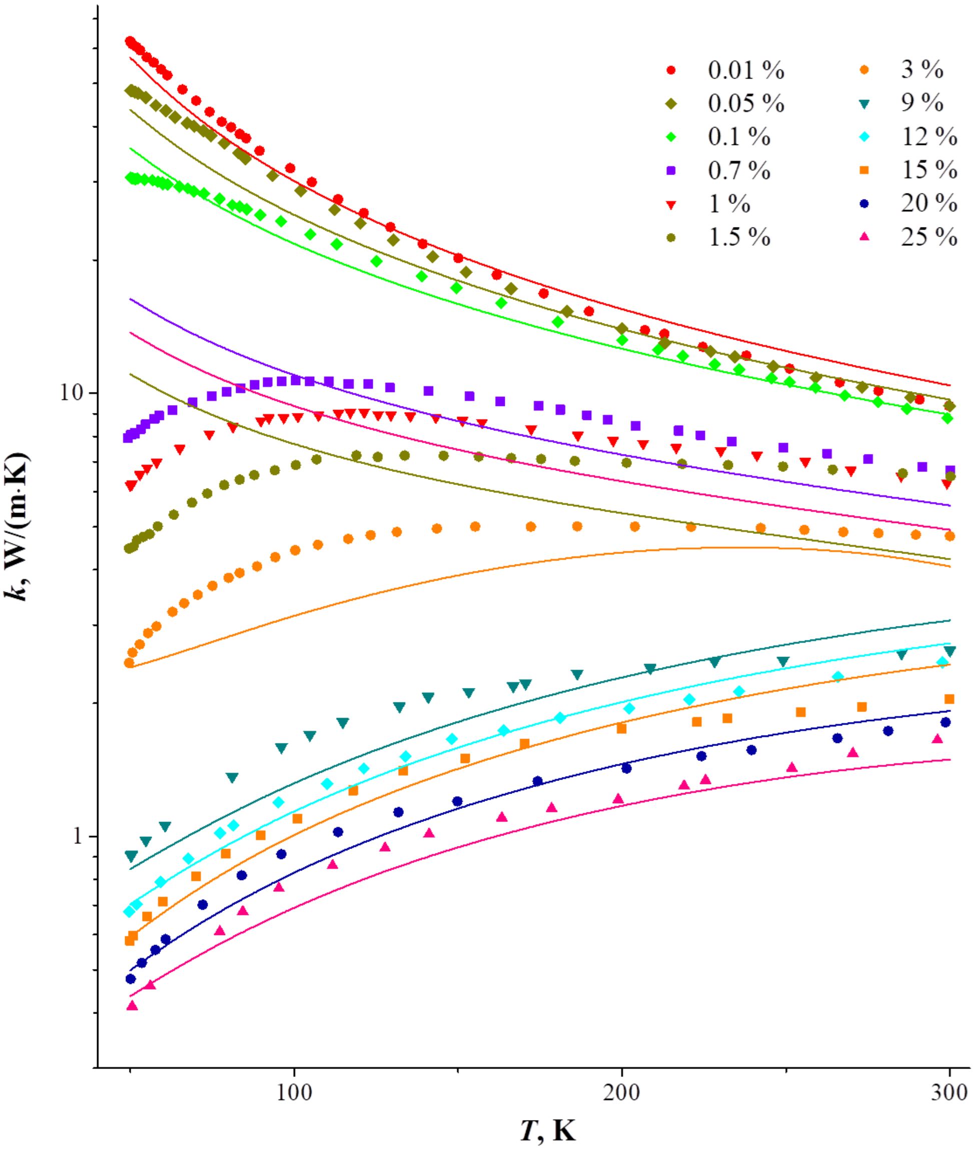

FIG. 1. Temperature-dependent thermal conductivity coefficient in $Ca_{1-x}Yb_xF_{2+x}$ solid solution single crystals: symbols refer to measured data points [8], and lines are fitted curves calculated by model (1)

range 50 – 100 K, the rise in thermal conductivity coefficient was fitted by the above polynomial, while after $k(T)$ passed the peak temperature, the whole equation (1) was applied. For high dopant concentrations, this equation was applied to fit the increasing thermal conductivity over the entire temperature range (50 – 300 K) with low values of the parameter A.

Our goal was to modify Liu et al.'s model [13] using Matthiessen's rule.

2. Results and discussion

The model we proposed and used to calculate the temperature-dependent thermal conductivity coefficient for $M_{1-x}R_x\mathrm{F}_{2+x}$ heterovalent solid solutions is as follows

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

where A is the amorphous specific resistance contribution; β is the parameter depending on the dopant; k_0 is the thermal conductivity coefficient of an undoped crystal; d is the dopant concentration; and D, B and C are factors of the polynomial for the amorphous thermal conductivity coefficient.

Keeping in mind that the range of temperatures we studied starts at 50 K, which is not a very low temperature, and the heat capacity, which directly influences the thermal conductivity coefficient, rises more slowly than by the $C \sim T^3$ law, we lowered the polynomial order to the second order. Also, we added the zero order factor D, whose meaning is the "remnant" thermal conductivity when the $k(T)$ is extrapolated to $T = 0$. Liu et al. [13] took k_0 as $k_0 = 3193T^{-1}$. Liu et al. [13] obtained this simple expression as a fit to the $k(T)$ data set for the $\mathrm{Ca}_{1-x}\mathrm{Yb}_x\mathrm{F}_{2+x}$ sample that had the least dopant level ($x = 0.01$ mol %) taken from our data [8]. However, the $k \sim T^{-1}$ law is approximately fulfilled only within a limited (near-room) temperature range, and only for some compounds. Without making serious corrections and complications, we selected $k_0 = 4575T^{-1.08}$ with the least deviations from experimental data, similar to the expression Liu et al. used [13]. As the parameter β, we took $\beta = 0.20$, which slightly differs from the $\beta = 0.16$ in Liu et al.'s model [13].

Figure 2 shows the fits by our model (2) for the entire dataset comprised of the $k(T)$ values we measured for twenty $\mathrm{Ca}_{1-x}\mathrm{Yb}_x\mathrm{F}_{2+x}$ solid solution compositions. In all cases, model (2) was used in the same manner, in the same form, and for the entire range of temperatures studied (50 – 300 K). One can observe a very close match of the behaviors of measured and fitted $k(T)$ curves over the entire concentration range.

As for the parameter A, its values that we selected show a concentration dependence little differing from the one described by a log function with a constant term (Fig. 3).

3. Conclusion

Altogether, our mathematical model has shown a good ability to fit the temperature-dependent behavior of the thermal conductivity coefficient in heterovalent fluoride solid solutions, with their diversity, which solid solutions experience a composition-driven transition from the crystal-like to glass-like behavior of thermal conductivity. When tested for $\mathrm{Ca}_{1-x}\mathrm{Yb}_x\mathrm{F}_{2+x}$ solid solution, the model has shown a promise for use with an option for further improvements.

In the future, we intend to correct the expressions for the model parameters and test the model for a wider range of similar compounds, as well as to analyze the model parameters depending on the type of compound.

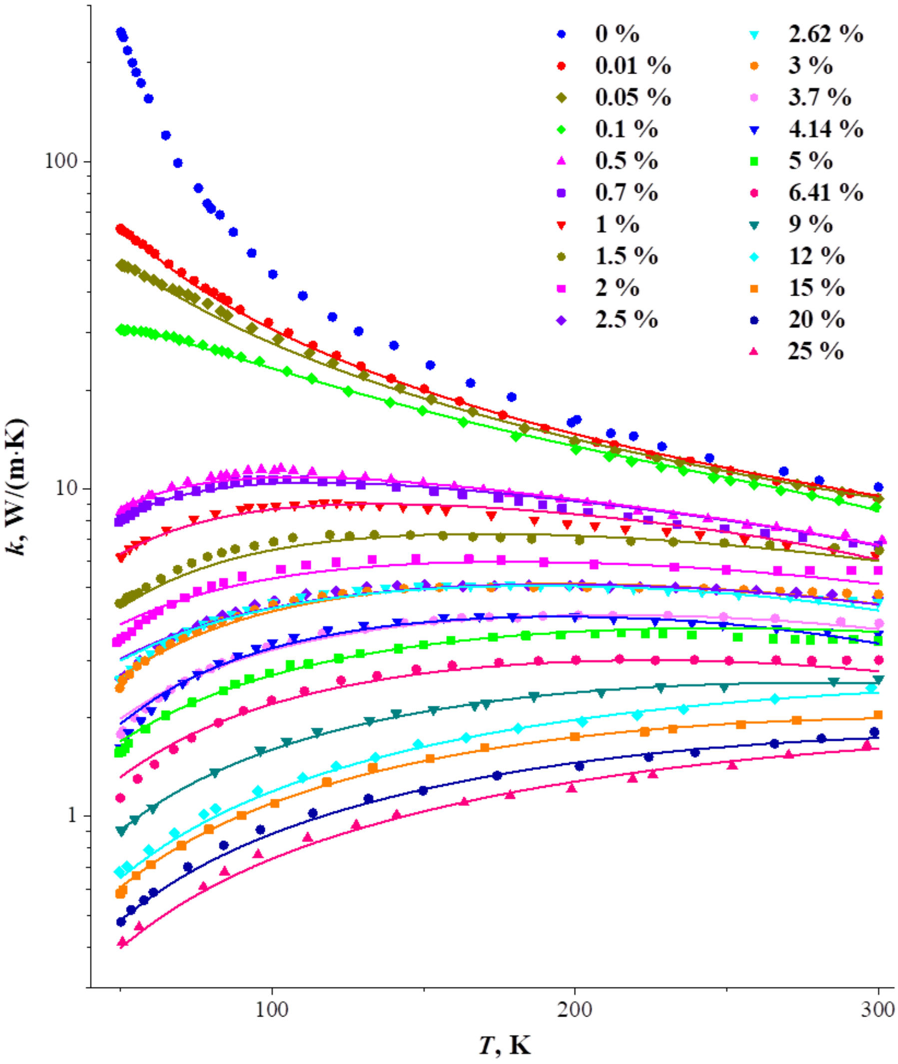

FIG. 2. Temperature-dependent thermal conductivity coefficient for $Ca_{1-x}Yb_xF_{2+x}$ solid solution single crystals: symbols refer to measured data points [8], and lines are fitted curves calculated by model (2)

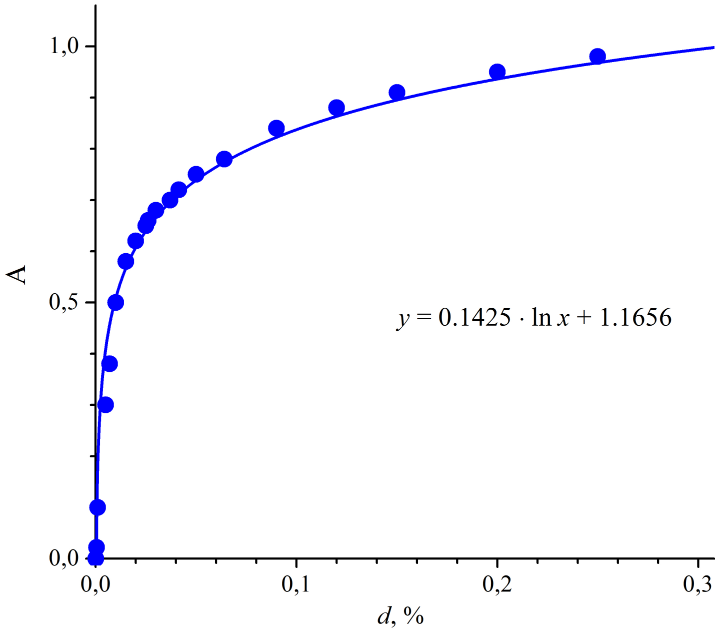

FIG. 3. Parameter A versus YbF_3 concentration in $Ca_{1-x}Yb_xF_{2+x}$ solid solution

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Information about the authors:

Pavel A. Popov – Petrovsky Bryansk State University, 14 Bezhitskaya str., Bryansk, 241036 Russia; ORCID 0000-0001-7555-1390; tfbgubry@mail.ru

Alexander V. Shchelokov – Petrovsky Bryansk State University, 14 Bezhitskaya str., Bryansk, 241036 Russia; ORCID 0009-0001-4090-2506; alexandershchelokov@mail.ru

Pavel P. Fedorov – Prokhorov General Physics Institute of the Russian Academy of Sciences, 38 Vavilova str., Moscow, 119991 Russia; ORCID 0000-0002-2918-3926; ppfedorov@yandex.ru

Conflict of interest: the authors declare no conflict of interest.