STRUCTURAL CHARACTERISTICS OF ALKALINE EARTH FLUORIDES AND THEIR THERMAL CONDUCTIVITY: SrF_2 WITH YF_3 AND LuF_3 IMPURITIES

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The relationship between structural characteristics and thermal conductivity of crystals is examined. Thermal conductivity data are obtained for strontium fluoride crystals, both pure and doped with YF_3 and LuF_3.

The introduction of trivalent impurities into strontium fluoride leads to regular changes, typical of crystals with point defects, in thermal conductivity, and correspondingly, thermal resistance (Fig. 1A, B). The thermal resistance of two pure specimens (Nos. 1, 2) differed insignificantly, and the additional thermal resistance of specimen No. 2 was connected with an uncontrolled impurity, evidently oxygen, introduced in growth of the monocrystal (data on the electrical conductivity of specimen No. 2 indicate strong hole conductivity; the most probable impurity producing hole conduction in strontium fluoride is oxygen).

The slope of the temperature curves of thermal resistance of the pure and doped crystals (to 0.5 mole% impurity content) is constant at $A_1 = 4.3 \cdot 10^{-4}$ m/W. At the same time the initial ordinate A_2 of the straight lines $A_1T + A_2$ systematically increases with increase in impurity content. It seems that the negative A_2 values in pure SrF_2 specimens, just as in CaF_2, are related to participation in heat transfer of optical branches, developed in the complex fluorite structure. As a result, the net thermal conductivity is composed of two components, one of which is due to acoustic oscillations, scattering through three phonon interactions [$\lambda_1 = (A_1T)^{-1}$], while the other describes transfer by optical branches formed basically by four phonon interactions (since three phonon scattering is impeded by conservation laws [2]), so that $\lambda_2 \simeq A_2 (A_1T)^{-2}$. The slope of the straight lines W changes only at elevated impurity concentrations ($A_1 = 3.8 \cdot 10^{-4}$ m/W at 1 mole% and $2.4 \cdot 10^{-4}$–$2.64 \cdot 10^{-4}$ at 3 mole%). However a linear relationship can be seen for the additional impurity resistance $W_N = A_2(N) - A_2(0)$ [where $A_2(0)$ characterizes pure specimen No. 1) for all impurity concentrations: $W_N = 6.46 \cdot 10^{-2} \pm 0.48 \cdot 10^{-2}\ N_I\%$ m·deg/W for specimens doped with Y, and $W_N = 5.5 \cdot 10^{-2} \pm 0.48 \cdot 10^{-2}\ N_I\%$, m·deg/W for specimens containing Lu. A reduction in A_1 contradicts known relationships describing the thermal conductivity of lattices with point defects [3]. This phenomenon is also observed at increased impurity concentrations in CaF_2 and can be explained by a certain readjustment of the oscillatory spectrum, upon which interaction of acoustic and optical phonons decreases.

The preservation of linearity in W_N as a function of N (Fig. 2) makes possible the assumption that, as before, W_N has a purely defect origin even at high impurity concentrations. In this case one may utilize a linear representation of net thermal resistance for crystals with point defects, scattering in which occurs according to the Rayleigh rule [3]. In the theoretical formulation W_N proves to be related to the propagation rates of long wave phonons, the Debye temperature, the mean atomic (molecular) volume, and the logical deformation parameter. All of these values are known for CaF_2 [4]. Due to the lack of corresponding information for SrF_2, we will define a theoretical value for W_N, using Lindeman's rule for evaluation of Θ_D and v, with a constant referred to the structurally similar fluorite lattice. We obtain $W_N = 95.7 \cdot 10^{-2}$–$10.8 \cdot 10^{-2}\ N_I\%$, m·deg/W. For purely isotopic dislocations the parameter $L_1 = (\Delta M/\overline{M})^2$, where $\Delta M = M_d - \overline{M}$. In the crystal doped with Lu the theoretical description agrees satisfactorily with experiment, if only the mass defect is considered ($L_I \simeq 0.7$). However, in crystals doped with Y the mass defect is small ($L_I \simeq 0.02$), and the additional thermal resistance apparently must be ascribed to deformation distortions. The low degree of lattice deformation in the Lu-

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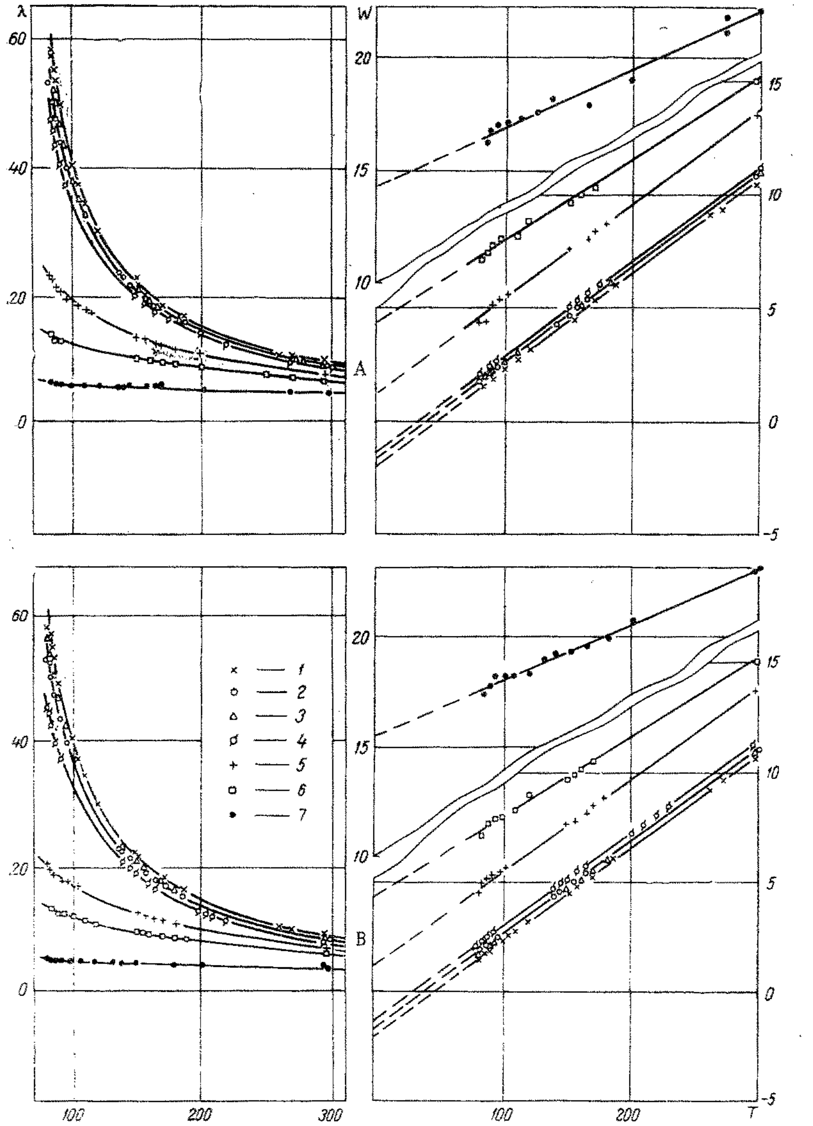

Fig. 1. Temperature (°K) dependence of thermal conductivity (W/m·deg) and thermal resistance (10^2 m·deg/W) of SrF_2 with additions of YF_3 (A) and LuF_3 (B): 1) SrF_2 No. 1; 2) SrF_2 No. 2; 3) 0.03 mole %; 4) 0.1 mole %; 5) 0.5 mole %; 6) 1 mole %; 7) mol. %).

doped crystals may be produced by the strong associative bond between the trivalent substitution impurity (in the cation sublattice) and the compensating excess charge of the fluorine ion (in the octahedral interstice). Such a defect center structure is known in the fluorite lattice from the studies [5, 6]. The associative bond between the ion Y^{3+} and the interstitial anion is significantly weaker. This was noted in the electrical conductivity measurements performed on the doped crystals (the bonding energy difference is approximately 0.1-0.2 eV). Large lattice deformations are also established in CaF_2 crystals doped with Y (the purely deformation portion of $W_N \cong 6 \cdot 10^{-2} N_I\%$). On the whole, under the influence of a trivalent impurity, SrF_2 deforms less than CaF_2. Two possible causes are the higher polarity of Sr^{2+} ions, due to which displacement of the fluorine ion in the octahedral interstice is made easier, and the increase in the ratio of ionic radii of Sr^{2+} on the one hand, and Y^{3+}, Lu^{3+} on the other (especially for the latter). One more observation must be made concerning the behavior of thermal conductivity in specimens with low impurity content (0.03 mole %). Although growth conditions for these specimens and the oxygen contaminated crystals (No. 2) did not differ, nevertheless, the thermal resistance of the doped crystals was below the W values of the undoped No. 2 specimens. Parallel measurements of electrical conductivity permit the assumption that at concentrations of the order of 0.01 mole % Y or Lu compensation occurs between the uncontrolled impurity producing mobile vacancies in the anion sublattice and the trivalent metallic impurity,

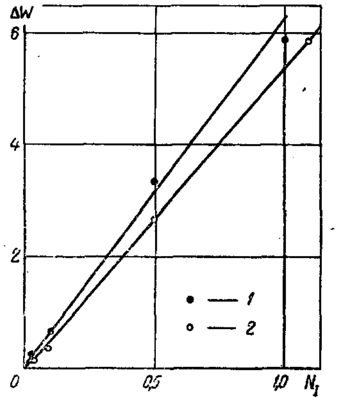

Fig. 2. Supplementary impurity resistance ($4.18 \cdot 10^2$m·deg/W) versus impurity concentration (mole %): 1) doped with YF_3; 2) doped with LuF_3.

which creates mobile interstitial anions in the lattice (the ratio between vacancy and interstitial anion concentrations is regulated by the effective mass rule). If it is assumed that the oxygen concentration in the doped crystals does not differ from that in the pure crystals (No. 2), then the compensation phenomenon can lead to a reduction in thermal resistance. This indicates that the scattering section of the complex consisting of the oxygen ion with vacancy is greater than the scattering section of the combination of the interstitial ion (Y^{3+} or Lu^{3+}) and the oxygen ion.

NOTATION

N_I, molar impurity content, %; λ, thermal conductivity; W, thermal resistance; v, propagation velocity of longwave phonons; θ_D, Debye temperature; V_0, mean atomic volume; L_I, local deformation parameter; M_d, defect mass; $\overline{M}$, mean molecular matrix mass.

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