

Molar heat capacity and thermal conductivity of single crystals of ZnMgSe substitution solid solution

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Determined for the first time are the temperature dependences of thermal conductivity coefficient and molar heat capacity of single crystals of the substitution solid solution $Zn_{1-x}Mg_xSe$ in 25–300°C temperature range. The obtained data are compared with those for control samples of ZnSe single crystal and polycrystalline ZnSe-CVD. The dependence of the density of single crystals of the substitution solid solution $Zn_{1-x}Mg_xSe$ on the concentration of magnesium was found for the first time.

Впервые получены температурные зависимости коэффициента теплопроводности и молярной теплоемкости монокристаллов твердого раствора замещения $Zn_{1-x}Mg_xSe$ в диапазоне температур 25–300°C. Проведено сравнение полученных данных с контрольными образцами монокристаллического ZnSe и поликристаллического ZnSe-CVD. Впервые определена зависимость плотности монокристалла твердого раствора замещения $Zn_{1-x}Mg_xSe$ от концентрации магния.

1. Introduction

Production of materials with new physical parameters is a topical task for semiconductor physics. One of the possible ways of handling this problem is the obtaining of solid solutions of the existing materials. IR optics calls for both narrow-band semiconductor crystals used as IR-radiation receivers, night vision devices, etc., and wide-band materials for middle IR-region lasers. One of the latter materials is $Zn_{1-x}Mg_xSe$ [1], a new crystal produced at the Institute for Single Crystals.

$Zn_{1-x}Mg_xSe$ is a wide-band crystal of substitution solid solution ($E_g = 2.7...3.3$ eV, $x = 0.03...0.60$). At magnesium concentrations higher than $x = 0.13$ this crystal possesses the hexagonal structure of wurtzite that points to the presence of anisotropy of its physical properties. The structural, optical, mechanical, electrophysical and piezoelectric properties of ZnMgSe single crystals

and the scope of their practical application were investigated in [2–5].

The new active materials ($Zn_{1-x}Mg_xSe:Cr^{2+}$; $Zn_{1-x}Mg_xSe:Fe^{2+}$; $Zn_{1-x}Mg_xSe:Cr^{2+}:Fe^{2+}$) meant for tunable lasers for middle IR region were obtained on the base of $Zn_{1-x}Mg_xSe$ at the Institute for Single Crystals, NAS of Ukraine [6]. This aroused great interest to detailed investigations of a number of physical (including thermal) properties of $Zn_{1-x}Mg_xSe$. However, the thermal characteristics (such as heat capacity and thermal conductivity) of the mentioned single crystals have not been studied so far. At the same time, determination of these parameters is necessary while developing and designing laser generators with active elements based on the studied crystals.

2. Experimental

The measurements were performed with $Zn_{1-x}Mg_xSe$ single crystals grown in graphite crucibles by the vertical Bridgman

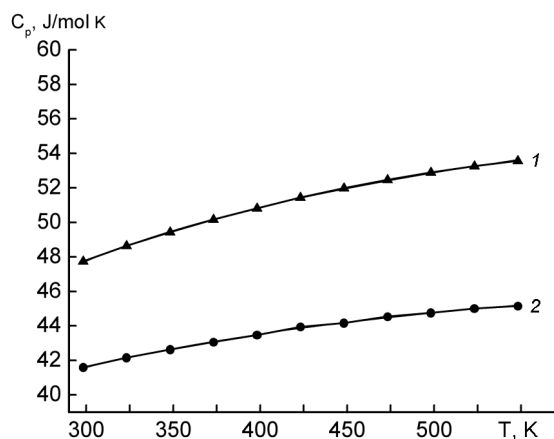


Fig. 1. Temperature dependences of molar heat capacity for the studied crystals: 1 — ZnSe; 2 — $Zn_{0.6}Mg_{0.4}Se$.

method under excessive pressure of inert gas. For control, we used ZnSe single-crystalline samples grown by Bridgman method and polycrystalline ZnSe-CVD samples (with a porosity of 0.22 %). The obtained data cannot be compared with the characteristics of MgSe, in view of the absence of reference data on their of thermal conductivity and molar heat capacity. The investigated samples were shaped as disks with a diameter of 15 mm and a height of 10 mm (for heat capacity measurements) and 5 mm (for thermal conductivity measurements) and polished surfaces.

The temperature dependences of heat capacity (c) and thermal conductivity coefficient (χ) for $Zn_{0.6}Mg_{0.4}Se$ and ZnSe single crystals and polycrystalline ZnSe-CVD samples were measured in 25–300°C range using commercial setups of IT- c -400 and IT- λ -400 types, respectively. The work of these devices is based on calorimetric measurement methods.

In view of rather high error (running into ± 10 % of the measured value) of the used meters (running into ± 10 % of the determined value), the measurements were repeated not less than 10 times for all the samples. Afterwards the obtained data were averaged.

3. Results and discussion

The experimental results obtained while measuring the temperature dependences are presented in Fig. 1 and Fig. 2.

As seen from Fig. 1, within the whole of the investigated temperature range the molar heat capacity of ZnSe single crystals

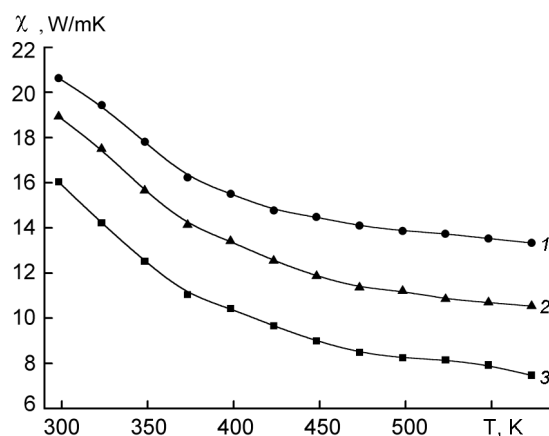


Fig. 2. Temperature dependences of thermal conductivity coefficients for the studied crystals: 1 — $Zn_{0.6}Mg_{0.4}Se$; 2 — ZnSe; 3 — ZnSe-CVD.

Table. Approximation coefficients for determination of the molar heat capacity of the investigated crystals

	a	b	c
ZnSe	49.6	$10.1 \cdot 10^{-3}$	$-4.3 \cdot 10^5$
$Zn_{0.6}Mg_{0.4}Se$	42.9	$5.9 \cdot 10^{-3}$	$-2.8 \cdot 10^5$

exceeds that of $Zn_{0.6}Mg_{0.4}Se$. At the same time the value of thermal conductivity coefficient for $Zn_{0.6}Mg_{0.4}Se$ within the whole of the studied temperature range is higher in comparison with the ones for ZnSe single crystal and ZnSe-CVD polycrystal (Fig. 2). This seems to be caused by the scattering of phonons by intergranular defects, including those present in the boundary-adjacent grain layer.

Analysis of the experimental data contained in Fig. 1 and 2 shows that at the studied temperatures the changes in the molar heat capacity and the thermal conductivity coefficient of $Zn_{0.6}Mg_{0.4}Se$ single crystals are lesser than the ones for the control samples. This confirms the earlier reported fact [7] that the thermal stability of $Zn_{1-x}Mg_xSe$ is higher in comparison with the one of ZnSe.

For inorganic substances the interpolation of temperature dependence of the heat capacity has the form $c_p = a + b \cdot T + c \cdot T^{-2}$. For the investigated crystals the coefficients a , b , c , are presented in Table.

Moreover, in the present work the density of $Zn_{1-x}Mg_xSe$ single crystals with $x = 0.25$; 0.4; 0.5 was experimentally studied for the first time (Fig. 3).

The densities of the source crystalline materials ZnSe (sphalerite structure) and MgSe (rock salt structure) are equal to 5.23 g/cm³ and 4.2 g/cm³, respectively.

The experimental data and the theoretical dependence (dotted line) for the density of Zn_{1-x}Mg_xSe solid solution are presented for the crystals possessing the hexagonal structure of wurtzite where the concentration of magnesium ranges between 6.5 and 30 at. %.

The theoretical density dependence was calculated from the X-ray structure analysis data on the lattice parameters of Zn_{1-x}Mg_xSe single crystals with different magnesium concentrations [2].

The obtained theoretical dependence is well approximated by the second-order polynomial: $\rho = A + B \cdot x + C \cdot x^2$, where $A = 5.23474$; $B = -2.38281$; $C = 0.96963$.

As is seen, the experimental data are in a good agreement with the calculated ones.

4. Conclusions

For the first time, the temperature dependences of the thermal characteristics of Zn_{1-x}Mg_xSe solid solution single crystals were determined. It was established that within the studied 25–300°C temperature range their thermal conductivity coefficient exceeded the corresponding value for ZnSe, whereas the heat capacity value was lower than the one of all the reference samples.

The dependence of the density of hexagonal Zn_{1-x}Mg_xSe single crystal on magnesium concentration was obtained for the first time. Proposed is an empiric formula which describes this dependence for the concentrations ranging between 6.5 and 30 at. %.

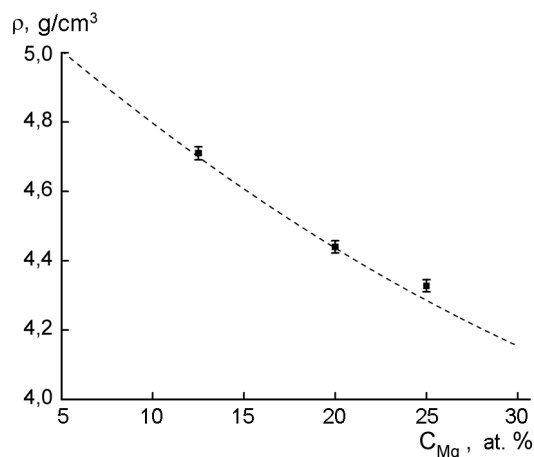


Fig. 3. Dependence of the density of Zn_{1-x}Mg_xSe single crystal on the concentration of magnesium for wurtzite-type crystalline structure.

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Теплоємність і теплопровідність монокристалів твердого розчину заміщення ZnMgSe

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Вперше отримано температурні залежності коефіцієнта теплопровідності і молярної теплоємності монокристалів твердого розчину заміщення Zn_{1-x}Mg_xSe у діапазоні температур 25–300°C. Проведено порівняння отриманих даних з контрольними зразками монокристалічного ZnSe і полікристалічного ZnSe-CVD. Вперше визначено залежність щільності монокристала твердого розчину заміщення Zn_{1-x}Mg_xSe від концентрації магнію.