Low Temperature Specific Heat of BiOX (X = Cl, Br, and I) Single Crystals

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Low temperature specific heat of layered bismuth oxyhalide crystals has been studied in the temperature range from 2 to 50 K in zero and 8 T magnetic field. The expected Debye-like behaviour at the lowest temperatures (below 4–5 K) is established. Linear dependences of entropy and the Debye temperature as cross-correlation parameters are established. The small values of the Debye temperature and peculiarities of phonon spectra at lowest temperatures are discussed.

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1. Introduction

Oxyhalides of bismuth BiOX (X = Cl, Br, I) are very interesting materials which find various applications as X-ray luminescent screens, as anti-Stokes converters, photocatalist and as usual luminophors [1]. The great interest for these materials is strongly related to the influence of dimensionality on the behaviour of physical properties.

The present works deals with the analysis of the specific heat of BiOX to search of the influence of dimensionality to deviation from the Debye classical behaviour.

2. Experimental details

BiOX pure samples was prepared by dissolving 99.99 pure bismuth oxides in hydrochloric acid, evaporating to form the hydrated chlorides, dehydrating the latter under vacuum, heating at $\approx$ 380–700 °C in a X_2 atmosphere, cooling to room temperature, and washing the product to remove BiX_3. The BiOX single crystals were prepared by the vapour gas transport reaction method in closed volume.

The specific heat was measured in the temperature range from 2 to 50 K in zero and 8 T magnetic field. The measurements were performed in a Physical Properties Measurement System (PPMS) from Quantum Design. The specific heat measurement system performs

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fully automated relaxation type heat capacity measurements using so called "two-tau model analysis" to accurately simulate the effect of the heat flow in the system.

3. Results and discussion

At temperatures below 4.5 K, the specific heat of BiOX shows (Fig. 1) a classical behaviour with a T^3 temperature variation. Between 13 K (BiOCl, BiOBr) and 15 K (BiOI), deviations from the T^3 law appear and are explained by means of four Einstein oscillators. The values of the Debye temperature θ_D are 205 K, 168 K and 146 K for BiOCl, BiOBr, and BiOI, respectively. This range of temperatures is in favour of a predominant ionic nature of the bonds.

In Fig. 2 there are shown dependences of the Debye temperature θ_D vs. $1/\sqrt{\mu_{BiOX}}$ and entropy ΔS_{298} vs. molecular mass μ_{BiOX} BiOX compounds. The Debye temperature dependence is in very good agreement with the Anderson relationship [2] $\theta_D = 1.27 \frac{h}{k_B} \sqrt{\frac{Br_0}{\mu_{BiOX}}}$, where μ_{BiOX} is molecular mass of BiOX compounds, B — the elasticity module, r_0 — equilibrium radius of cell, respectively. We calculated the entropy values ΔS_{298} from $C(T)$ dependences (see Fig. 1) by the numerical integral method as $\Delta S_{298} = \int_{T_{min}}^{298.15} \frac{C_p}{T} \, dT$. The entropy of BiOX increases linearly with increase of μ_{BiOX}. The values of entropy are $\Delta S_{298} = 101.7, 108.6$ and 119.5 J/(mol K) for BiOCl, BiOBr and BiOI, respectively.

In conclusion, we have observed at least two domains in the variation of the specific heat. Up to approximately 4 K the behaviour follows the classical Debye
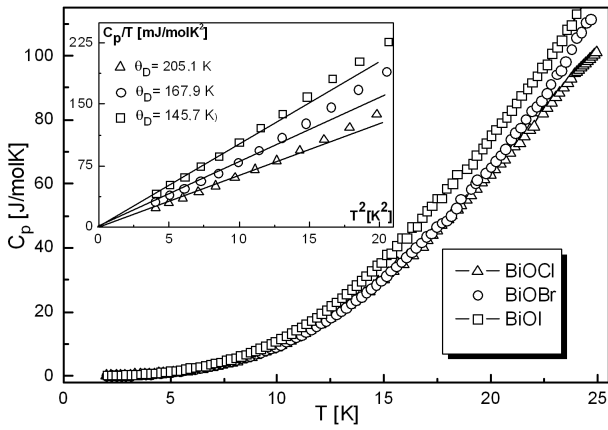
Fig. 1. The temperature dependence of specific heat of BiOX in both C vs. T and C/T vs. T^2 (the inset) representations.
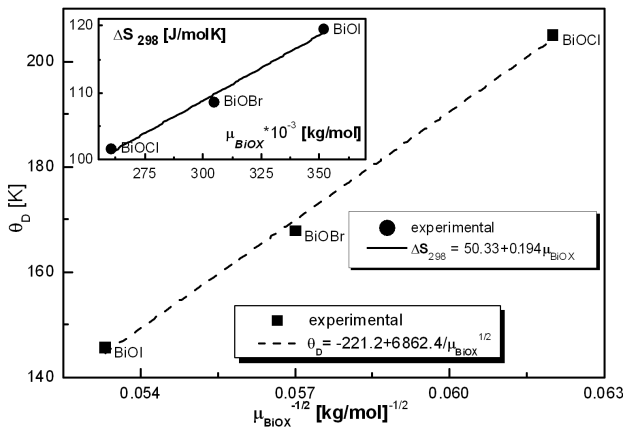

Fig. 2. Dependence of the Debye temperature θ_D vs. $1/\sqrt{\mu_{\mathrm{BiOX}}}$ of BiOX. The inset shows dependence of entropy vs. molecular mass μ_{BiOX} of BiOX.

type. Above this temperature, the behaviour can be explained by low frequency optical phonons synthesized by four Einstein oscillators. Finally, a deviation from the T^3 behaviour has been observed for increasing temperature ($T > 12$–15 K) which may be due to the two-dimensional or multilayer character of BiOX structure [3].

Acknowledgments

References

[1] V.V. Bunda, S.O. Bunda, in: *Physics of Electronic Materials*, Vol. 2, *2nd Int. Conf. Proc. Kaluga (Russia) 2005*, p. 134.

[2] O.L. Anderson, in: *Physical Acoustics*, Vol. III-B, Ed. W.P. Mason, Academic, New York 1965, p. 43.

[3] V.V. Bunda, S.A. Bunda, M. Kajňaková, A. Feher, E. Syrkin, S.B. Feodosyev, *Low Temp. Phys.*, in press.