Specific heat of $CuTa_2O_6$:Sb semiconductors

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In environmental protection, materials are sought that can be used in the photodegradation of dyes under the influence of visible light irradiation. One such may be $CuTa_2O_6$, which exhibits significant photocatalytic activity in the degradation of methyl orange and exhibits excellent stability; it is therefore a promising material for potential use in a practical photocatalyst [1]. The $CuTa_{2-x}Sb_xO_6$ solid solution (x=0.0, 0.1, 0.2, 0.3 and 0.5) crystallizes in a tetragonal system and adopts the $CuTa_2O_6$ structure. The $CuTa_{2-x}Sb_xO_6$ phase was obtained by solid-state reactions both from oxides: CuO, α-Sb_2O_4 and Ta_2O_5, as well as from separately obtained compounds: $CuSb_2O_6$ and $CuTa_2O_6$. The band gaps estimated by the Kubelka-Munk method decreased with increasing antimony ions from E_g = 2.94 eV for x = 0.0 to E_g = 2.64 eV for x = 0.5 [2].

Specific heat C(T) was measured in the 2–300 K temperature range and in the external magnetic field up to 60 kOe using a PPMS platform equipped with a vibrating sample magnetometer (VSM) option (Quantum Design, San Diego, California, USA). For the samples under study, the value of C per molecule reaches the value of 3R according to the Dulong-Petit law (where R is the gas constant). The C(T) data well approximate the Debye-Einstein (DE) model [3]:

$$C(T) = \gamma_0 T + 9nR(1-d)\left(\frac{T}{\theta_D}\right)^3 \int_0^{\frac{\theta_D}{T}} \frac{x^4 e^x}{(e^x-1)^2}\,dx + 3nRd\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{\left(e^{\theta_E/T}-1\right)^2},$$

where the first term represents the specific heat of electrons ($C_{el} = \gamma_0 T$), and the remaining two terms account for the contribution of the crystal lattice, θ_D and θ_E are the Debye and Einstein temperatures, respectively, n is the number of atoms per formula, and d denotes the number of optical phonon modes. For the specific heat measurements, the powder samples were compacted in a disc form (10 mm in diameter and 1-2 mm thick) using the pressure of 18 MPa; then, they were sintered for 2 h at 873 K. The measurement results of the specific heat and the fitting parameters of the DE model are presented in Table 1.

Table 1. Specific heat parameters of solid solution $CuTa_{2-x}Sb_xO_6$: γ_0 is the Sommerfeld constant, T_{max} is the specific heat peak temperature in a magnetic field of 0 and 60 kOe.

x	γ_0 (mJ/molK^2)	θ_D (K)	θ_E (K)	n	d	T_{max} (H=0) (K)	T_{max} (H=60 kOe) (K)
0	18	312	576	9	0.30	11.1	13.3
0.2	14	316	494	9	0.25	11.1	13.3
0.3	16	317	551	9	0.29	8.8	12.5
0.5	11	313	475	9	0.27	8.3	10.5

At low temperatures, a sharp specific heat peak at T_{max} was observed, which broadens and shifts towards higher temperatures with increasing magnetic field. This may mean the appearance of ferromagnetic magnon excitations. However, as the antimony ions content in the sample increases, this effect shifts towards lower temperatures (Table 1).

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