THERMOCHEMICAL DATA OF ARGYRODITE-TYPE IONIC CONDUCTORS: Cu_6PS_5Hal (Hal = Cl, Br, I)

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ABSTRACT

The molar heat capacities of Cu_6PS_5Hal (Hal = Cl, Br, I) have been measured in the temperature range 2 to 500 K. From these data the thermodynamic standard values of entropy, enthalpy and Gibbs free energy were calculated, the heats of formation were computed from the results of vapour pressure measurements and specific heat data. The structural phase transitions at 241 K, 257 K and 272 K of the three compounds were characterized by their thermodynamic parameters. In Cu_6PSCl a new phase transition was found at 165 K.

INTRODUCTION

Compounds of the general formula Me_6PS_5Hal (Me = Ag, Cu; Hal = Cl, Br, I) are members of a new family of tetrahedrally close-packed structures, denoted argyrodites (ref.1). These compounds recently attracted interest because of the incomplete occupancy of the metal-ion sites, which leads to the appearance of order-disorder phenomena, phase transitions and ionic conductivity (ref.2).

In this paper we report the first measurements of the specific heat of copper-argyrodites in order (i) to calculate the basic thermodynamic functions, which have been required to optimize crystal growth by chemical vapour transport (CVT) (ref.3), (ii) to determine quantitatively the thermodynamical parameters of the earlier found structural phase transitions (ref.1) and (iii) to investigate the heat capacity at low temperatures.

EXPERIMENTAL

The samples were synthesized by reacting stoichiometric amounts of high purity elements in evacuated and sealed quartz ampoules for 6 days at 600°C (ref.1,2). For the experiments pressed pellets and single crystals with a typical size from 10 to 500 mm^3 were used.

The heat capacities have been measured with an adiabatic calorimeter at low temperatures (T < 100 K (ref.4)) and by use of a differential scanning calorimeters (Perkin-Elmer DSC-2) above 100 K (ref.5). The overall calorimetric error is estimated to be less than 1.0 % at T < 100 K and 1.5 % for T > 100 K.

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Table 1

Thermochemical data of Copper argyodites (in KJ/Mol)

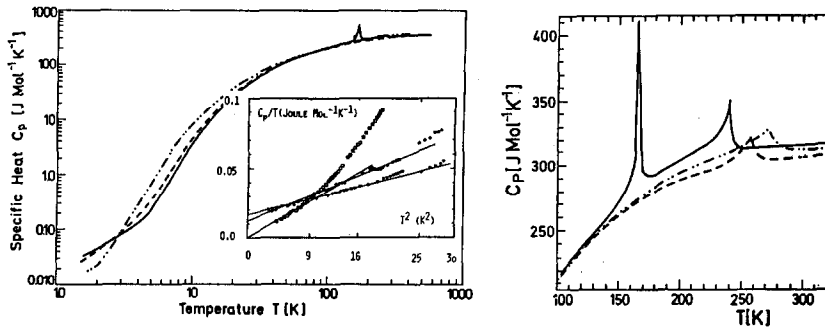| Compound	$\Theta_0[K]$	$H^0_{298}-H^0_0$	S^0_{298}	$G^0_{298}-G^0_0$	H^0_{298}	H^{trans}	S^{trans}
Cu_6PS_5Cl	269	72.34	0.502	-79.854	510±15	0.478	0.00198
Cu_6PS_5Br	232	61.65	0.497	-78.16	477±15	0.505	0.00197
Cu_6PS_5J	204	64.98	0.492	-80.96	439±15	0.507	0.00187

Figure 1 (left) and 2 (right).

Specific heat of Copper argyrodites:

Cu_6PS_5Cl (—), Cu_6PS_5Br (— — —), Cu_6PS_5J (— ∙∙ —).

Insert shows C_p/T vs T^2 below 10 K.

RESULTS

The measured specific heats C_p of the copper-argyrodites as function of temperature are shown in Fig. 1 in a double logarithmic scale. The smoothed curves have been obtained from the best polynomial fit (standard deviation < 0.7 %) to the more than 300 individual experimental points, measured below 100 for each component. The low temperature data are depicted in more detail in the insert of Fig.1 in terms of C_p/T vs T^2. The temperature dependence of $C_p(T)$ above 100 K, where the phase transitions occur, are represented in Fig. 2.

Integration of the fitted $C_p(T)$-curves yields the standard enthalpy increment $(H^0_{298}-H^0_0)$, the standard entropy S^0_{298} and the function $(G^0_{298}-G^0_0)/T$, which are tabulated in Tab. 1. More details of the procedure of polynomial fit and the integration of $C_p(T)$ and the quantitative values for the specific heats will be given elsewhere together with C_p-results on other argyrodites: Ag_6PS_5Hal (Hal = Cl, Br, I) and Me_7PS_6 (Me = Cu, Ag) (ref.6). The Debye temperatures Θ_0 at low

temperatures have been determined using the Debye's T^3-law (insert of Fig. 1).
Table 1 contains the resulting Θ_0-values. Finally we computed the characte-
ristic thermal parameters of the structural phase transitions at 241 K, 256 K
and 273 K, having the enthalpy values ΔH_{tr} = 478, 505, 507 J/Mol and the entro-
pies ΔS_{tr} = 1.98, 1.96, 1.87 J/Mol K for Cu_6PS_5Cl, Cu_6PS_5Br and Cu_6PS_5I, respec-
tively. In order to evaluate $c_p^{trans}(T)$ we had to reconstruct the lattice heat
capacity in the vicinity of the transition by inspection of the change of the
Debye temperature with temperature, $\Theta(T)$ (ref.6).

DISCUSSION
Lattice specific heat

At high temperatures ($T > \Theta$) Neuman-Kopp's rule is fulfilled and the specific
heats have identical values, being $C_p \approx 325$ J Mol^{-1} K^{-1}. At temperatures below
100 K the C_p-data differ considerably due to the different molecular masses of
the constituents: The increase of the halogen-atom mass leads to a systematic
decrease of the Debye temperature Θ_0 in these isotypic structures.

The specific heat of all compounds does not obey Debye's T^3-law, which is
expected for insulating materials at low temperatures. We attribute the anoma-
lous quasilinear heat capacity observed below $T \lesssim 10$ K (fig. 1, insert) to
structural disorder in the Cu-cation sublattice by which the Cu-ions can move
by quantum-mechanical tunneling from one lattice site to another. The occur-
rence of tunneling processes in argyrodites, which is similar to tunneling in
amorphous materials and tunneling processes in other ionic conductors, has been
discussed in more detail recently (ref.6).

PHASE TRANSITIONS

The phase transitions (see Fig. 2) have already been reported (ref.1,2), but
not analysed quantitatively. Since the temperature scale in calorimetric mea-
surements is much more precise than in crystallographic structure investiga-
tions, this may explain the partially considerable differences of the tempera-
tures of transitions between the present data and those reported previously
(ref.1,2). The transitions mark the structural change from the cubic high tem-
perature phase (F43m) into a monoclinic low temperature phase Cc. The tempera-
ture dependence of $c_p^{tr}(T)$ is typical for a second order transition, confirmed
by structural investigations which illuminate that the transition from "order"
to "disorder" is smeared out over a broad temperature range. We could not de-
tect any hysteresis. The transition enthalpies and entropies (see Tab. 1) are
identical for the three compounds. The second transition in Cu_6PS_5Cl, T_c = 165K,

has been detected for the first time. This transformation has not yet been identified structurally.

Therefore an interpretation is rather difficult. However, there are indications that it is a crystallographic transition into a further low temperature phase of type Pc (ref.4).

HEATS OF FORMATION

The heats of formation were calculated from the relations:

$$H^0_{298}(\text{Argyrodite}) = \Delta H_T - \int_{298}^{T} C_p(T)dT \text{ and } \Delta H_T(\text{Cu}_6\text{PS}_5\text{Hal}) = \sum r_i H^T_i - \Delta_D H_T$$

where the first term on the right hand side representing the sum of the heats of formation $r_i H^T_i$ of the dissociation products, can be taken from tabulated data and the second term, the dissociation enthalpy $\Delta_D H_T$ is given by the temperature dependence of the dissociation pressure (ref.3) due to the second law method. The results which agree with preliminary calorimetric investigations of the reaction heat ΔH_T are listed in Table 1.

CONCLUSION

The thermochemical data of $\text{Cu}_6\text{PS}_5\text{Hal}$ (Hal = Cl, Br, I) derived from the measured specific heats made it feasible to calculate vapour phase equilibria and to study growth conditions for CVT of copper-argyrodites (ref.3). Better quality and crystals of larger size have been obtained, in order to perform structure determinations at low temperatures.

ACKNOWLEDGEMENT

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