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CALORIMETRIC INVESTIGATIONS ON THE $SbNbO_4$–$SbSbO_4$ SYSTEM

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Enthalpies of formation and molar heat capacities of $SbNb_{1-z}Sb_zO_4$ ($z = 0.00, 0.07, 0.14, 0.20, 0.38, 1.00$) were determined by solution calorimetry in NaOH/KOH (483 K), drop calorimetry and DSC (320–673 K). The molar heat capacities depend nearly linearly on the Sb(V)-content. The integral molar enthalpies of mixing are positive. A subregular solid solution model permits a good description of the thermodynamic properties of the mixed crystals.

The antimony(III)-orthoniobates-orthoantimonates(V) $SbNb_{1-z}Sb_zO_4$ belong to a promising new group of ferroelectric mixed oxides with high pyro- and piezoelectric sensitivity; the antimony ions are present in two valence states in the crystal lattice. The dielectric properties of the mixed crystals are considerably altered by a variation of the Sb/Nb-stoichiometry [1, 2]. Although the end members of the system are isotypic (orthorhombic cervantite or stibiotantalite lattice [3]), a discontinuity exists in the series of solid solutions (at 1070 K for $0.32 < z < 0.48$ [1, 2]). The thermodynamic properties of the solid solutions have not yet been investigated, although informations about favorable ways for the preparation could be derived from a thermodynamic study.

Isoperibolic solution calorimetry in hydroxide melts and e.m.f. measurements reported elsewhere [4] were employed successfully to determine thermodynamic data of the end phases $SbNbO_4$ and $SbSbO_4$.

Experimental

Preparation of the substances

Attempts at preparation of the mixed crystals by hydrothermal (H_2SO_4/H_2O_2, 520 K, 150 atm [5]) and chemical synthesis (coprecipitation and sintering of the hydroxides [6]) were not satisfying, because the reactions were incomplete. The substances could be prepared by solid state reaction of Sb_2O_3 (99.999%, Ventron),

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Nb_2O_5 (99.9+%, Ventron) and Sb_2O_4 (99.999%, Ventron) at 900 K (500 h) in evacuated and sealed glass ampoules (Supremax, Schott). The solid solutions were controlled by X-ray diffraction and by chemical analysis after dissolving in concentrated HCl in an autoclave (393 K), the Sb(III) and Sb(V) contents were checked bromato- and iodometrically [7].

Calorimetry

The mixed crystals (0.02–0.08 g) were dissolved in less than 20 s in molten mixtures (28 g) of KOH (60 mol%) and NaOH (40 mol%) at 483 K. The solution calorimeter is of the isoperibolic type [4]. Molar heat capacities (320–673 K) were determined by drop calorimetry in air [8, 9] and differential scanning calorimetry (DSC–2 Perkin–Elmer) under argon. In the isoperibolic calorimeters, the temperature was recorded with thermistors, calibration being performed electrically (solution calorimeter) or with α-Al_2O_3 (drop calorimeter).

Results and discussion

The formation of antimony tetroxide and antimony niobate from the oxides

$$0.5\,Sb_2O_3 + 0.5\,M_2O_5 \rightarrow SbMO_4 \quad (M = Sb(V) \text{ or } Nb(V)) \qquad (1)$$

is an exothermic process for Sb_2O_4 ($\Delta_R H$ (483 K) = (-25 ± 4) kJ mol^{-1}), but endothermic for $SbNbO_4$ ($\Delta_R H$ (483 K) = $(+2.8 \pm 3.6)$ kJ mol^{-1}). The positive enthalpy of formation of antimony niobate is in accordance with the temperature dependence of the decomposition pressure. The high entropy of formation of the compound [4], for which no conclusive explanation can be given, is responsible for its thermodynamic stability. The linear equation of molar heat capacity of antimony tetroxide [10] was checked experimentally (Fig. 1). For antimony niobate a quadratic

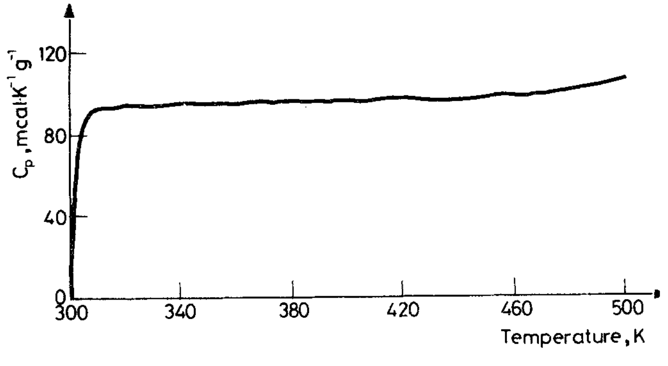

Fig. 1 Heat capacity curve of Sb_2O_4 (DSC–2, argon)

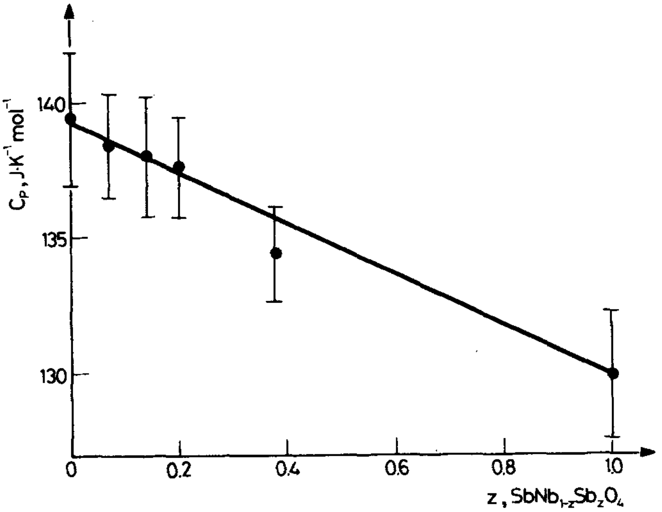

Fig. 2 Mean molar heat capacities ($T = 320$–673 K) of antimony(III) niobates antimonates(V)

C_p equation ($C_p/(\text{JK}^{-1}\ \text{mol}^{-1}) = 115.4 - 7.04 \cdot 10^{-3}\ T/K + 1.068 \cdot 10^{-4}\ T^2/K^2$, $T = 300$–873 K) was derived, that is in agreement with the DSC measurement of Ponomarev et al. [11]. In air an oxidation of $SbNbO_4$ was observed at 873 K, accompanied by vanishing of its initially brown colour; drop experiments in vacuum were used for calculation of C_p at this temperature.

Heat contents of the mixed crystals (320–673 K) depend nearly linearly on the molar fraction of Sb_2O_4 (Fig. 2), although the ferroelectric phase transitions of the mixed crystals, but not those of $SbNbO_4$ and Sb_2O_4, occur in this temperature interval. The phase transitions should therefore be of nearly second order, the small C_p anomaly falling in the experimental errors; this conclusion is confirmed by dielectric and conductivity measurements [2, 12]. The smaller heat capacity of the two-phase sample of global composition $SbNb_{0.62}Sb_{0.38}O_4$ might be due to the absence of the ferroelectric phase transition in the Sb(V)-rich phase [1]. Mean molar heat capacities can be directly assessed from the heat contents; Neumann–Kopp's rule referred to $SbNbO_4$ and Sb_2O_4 is fulfilled and the thermodynamic mixing quantities are therefore independent of temperature.

Integral molar enthalpies of mixing according to a reaction

$$(1-z)\,SbNbO_4 + z\,SbSbO_4 \rightarrow SbNb_{1-z}Sb_zO_4 \qquad (2)$$

can be derived from the molar enthalpies of solution of the mixed crystals in NaOH/KOH-mixtures (Table 1). The integral heats of mixing are always positive, indicating weaker interactions in the lattice by incorporation of Sb(V) ions. Positive

Table 1 Molar enthalpies of solution (NaOH/KOH, 483 K) $\Delta_S H$, integral molar enthalpies of mixing $\Delta_M H$ (cal: from calorimetry, mod: subregular model) and integral Gibbs free energies of mixing $\Delta_M G$ of $SbNb_{1-z}Sb_zO_4$ (in kJ mol^{-1})

z	$\Delta_S H$	$\Delta_M H_{cal}$	$\Delta_M H_{mod}$	$\Delta_M G$
0.00	-124.2 ± 1.8			
0.07	-122.7 ± 1.7	$+1.2 \pm 3.4$	$+1.2$	-0.7
0.14	-119.5 ± 2.5	$+0.7 \pm 4.2$	$+2.3$	-2.4
0.20	-119.3 ± 2.4	$+2.7 \pm 4.0$	$+3.0$	-1.1
1.00	-86.0 ± 1.0			

deviations from ideality are found in nearly all mixed crystal series with isovalent substitution of ions on the same lattice sites [13].

As the system deviates from ideality and as an asymmetric discontinuity in the mixed crystal series occurs, the solid solutions were tentatively described by a subregular model; the integral molar Gibbs free energy of mixing is written as:

$$\Delta_M G = z(1-z)(A(1-z)+Bz)+RT(z \ln z+(1-z)\ln(1-z)) \qquad (3)$$

The interaction parameters A (19.8 kJ mol^{-1}) and B (14.5 kJ mol^{-1}) were calculated from the limits of solubility of the system [13]. The heats of mixing determined from equation (3) are in good agreement with experimental results (Table 1). The ideal entropy of mixing in the subregular model means that Sb(V) and Nb(V) ions should be distributed nearly randomly on the accessible lattice sites. A random distribution seems quite possible because of the similar ionic radii ($r(Nb^{5+}) = 69$ pm, $r(Sb^{5+}) = 60$ pm [14], although the high ionic charge does not favour a statistical repartition [13].

The Gibbs free energies of mixing calculated from calorimetric heats of mixing and ideal entropy of mixing are always negative at 900 K (Table 1), which accounts for the spontaneous formation of mixed crystals from $SbNbO_4$ and Sb_2O_4 at this temperature (see "preparation").

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Zusammenfassung — Bildungsenthalpien und molare Wärmekapazitäten von $SbNb_{1-z}Sb_zO_4$ ($z = 0$, 0,07, 0,14, 0,20, 0,38, 1) wurden durch Lösungskalorimetrie in NaOH/KOH-Schmelze bei 483 K bzw. Einwurfkalorimetrie und DSC (320–673 K) bestimmt.Die molare Wärmekapazität hängt nahezu linear vom Sb(V)-Gehalt ab. Die integralen molaren Mischungsenthalpien sind positiv. Die thermodynamischen Eigenschaften der Mischkristalle lassen sich mit einem subregulären Modell für feste Lösungen gut beschreiben.

Резюме — Методами жидкостной калориметрии в NaOH(KOH) (483 K), капельной калориметрии и ДСК (320—673 K) определены молярные теплоемкости и энтальпии образования системы $SbNb_{1-z}Sb_zO_4$ $z = 0$, 0,07, 0,14, 0,20, 0,38 и 1,00. Молярные теплоемкости почти линейно зависят от содержания пятивалентной сурьмы. Интегральные молярные энтальпии смешения являются положительными величинами. Модель полусистематического твердого раствора дает хорошее описание термодинамических свойств смешанных кристаллов.