Thermochimica Acta, 13 (1975) 357–360
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Note

Thermodynamic properties of Y,Th and U,MX_3 compounds with IIIA and IVA elements

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(Received 20 June 1975)

After the determination of some thermodynamic properties of rare earths (RE) intermetallic compounds, having the REX_3 composition and crystallizing with the $AuCu_3$ type of structure[1–3], we have drawn our attention to other isomorphous compounds formed by yttrium, thorium and uranium with the same partner elements.

The first aim of the present work was to verify the validity of some relationship, found for the REX_3 phases[3], which correlate the heats of formation of these compounds to the dimensions of the involved elements. Moreover, as Y, Th and U have an important role in nuclear technology, it was thought that a knowledge of the physico-chemical properties of such compounds could be of some interest for their further applications.

EXPERIMENTAL

Dynamic differential calorimetry (DDC) has been employed to evaluate the heats of formation of the title compounds. The method has been described elsewhere for $RESn_3$ phases[1] and no significant changes have been made in this instance.

Rare metals used in this investigation were obtained from Koch-Light Laboratories, England, with a purity of 99.95%; the other elements, from the same source, had a purity of 99.999%. Samples ranging from 1.0 to 2.0 g each were prepared from stoichiometric amounts of powder of the two metals, well mixed and pressed directly into the "reaction" Mo containers. Oxidizable substances were manipulated in a dry-box under ultrapure argon. As already observed for the analogous phases of the RE, the reaction is exothermic, fast and leads to the complete formation of the desired compound.

The thermograms were obtained at a heating rate of 20 or 10°C min^{-1} and the magnitude of the thermal effect due to the reaction was evaluated from the corresponding calibration curves. Reproducibility of the results was ensured by preparing several samples for each compound and considering only those alloys for which micrographic and X-ray analysis assured the presence of a single phase.

X-ray examination confirmed the structure ($AuCu_3$-type) and the lattice constant values were found in good agreement with current literature data.

$ThPb_3$ and $ThTl_3$ have not been examined micrographically due to their high reactivity (ignite immediately in air).

As the reactions start at different temperatures (T_r) but always between solid Y, Th or U and liquid Sn, In, Pb, Tl or Ga, the heats of formation have been corrected for the heats of fusion of the partner elements and, assuming the validity of the Neumann and Kopp's rule, could be referred at 298 K, corresponding to the reaction:

$$M(s)+3X(s) = MX_3(s)+\Delta H_f$$

The total error which affects these results is evaluated to be of the order of 5–6%.

DISCUSSION

All the examined compounds, as already known, crystallize with the cubic $AuCu_3$ type of structure, except YSn_3 which does not exist or crystallizes with a different structure. Several attempts to determine the heats of formation of YTl_3 and UTl_3 failed: the reaction between these two elements and Tl spread over a temperature range of about 250°C and the peak area of the reaction is not well defined to be measured with sufficient accuracy. Table I contains the results obtained in the present investigation, together with those existent in the literature.

TABLE I

HEATS OF FORMATION (kcal g-at.$^{-1}$) AT 298 K FOR (Y, Th, U)X_3 COMPOUNDS AND "REACTION TEMPERATURE" (°C) T_r.

Comp.	ΔH_f	T_r	*Ref.*	*Comp.*	ΔH_f	T_r	*Ref.*
YIn_3	−10.0	480°	this work	USi_3	−8.2	—	9
YPb_3	−9.0	340°	this work	UAl_3	−6.5	—	10
YTl_3[a]	−8.5	—	this work	UGe_3	−6.4	—	9
				UGa_3	−6.1	160°	this work
$ThSn_3$	−9.7	520°	this work	USn_3	−5.6	—	9
$ThIn_3$	−9.0	500°	this work	UIn_3	−3.8	430°	this work
$ThPb_3$	−7.0	520°	this work	UPb_3	−3.7	—	9
$ThTl_3$	−6.2	570°	this work	UTl_3[a]	−3.6	—	this work

[a] Extrapolated values.

As already observed for the analogous, isomorphous RE compounds, the stability of these phases, for a given M element, increases in the series Tl, Pb, In, Sn and in the case of the U compounds the series goes on with Ga, Ge, Al, Si.

All the data, for Th and U, were fitted to a straight line, on plotting the heats of formation vs. the radii ratio $r(M)/r(X)$, where $r(M)$ is the ionic radius for tetravalent Th and U, and $r(X)$ is the ionic radius for the X element, corresponding to its higher valency state. For uranium we have used the tetravalent ionic radius as recent works of Misiuk, Mulak and Czopnik[4,5] indicate that this is the most probable electronic configuration of U in these compounds. The values of the ionic radii are taken from Ahrens[6]. The equations for the two straight lines are:

$$\Delta H_f = -9.94\, r(\mathrm{Th})/r(\mathrm{X}) + 4.40\ (\pm 0.55\ \mathrm{kcal\ g\text{-}at.}^{-1})\ \text{for Th compounds}$$

and

$$\Delta H_f = -3.56\, r(\mathrm{U})/r(\mathrm{X}) + 0.03\ (\pm 0.42\ \mathrm{kcal\ g\text{-}at.}^{-1})\ \text{for U compounds.}$$

The data for the Y compounds can be fitted to the straight line for the trivalent RE compounds; it is well known, indeed, that yttrium in many instances behaves like a rare earth.

This correlation is just the same as that found for divalent or trivalent rare earths phases[3], as is shown in Fig. 1, where we have collected all the existent data for these compounds. For trivalent RE some data have been omitted when overlapping occurred. Then, using this correlation, it is possible to evaluate the probable values for YTl_3 and UTl_3 which are −8.5 and −3.6 kcal g-at.$^{-1}$, respectively.

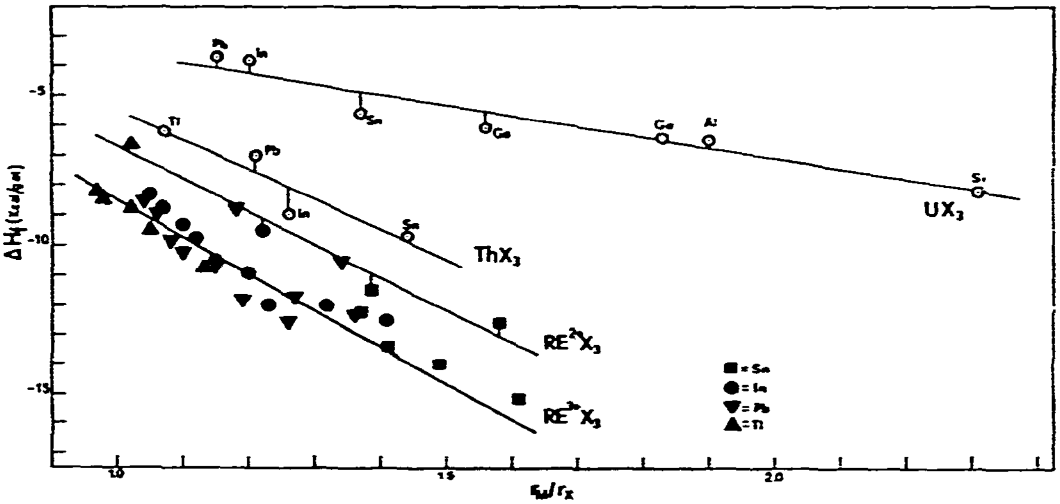

Fig. 1. Heats of formation vs. ionic radii ratio.

The apparently low values for uranium compounds can be explained taking into account the relation due to Miedema[7], which makes possible the evaluation of the heats of formation of several intermetallic compounds. One of the two factors which contributes to the heat of formation of a metallic phase, namely the electron density at the boundary of the Wigner-Seitz cell: n_{WS}, has a very high value for uranium in respect to those for Y, Th and RE. As this factor gives an unfavourable, positive contribution to the ΔH_f, low values of the heats of formation of uranium compounds can be expected. Moreover, as shown by Iandelli and Ferro[8], in RE, Y and Th compounds, the observed M–X distances are lower than those calculated from atomic radii, thus to indicate a "contraction" in the formation of the corresponding phases. Uranium compounds show on the contrary an "expansion" of these distances, the structure being apparently built up on X–X more than on M–X contacts. This fact could explain, once more, the low values of the heats of formation for the UX_3 compounds.

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