Thermochimica Acta, 144 (1989) 151–157
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL BEHAVIOUR OF MIXED TUNGSTATES $ASc(WO_4)_2$ (A = Li, Na, K, Rb AND Cs)

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(Received 9 August 1988)

ABSTRACT

The A_2WO_4–$Sc_2(WO_4)_3$ system, where A = Li, Na, K, Rb and Cs, has been reinvestigated. Four different phases 9:1, 5:1, 2:1 and 1:1 have been obtained and characterized. A reversible transition in $NaSc(WO_4)_2$ (1:1) and three reversible transitions in $Na_4Sc_2(WO_4)_5$ (2:1) have been established. The kinetics and mechanism of formation of $ASc(WO_4)_2$ are evaluated by TG and DTA.

INTRODUCTION

Compounds of mixed oxides have a large number of technological applications. Recently, scandium tungstates have been found to be potentially useful as luminescent materials [1]. Phase relationships of A_2WO_4–$Sc_2(WO_4)_3$ where A = Li, Na, K, Rb and Cs have been reported in the literature [2–4]. However, the available information is not comprehensive. Although phases with composition 9:1, 5:1 and 1:1 have been reported there is no information about other existing intermediate phases. This could be because of the temperature dependent and thermally unstable nature of these phases. In view of the scanty information, the system A_2WO_4–$Sc_2(WO_4)_3$ has been reinvestigated to gain better understanding of solid state behaviour of the phases formed.

EXPERIMENTAL

Different intimately mixed compositions of the mixture A_2WO_4–$Sc_2(WO_4)_3$ were used for the preparation of different phases in the temperature range 400–1000 °C. The mixtures were heated for approximately 60–90 h in a tubular furnace under controlled temperature conditions. Slow heating rates (2–4 °C min^{-1}) were used. The compounds were purified by thorough washing with boiling water, filtering, drying and refiring at 800 °C. The final products were analysed by TG, DTA and X-ray unit techniques.

A Stanton thermobalance (model HT) was used for TG studies. A locally set up DTA unit was used for DTA work. A Philips PW 1010 X-ray unit with a PW 1051 diffractometer was used for X-ray diffraction studies.

For the determination of kinetics and mechanisms of formation, intimate mixtures of (a) $A_2CO_3 + 4WO_3 + Sc_2O_3$ for TG and (b) $A_2WO_4 + Sc_2(WO_4)_3$ were used for DTA. The weight losses corresponding to the formation (in the case of TG) and the exothermic peak (in the case of DTA) were used for the evaluation. Sample weights of 600 mg for TG and 200 mg for DTA were used.

RESULTS AND DISCUSSION

The system Na_2WO_4–$Sc_2(WO_4)_3$ has been reported by Komissarova et al. [2], Klevtsov et al. [3] and Karpov et al. [4]. The compositions reported are 9 : 1, 5 : 1 and 1 : 1. In the present investigations 9 : 1 to 1 : 9 compositions of the mixture are attempted. Amongst these compositions, 2 : 1 phase $Na_4Sc_2(WO_4)_5$ in the sodium tungstate rich region could be predominantly observed, in addition to 9 : 1, 5 : 1 and 1 : 1 phases (Table 1). However, this 2 : 1 phase is found to be temperature dependent. On annealing, this phase disproportionates to 1 : 1 phases $NaSc(WO_4)_2$ and A_2WO_4 (Fig. 1). In compositions beyond 1 : 1, another phase corresponding to 2 : 3 composition is obtained, but this phase is also found to be thermally unstable and could not be isolated from the 1 : 1 phase. X-Ray patterns recorded are diffuse and could not be used to clearly distinguish the separate entities. The identifica-

TABLE 1

XRD pattern of $Na_4Sc_2(WO_4)_5$

d (nm)	*I*	*d* (nm)	*I*
0.9992	20	0.2270	20
0.5717	18	0.2217	20
0.5505	12	0.2113	10
0.5011	100	0.2099	15
0.4707	20	0.1985	5
0.4599	5	0.1918	10
0.3770	95	0.1892	20
0.3232	20	0.1791	25
0.3132	15	0.1759	25
0.3038	90	0.1716	5
0.2988	70	0.1677	10
0.2867	20	0.1614	5
0.2742	5	0.1542	20
0.2508	40	0.1523	20
0.2304	5	0.1447	15

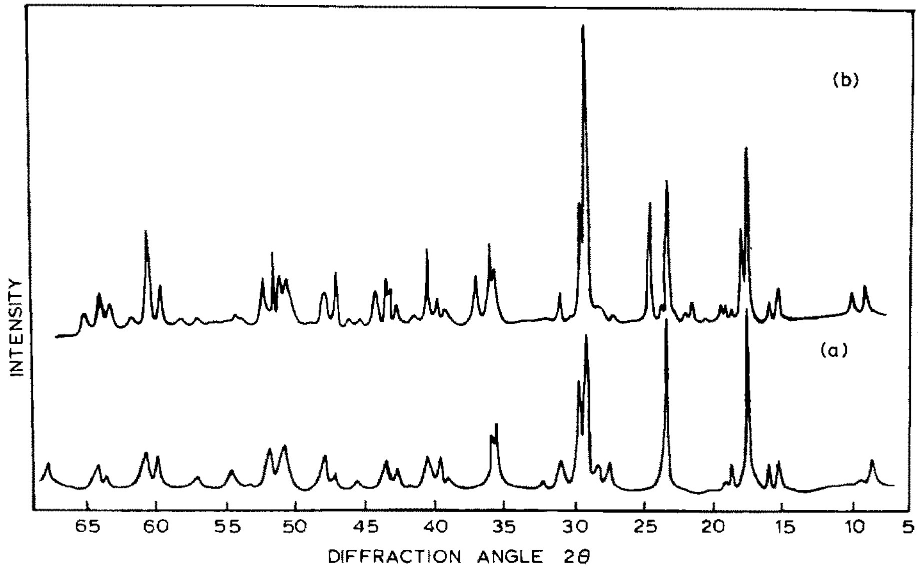

Fig. 1. X-ray diffraction patterns of $Na_4Sc_2(WO_4)_5$: (a) unannealed; (b) annealed.

tion of phases was impossible because of the incongruent melting nature of the phases beyond 1 : 1 composition.

Phase transitions

The formation of 1 : 1 phase $NaSc(WO_4)_2$ is found to occur at the sodium tungstate transition temperature ($\sim 660\,^\circ C$). The sodium tungstate undergoes $\alpha \rightarrow \beta$ transition at this temperature which indicates that the β-phase of sodium tungstate is taking part in the formation reaction.

A reversible transition is observed in the above compound at 835 °C, before melting at 860 °C. Similarly, three reversible transitions are also observed in the 2 : 1 phase $Na_4Sc_2(WO_4)_5$ (671, 713 and 833 °C) before melting at 859 °C (Fig. 2).

Kinetics

The kinetics and mechanism of formation of $ASc(WO_4)_2$ where A = Li, Na, K, Rb, Cs have been evaluated for the reactions

$$A_2CO_3 + 4WO_3 + Sc_2O_3 \rightarrow 2ASc(WO_4)_2 + CO_2$$

and

$$A_2WO_4 + Sc_2(WO_4)_3 \rightarrow 2ASc(WO_4)_2$$

by TG and DTA respectively (Figs. 3 and 4).

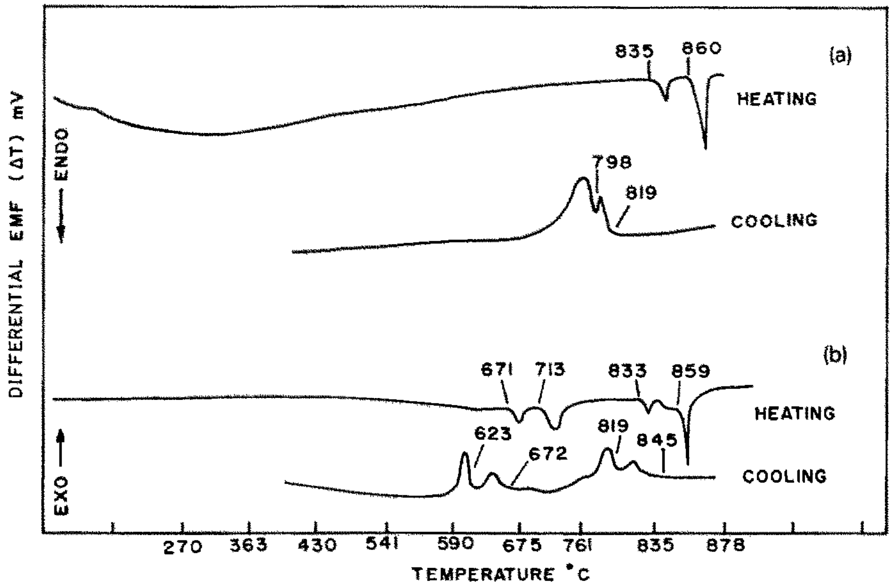

Fig. 2. DTA curves of (a) $NaSc(WO_4)_2$ and (b) $Na_4Sc_2(WO_4)_5$.

Different reaction mechanism models are used [6]. However, these reactions are found to follow the diffusion controlled reaction mechanism of Jander [7] (Fig. 5) and Ginstling and Brounshtein [8] (Fig. 6) respectively.

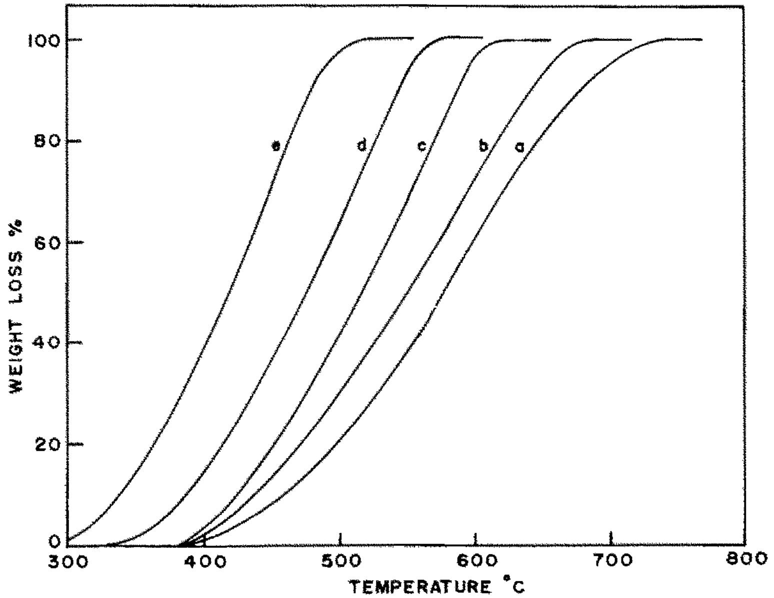

Fig. 3. TG curves of $A_2CO_3 + Sc_2O_3 + 4WO_3$ mixtures where A = Li (a), Na (b), K (c), Rb (d) and Cs (e).

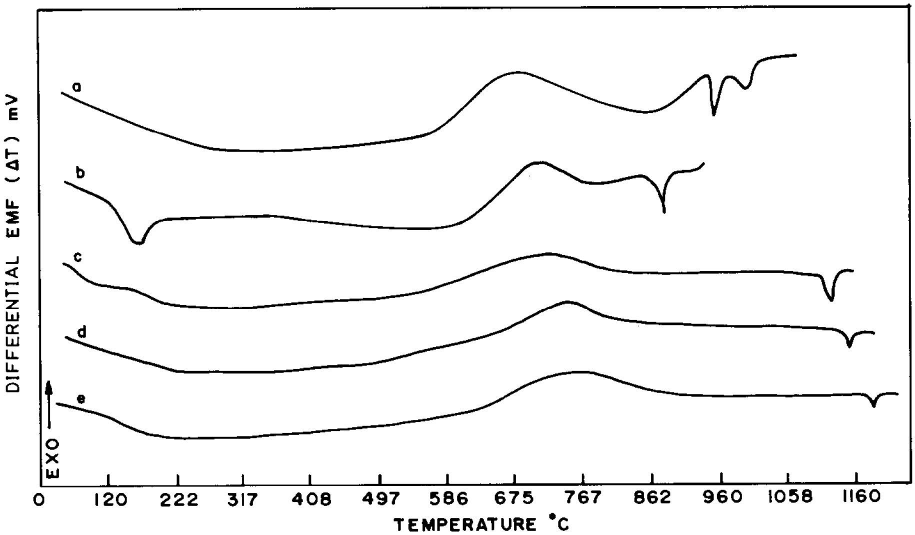

Fig. 4. DTA curves of $A_2WO_4 + Sc_2(WO_4)_3$ (1 : 1) mixtures where A = Li (a), Na (b), K (c), Rb (d) and Cs (e).

Modified forms of their expressions are used to suit dynamic processes. On differentiating with respect to t, substituting $d\alpha/dT$ for $d\alpha/dt$, $K = Ze - E/RT$, and $\beta = dT/dt$ and taking logarithms as follows we obtain

$$\log \frac{d\alpha}{dT}\left[1-(1-\alpha)^{1/3}\right]\left[(1-\alpha)^{-2/3}\right] = C - \frac{E}{2.303RT} \qquad (1)$$

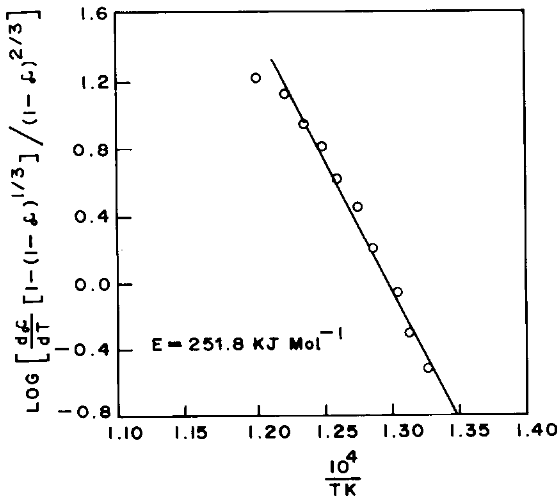

Fig. 5. Typical plot for kinetics of formation of $NaSc(WO_4)_2$ from $Na_2CO_3 + Sc_2O_3 + 4WO_3$ by TG following the Jander model [7].

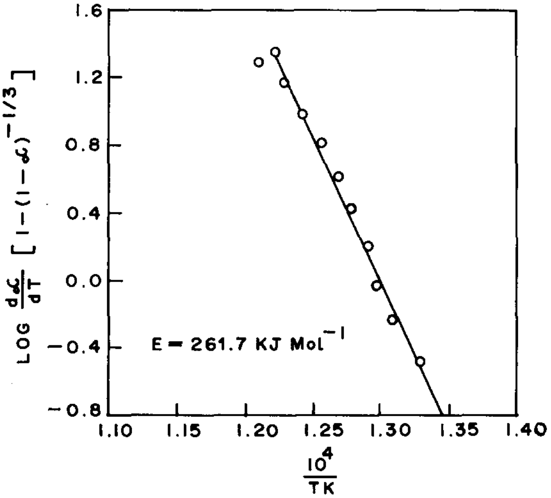

Fig. 6. Typical plot for kinetics of formation of $NaSc(WO_4)_2$ from $Na_2WO_4 + Sc_2(WO_4)_3$ (1 : 1) by DTA following the Ginstling and Brounshtein model [8].

(Jander [7]) and

$$\log \frac{d\alpha}{dT}\left[1-(1-\alpha)^{-1/3}\right] = C - \frac{E}{2.303RT} \qquad (2)$$

Ginstling and Brounshtein [8] where C is a constant and all other notations have their usual meaning. Using these expressions straight line plots are obtained for these reactions and activation energy values (E) as also frequency factor values (Z) are evaluated. The activation energies are in the ranges 247.2–268.4 kJ mol^{-1} and 254.2–273 kJ mol^{-1} in the case of eqns.

TABLE 2

Kinetic data for the formation of $ASc(WO_4)_2$ (A = Li, Na, K, Rb and Cs) from different reactant mixtures

Compound	Reactant mixture A [a] (TG data, Jander model [7])		Reactant mixture B [b] (DTA data, Ginstling and Brownshtein model [8])	
	Activation energy (kJ mol^{-1})	Frequency factor (s^{-1})	Activation energy (kJ mol^{-1})	Frequency factor (s^{-1})
$LiSc(WO_4)_2$	247.2	4.5×10^{12}	254.2	5.1×10^{12}
$NaSc(WO_4)_2$	251.8	4.8×10^{12}	261.7	5.5×10^{12}
$KSc(WO_4)_2$	262.6	5.4×10^{12}	269.4	5.6×10^{12}
$RbSc(WO_4)_2$	265.3	5.5×10^{12}	271.4	5.7×10^{12}
$CsSc(WO_4)_2$	268.4	5.6×10^{12}	272.0	5.8×10^{12}

[a] Reaction A: $ACO_3 + 4WO_3 + Sc_2O_3 \rightarrow 2ASc(WO_4)_2 + CO_2$.

[b] Reaction B: $A_2WO_4 + Sc_2(WO_4)_3 \rightarrow 2ASc(WO_4)_2$.

(1) and (2) respectively (Table 2). Similar studies have been reported [2–5] in the case of $ASc(MoO_4)_2$.

Reaction mechanism

In these reactions the diffusion is the rate controlling step. The tungstic oxide is the mobile species and diffusion of this through the product layer controls the rate. This diffusion takes place according to vacancy mechanism. Control of the chemical reaction is localised in a reaction zone and formation of crystal nuclei and growth of reaction product takes place uniformly. High activation energy values obtained in these reactions support this assumption. Similar observations were also made in rare earth molybdate formation studies [9].

CONCLUSION

In the system A_2WO_4-$Sc_2(WO_4)_3$ the 9 : 1, 5 : 1, 2 : 1, 1 : 1 and 3 : 2 phases are possible. These phases are temperature dependent and indicate incongruent melting behaviour. The kinetics are governed by a diffusion controlled reaction mechanism.

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