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THERMOANALYTICAL STUDIES ON SOME TETRAHEDRAL A_3AsO_4-TYPE COMPOUNDS

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ABSTRACT

Tetrahedral orthoarsenates, A_3AsO_4 (A = Li, Ag and Tl) have been prepared and characterized by chemical, thermal and X-ray diffraction analyses. Amongst these orthoarsenates, the thallous compound has the lowest thermal stability, undergoing melting before decomposition. While silver orthoarsenate undergoes a crystallographic phase transition from the low-temperature primitive cubic to a high-temperature face centered cubic form before decomposition, lithium orthoarsenate is highly stable at least up to 1600 K, though it also undergoes a polymorphic transition.

INTRODUCTION

Compounds of the type A_3XO_4 (A = monovalent metal, X = P, As, V) show reversible phase transitions. Phase transitions in Li_3PO_4 [1,2] and Li_3AsO_4 [3] have been reported with crystallographic data of the low- and high-temperature polymorphs. Similarly, Li_3VO_4 has been investigated in detail by thermoanalytical techniques [3,4]. All these transitions are found to be reversible in nature.

In the present investigations, the thermal behaviour of Li_3AsO_4, Ag_3AsO_4 and Tl_3AsO_4 has been studied.

EXPERIMENTAL

Preparation

Lithium arsenate, Li_3AsO_4, was prepared [5] by reacting lithium carbonate and standard arsenic acid. The precipitate was washed with distilled water and heated to 775 K for 10 min.

Silver arsenate, Ag_3AsO_4, was prepared [6] by mixing solutions of silver nitrate and arsenic acid. The chocolate brown precipitate was washed with

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distilled water and heated to 775 K for 30 min.

Thallous arsenate, Tl_3AsO_4, was prepared [5] by reactions of thallous carbonate with a solution of arsenic oxide in concentrated nitric acid. The pale yellow precipitate was washed with distilled water and dried in the air at 380 K.

Chemical analysis

The compounds were analysed chemically for As as well as the monovalent metal content to confirm the composition.

Thermal analysis

Thermogravimetric analysis (TG) was carried out on a Stanton thermobalance of 1 mg sensitivity. A 200 mg sample was heated in the thermobalance to 1600 K at a heating rate of 4° min^{-1}.

Differential thermal analysis (DTA) was carried out on a DTA unit built in this laboratory using platinel thermocouples for differential output. The differential EMF and the temperature measuring thermocouple EMF were recorded on a Rikadenki X–Y recorder. A 100 mg sample was taken for each run. Calcined Al_2O_3 was used as reference material. DTA runs were taken up to 1270 K during heating and cooling at a rate of 10° min^{-1}.

X-Ray diffraction analysis

Room temperature X-ray patterns were taken on a Philips PW 1010 X-ray generator with a PW 1051 diffractometer using nickel filtered Cu K_α radiation. High-temperature X-ray diffraction patterns were taken on a similar diffractometer with an MRC model X-86-N3 high-temperature attachment.

RESULTS AND DISCUSSION

The results of the thermogravimetric analysis of the orthoarsenates are given in Fig. 1. Lithium arsenate is found to be stable from room temperature to 1600 K in air, while in the case of silver arsenate, the decomposition sets in at about 1400 K and is found to be nearly complete by 1600 K. Thallous arsenate is found to be comparatively less stable at high temperatures; decomposition starts around 970 K and is complete at about 1470 K.

DTA curves of lithium arsenate are given in Fig. 2. The compound shows, on heating, an endothermic peak in the temperature interval of 1055–1100 K, while on cooling, it appears at 900–830 K as an exothermic peak, showing thereby a reversible crystallographic transformation involving considerable

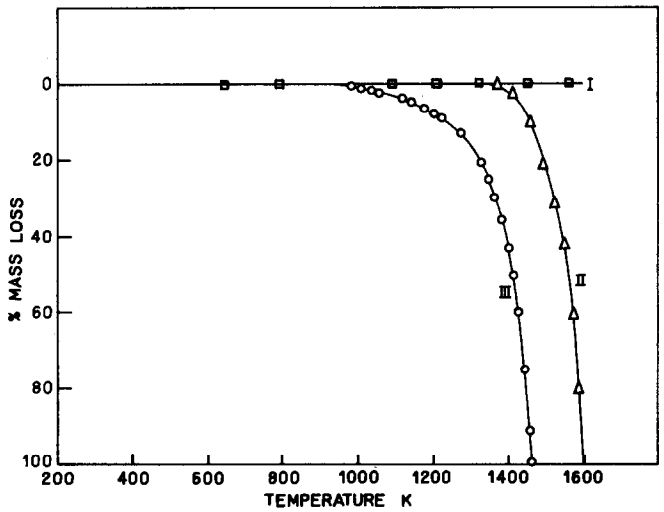

Fig. 1. TG curves of orthoarsenates. I, Li_3AsO_4; II, Ag_3AsO_4; III, Tl_3AsO_4.

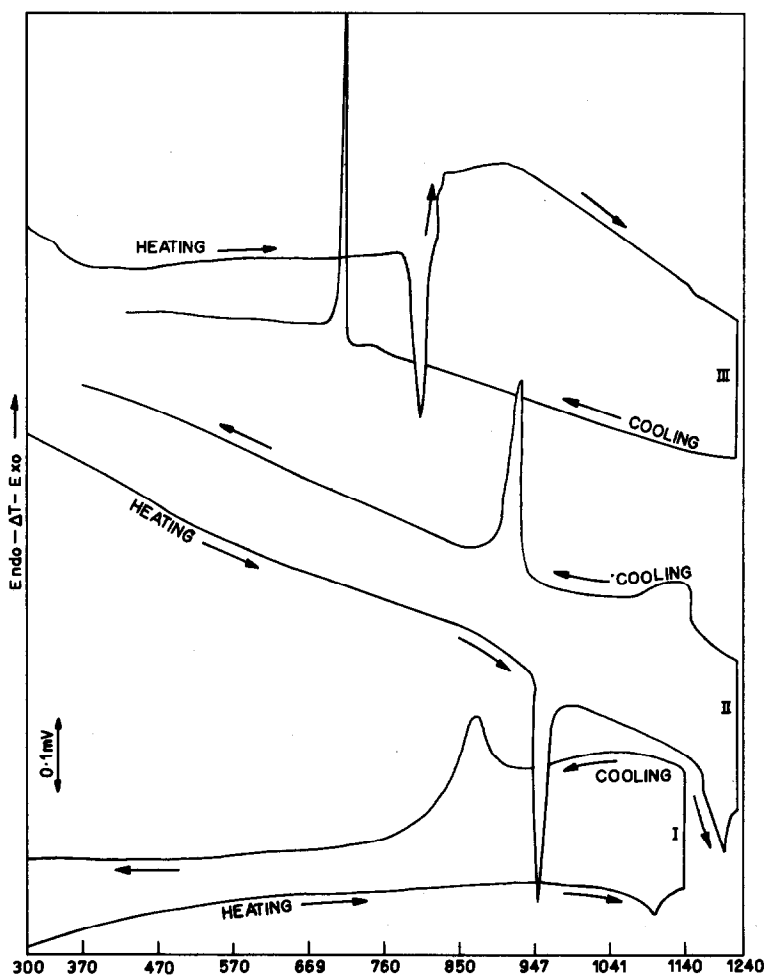

Fig. 2. DTA curves of orthoarsenates. I, Li_3AsO_4; II, Ag_3AsO_4; III, Tl_3AsO_4.

hysteresis. The reported $\beta \rightarrow \gamma$ transition of the lithium arsenate is observed in the high-temperature XRD studies. The low-temperature orthorhombic structure changes over to another orthorhombic structure at high temperature. XRD data of the high-temperatre γ-Li_3AsO_4 are given in Table 1.

In the case of silver arsenate, as shown in Fig. 2, two endothermic peaks are observed on heating at temperatures of 975–1000 and 1200–1235 K. On cooling, the exothermic peaks are seen at 960–925 and 1190–1185 K. In each case, no corresponding mass loss is observed in thermogravimetry as seen in Fig. 1. The first peak has been identified as due to a reversible crystallographic transformation, while the latter is found to be due to melting of the compound. Table 2 shows the XRD data of the low- and high-temperature polymorphs of silver arsenate. The low-temperature form of Ag_3AsO_4 is

TABLE 1

XRD data of high-temperature γ-Li_3AsO_4 at 1025 K

d (nm)	I/I_0	hkl
0.5431	30	110
0.4091	95	120
0.3923	100	101
0.3686	65	111
0.3171	35	121
0.3144	40	200
0.2716	60	220
0.2693	30	040
0.2587	55	211
0.2510	30	002
0.2444	25	012
0.2331	25	102
0.2275	30	022
0.2097	15	300
0.2058	15	310
0.1980	25	051
0.1962	25	202
0.1930	35	212
0.1888	40	151
0.1843	25	222
0.1821	15	321
0.1795	10	060
0.1690	10	061
0.1673	15	003
0.1654	35	340
0.1635	20	052
0.1591	35	312
0.1582	45	152

orthorhombic: $a_0 = 0.6298$ nm; $b_0 = 1.0766$ nm; $c_0 = 0.5017$ nm; $Z = 4$.

TABLE 2

X-Ray diffraction data of high- and low-temperature phases of Ag_3AsO_4

Room temperature [a]			985 K [b]		
d(nm)	I/I_0	hkl	d(nm)	I/I_0	hkl
0.3066	25	200	0.2395	100	222
0.2743	100	210	0.2075	45	400
0.2503	75	211	0.1468	35	440
0.1940	12	310	0.1252	35	622
0.1770	25	222			
0.1701	45	320			
0.1640	60	321			
0.1534	30	400			
0.1371	30	420			
0.1339	35	421			
0.1309	10	332			
0.1140	25	520, 432			
0.1121	18	521			
0.1085	13	440			

[a] Cubic (P): $a_0 = 0.6137$ nm.
[b] f.c.c.: $a_0 = 0.8303$ nm.

primitive cubic with space group $T_D^4 P\bar{4}3N$ and is isotypic with Ag_3PO_4 [7]. The high-temperature form of Ag_3AsO_4 is face centred cubic and is isotypic with the high temperature form of Ag_3PO_4 [8].

The results of the DTA study of thallous arsenate are given in Fig. 2. On heating, a sharp endothermic peak is observed at 788–823 K, which is reproduced on cooling at about 713 K. Since there was no corresponding weight change in the TG and from observations of samples heated just at this transformation temperature and cooled to room temperature, the peak is attributed to melting of the compound.

The results show that, amongst the orthoarsenates, the thallous compound has the lowest thermal stability, melting at 788 K and decomposing above 970 K. The lithium compound is found to be highly stable at least up to 1600 K, though it undergoes a polymorphic transition around 1055 K. In the case of silver arsenate, though stable up to 1385 K the decomposition is preceded by polymorphic transition (975 K) and melting (1200 K). Considering the thermal hysteresis and heat changes involved, both the crystallographic transitions of lithium and silver arsenates are found to be of the first order.

The thermoanalytical studies show some interesting features of the decompositions of silver and thallium arsenates. Conforming to the mass losses observed in these compounds, the decomposition reactions can be repre-

sented by

$$Ag_3AsO_4 \rightarrow 3\ Ag\uparrow + 0.5\ As_2O_3\uparrow + 1.25\ O_2\uparrow \quad (1)$$

$$Tl_3AsO_4 \rightarrow 1.5\ Tl_2O\uparrow + 0.5\ As_2O_3\uparrow + 0.5\ O_2\uparrow \quad (2)$$

All the decomposition products vaporize/sublime at these temperatures and hence no residue is left. Apparently, the volatilization of silver may not be thought of at these temperatures. However, it is found that silver has considerable vapour pressure [9] above 1300 K and since silver is formed in the nascent state during the decomposition, the high rate of volatilization is understandable.

The shifts observed in the base lines in the DTA plot of silver arsenate during the heating and cooling cycle are to be considered as characteristics of the sample since the shift is completely reversible and is reproduced fully. Though the characteristics of the decompositions of the other compounds could not be ascertained, in the case of thallium arsenate due to the progressive volatilization of Tl_2O and As_2O_3, the base line continuously shifts towards the endothermic side with increase in temperature. Hence, on cooling, the shift in the base line is considerably reduced and after solidification the base line is stabilized.

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