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DOUBLE ARSENATES OF THORIUM AND MONOVALENT METALS. PART II. THERMAL AND ELECTRICAL PROPERTIES

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ABSTRACT

The thermal properties of the double arsenates, $M^ITh_2(AsO_4)_3$ [M^I = Li, Na, K, Ag and Tl] have been studied using thermogravimetric (TG), differential thermal analysis (DTA), high temperature X-ray diffraction and dilatometric techniques. The electrical behaviour of these compounds has been investigated by carrying out electrical conductivity measurements under different oxygen partial pressures and also by solid state electrolysis. The double arsenates are highly stable under different thermal conditions having no polymorphic transitions nor any change in the mechanism of conduction in the temperature range of the investigations.

INTRODUCTION

The preparation and crystallographic data of polycrystalline samples with the formula $M^ITh_2(AsO_4)_3$ (M^I = Li, Na, K, Ag and Tl) have been reported [1]. They are monoclinic, space groups *C*2/*c*, with four formula units per unit cell. Similar values of the lattice constants and the same space group extinctions between them suggest their close structural relationship.

Very little information is available in the literature on the thermal and electrical properties of the double arsenates of thorium and monovalent metals; only the decomposition temperatures of the lithium and sodium double arsenates have been reported [2]. The present paper describes the results of a study of the thermoanalytical and electric properties of these compounds.

THERMAL PROPERTIES

The investigations carried out consist of thermogravimetric studies (TG), differential thermal analyses (DTA), high temperature X-ray diffraction and thermal expansion measurements. The results of these investigations have been utilized in characterizing the thermal behaviour of these compounds.

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Experimental

Thermogravimetric analysis (TG) was carried out on a Stanton thermobalance of 1 mg sensitivity. A 500 mg sample was heated in the thermobalance up 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 500 mg sample was taken for each run. Calcined ThO_2 was used as reference material in order to match the density and specific heat of the double arsenates and thus stabilize the base line. DTA runs were taken up to 1270 K during heating and cooling at a rate of 10° min^{-1}.

Thermal expansion measurements were carried out employing a dilatometric technique. A Type LKB 3185 dilatometer with a constant heating rate of 6° min^{-1} was used for the dilatometric studies. Samples in the form of pellets (10 × 12.5 mm) sintered in air for 24 h at 1273 K were used.

Results and discussion

The results of the thermogravimetric analysis of the double arsenates are given in Fig. 1. As seen in the figure, the compounds undergo decomposition in one step. Lithium double arsenate decomposes in the temperature range

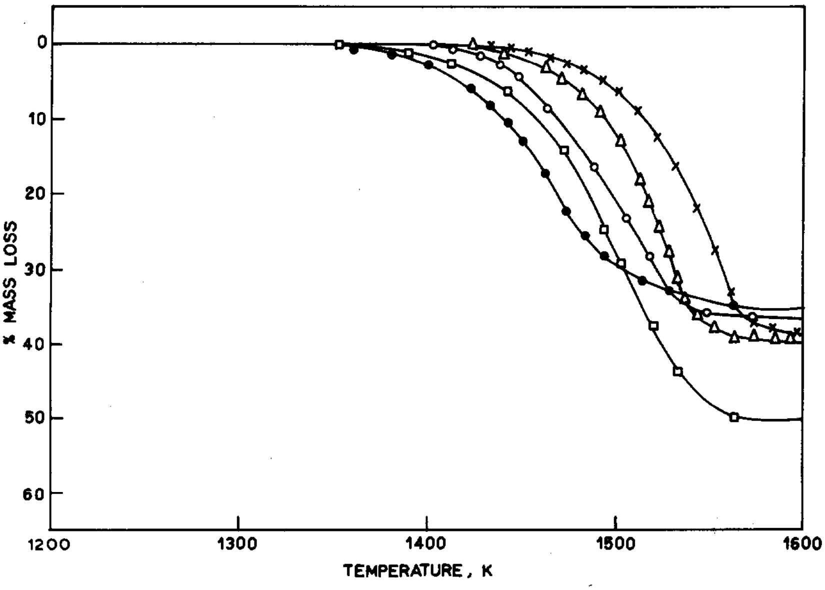

Fig. 1. TG curves of double arsenates of thorium. ○, $LiTh_2(AsO_4)_3$; ×, $NaTh_2(AsO_4)_3$; Δ, $KTh_2(AsO_4)_3$; ●, $AgTh_2(AsO_4)_3$; □, $TlTh_2(AsO_4)_3$.

1405–1550 K, while sodium and potassium double arsenates decompose at temperatures of 1435–1575 and 1425–1560 K, respectively. In the case of the silver double arsenate; the decomposition is found to take place between 1350 and 1580 K, whereas for the thallium compound the decomposition is found to be in the temperature range 1340–1560 K. It is to be noted that the mass losses in all cases do not reach equilibrium values even after the decompositions are over, since the decomposition products are monovalent metal oxides, arsenic oxide etc., which contribute to continued mass loss.

Differential thermal analysis of the double arsenates does not show any peak, indicating thereby that there are no polymorphic transitions in these compounds.

In Fig. 2, the values of the percent linear thermal expansion obtained for all the double arsenates are plotted as a function of temperature. The variation of the percent linear thermal expansion (ΔE) as a function of temperature (T in K) could be expressed by the standard equation obtained by a least square fit of the data in the range 300–1200 K.

$$\Delta E = A(\Delta T) + B(\Delta T)^2 + C(\Delta T)^3 \qquad (1)$$

where ΔT is the temperature differential. The values calculated using the equation are found to be in good agreement with the measured values; typical data for the silver double arsenate are given in Fig. 3. Data obtained

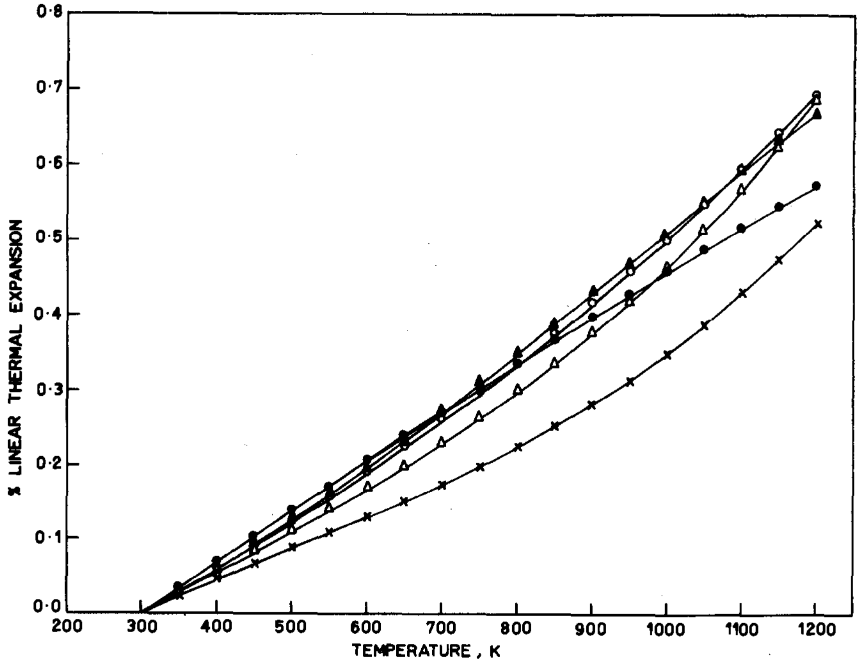

Fig. 2. Percent linear thermal expansion of $M^{I}Th_2(AsO_4)_3$ as a function of temperature. △, $LiTh_2(AsO_4)_3$; ×, $NaTh_2(AsO_4)_3$; ▲, $KTh_2(AsO_4)_3$; ●, $AgTh_2(AsO_4)_3$; ○, $TlTh_2(AsO_4)_3$.

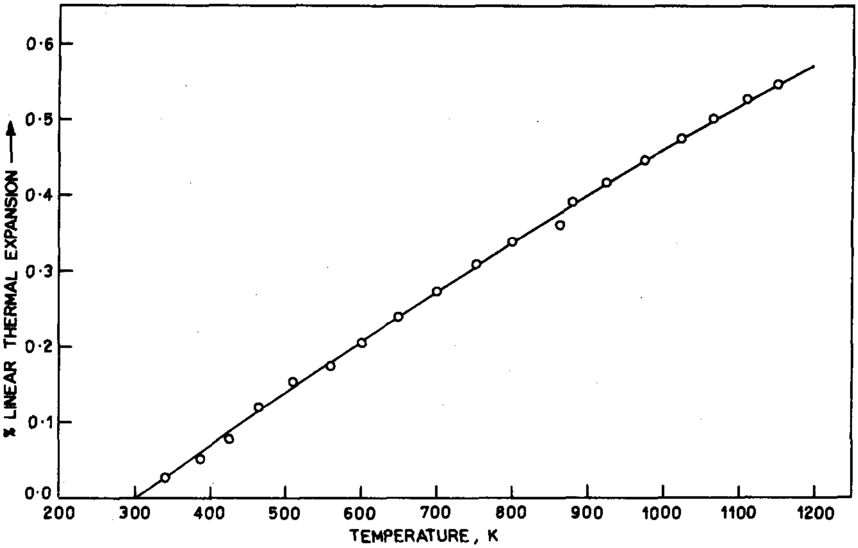

Fig. 3. Percent linear thermal expansion of $AgTh_2(AsO_4)_3$ as a function of temperature.

for the linear thermal expansion coefficients were computed to evaluate the temperature dependence of the coefficients and can be expressed by the standard equation

$$\alpha_l = A' + B'(\Delta T) + C'(\Delta T)^2 \tag{2}$$

where $\Delta T = T - 298$ and A', B' and C' have values 100 times less than the corresponding values of A, B and C of eqn. (1). The coefficient of average linear thermal expansion (α_l) for all the double arsenates studied falls more or less in the range $5-8 \times 10^{-6}$ K^{-1}.

ELECTRICAL CONDUCTIVITY

Of late, considerable work on substituted double phosphates has been published due to their excellent fast (monovalent) ion conduction properties [3–5]. For example, sodium zirconium phosphosilicates [4] are reported to have comparable Na^+ ion transport properties to that of β''-alumina. The close isomorphism [2] of the double arsenates with the corresponding phosphates leads to the inference that the compounds in question could be considered suitable for possible use as fast ion conductors. Hence, the electrical conductivity of these compounds was investigated.

Experimental

A two point probe method was used. Due to the high polarization of the samples in d.c. fields, the a.c. conductivity was measured with an a.c.

impedence bridge (General Radio Co., Model 1650-A). The measurements were carried out from room temperature to 1175 K at 1 kHz in pure oxygen, air and cylinder nitrogen corresponding to oxygen partial pressures of 1×10^5, 0.2×10^5 and 3×10^2 N/m^2. A cell assembly fabricated in the laboratory [6] was used for the conductivity measurements. In all measurements, before the sample (12.0 mm diam.×3.0 mm thick) was mounted in the holder, both its surfaces were coated with platinum paste (Dupont electronic grade 7553) and fired at 1000 K. The coating formed made good electrical contacts with the Pt foil electrodes. All specimens, after firing overnight at 1270 K, had densities in the range 85–90% theoretical. The conductivity was calculated using the well-known relationship between the samples dimensions and measured resistance

$$\sigma = \frac{1}{R} \times \frac{L}{A}$$

where L is the thickness of the pellet, A is the area and R is the measured resistance.

In order to obtain information about the nature of the mobile ionic species, solid state electrolysis was carried out on pellets (12.0 mm diam.×10.0 mm thick) of the double arsenates of lithium, silver and thallium. The same experimental set up used in a.c. conductivity measurements was employed. A direct current of ~2 mA was passed through the sample over a period of 7–8 days.

Results and discussion

The results of conductivity measurements carried out under different oxygen partial pressures are shown in Fig. 4. It is seen that the conductivity does not show any change corresponding to changes in the oxygen partial pressures within the ranges investigated. From the data, it is seen that all these compounds are semiconducting. The plots of log σ vs. $1/T$ are linear and do not show any discontinuity, thus confirming that the compounds have no polymorphic transition nor any change in the mechanism of conduction in the range of temperature of the investigations. Solid state electrolysis on the double arsenates conclusively proves that the conductivity is due to cationic transport of the monovalent metal ion, M^+. All the compounds have very nearly the same activation energy of conduction of about 1.0 eV.

The ionic conduction observed in these compounds is explained in the light of their crystal structures which are isotypic with the corresponding phosphates [2]. Since higher homologues in the series such as $Li_2Th(AsO_4)_2$ and $Na_2Th(AsO_4)_2$ are known, it is to be presumed that there are present at least two types of energetically nonequivalent interstices $M^I(I)$ and $M^I(II)$. Either by reducing the site occupancy at $M^I(I)$ or by partially occupying the

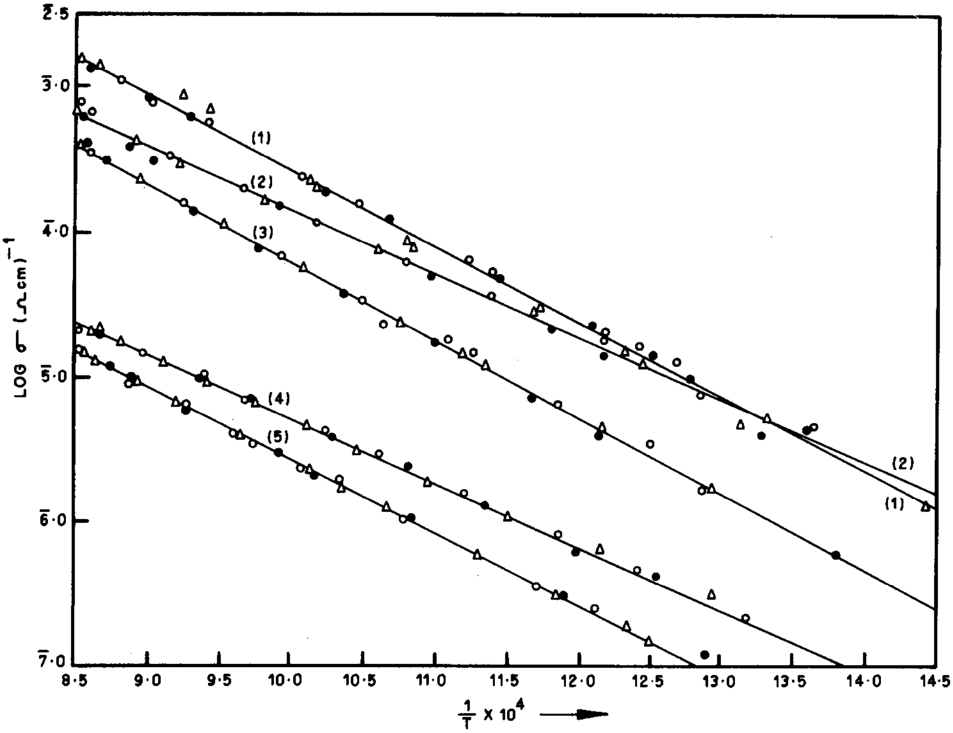

Fig. 4. Electrical conductivity of $M^{I}Th_2(AsO_4)_3$ under different oxygen partial pressures. (1), $AgTh_2(AsO_4)_3$; (2), $NaTh_2(AsO_4)_3$; (3), $LiTh_2(AsO_4)_3$; (4), $TlTh_2(AsO_4)_3$; (5), $KTh_2(AsO_4)_3$. ○, Cylinder nitrogen; △, pure oxygen; ●, air.

M^{I}(II) sites, the mobility of the M^{I} cations, and therefore the conductivity of the compounds, can be considerably enhanced. It is concluded that the monovalent metal thorium double arsenates are highly stable under different thermal conditions. Though their conductivity is very low, it can be considerably enhanced and it may be possible to obtain superionic conductors by modifying their compositions such that the partial occupancy of the available monovalent metal ion sites is ensured, such as is done in the case of sodium zirconium phosphosilicates.

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