Solid State Chemistry of Thallous Molybdate

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Thallous molybdate has been prepared by solid state reaction between thallous carbonate and molybdenum trioxide and characterized by chemical analysis, X-ray powder diffraction pattern, density measurement, thermogravimetry and IR spectrum. The electrical conductivity data of pressed pellet at different temperatures have also been reported.

METAL molybdates have been reported to be useful catalysts for desulphurization, dehydrogenation, oxidation and other types of reaction of industrial importance[1-6]. The formation and composition of polymolybdates of thallium(I) have been studied amperometrically[7] and the crystal structure of thallium(I) trimolybdate ($Tl_2Mo_3O_{10}$) has been determined[8]. Although thallous molybdate, Tl_2MoO_4, has been prepared from solution[9] and the phase diagram studies involving Tl_2MoO_4-MoO_3 have been made[10], little attention has been paid to the study of solid state chemistry of thallous molybdate. This paper describes the preparation of thallous molybdate in the solid state and its characterization by chemical analysis, powder X-ray diffraction pattern, density measurement, IR spectroscopy, TG and electrical conductivity.

Materials and Methods

Thallous carbonate (BDH), molybdenum trioxide (AR) and acetone (GR) were used without further purification.

Preparation of thallous molybdate — A very light yellow thallous molybdate has been prepared in the solid state by the method used for thallous tungstate[11]. A homogeneous (1:1) molar reaction mixture was taken in a gold crucible and heated at $540° \pm 10°$ for 3 hr. First, a mixture of yellow and black reaction product was formed which was finally converted to light yellow thallous molybdate on cooling, grinding and reheating at $580° \pm 10°$ two to three times for about 3 hr.

Thallium(I) in thallous molybdate was analysed by usual volumetric method[12]. The percentage of Tl(I) was found to be 71·4% (Calc. for Tl_2MoO_4: Tl, 71·9%).

Crystal structure — The powder X-ray diffraction pattern of thallous molybdate was taken with X-ray diffractometer using CuKα radiation. Attempts were made to compare the powder diffraction pattern of Tl_2MoO_4 with those of a number of compounds such as Tl_2WO_4, β-K_2CrO_4, Be_2SiO_4, Ca_2PbO_4, Li_2BeF_4, Li_2WO_4, K_2SO_4 and Na_2SO_4 from ASTM powder diffraction file. It has been found that none of these compounds were isostructural with Tl_2MoO_4. Therefore, the pattern was indexed by Hesse-Lipson's method. Agreement between observed and calcu-

lated $sin^2\theta_{hkl}$ values (Table 1) was satisfactory. Accuracy of the indexing was also checked by de Wolff criteria[13]. Figure of merit (Table 1) for thallous molybdate showed that indexing was correct. The lattice parameters of thallous molybdate were refined by least square method.

Density measurement — The density of thallous molybdate measured with a pyknometer using toluene as a displacing liquid was found to be 6·55 ± 0·06 g/ml at $35° \pm 0·1°C$.

Thermogravimetry (*TG*) — Thermogravimetry of thallous molybdate and an equimolar reaction mixture of thallous carbonate and molybdenum trioxide were carried out with the help of a thermogravimetric analyser (Fertilizer Corp. of India Ltd, Sindri). Gold crucible was used for the experiment. After TG, the sample was cooled slowly to about 40° in the furnace. An increase in the weight of the sample was observed.

IR measurements — The IR spectrum of thallous molybdate in KBr disc was measured in the range 4000-700 cm^{-1} using a Perkin-Elmer spectrophotometer model No. 137.

Electrical conductivity measurements — The electrical conductivity of the solid pressed pellet (pressure 5000 kg) of thallous molybdate employing two electrode method was measured in the temperature range 60-480° with a Toshniwal conductivity bridge

TABLE 1 — CRYSTAL DATA FOR THALLOUS MOLYBDATE

d (Å)	$sin^2\theta_{hkl}$		hkl	I/I_0
	Obs.	Calc.		
3·2549	0·0561	0·0558	110	100
3·2090	0·0577	0·0583	111	54
3·1754	0·0589	0·0586	104	48
3·0893	0·0622	0·0625	005	87
1·8879	0·1667	0·1674	300	21
1·8661	0·1707	0·1702	213	16
1·8344	0·1766	0·1774	302	30
1·7874	0·1860	0·1869	207	10
1·6313	0·2233	0·2232	220	8
1·5535	0·2463	0·2457	223	7
1·4407	0·2863	0·2857	225	11

$a=b=6·526$ Å; $c=15·417$ Å; $V=5·68 \times 10^{-22}$ cm^3; $z=4$; and $M=11$.

operated at 50 Hz. The pellet was held between two gold electrodes of suitable size which was then placed in a furnace.

Results and Discussion

The reaction between thallous carbonate and molybdenum trioxide leading to the formation of a very light yellow thallous molybdate may follow either route A or route B and C as shown below.

$$Tl_2O + CO_2$$

$$Tl_2CO_3 \quad\quad C \mid MoO_3$$

B / \ A

MoO_3

$$Tl_2MoO_4 + CO_2$$
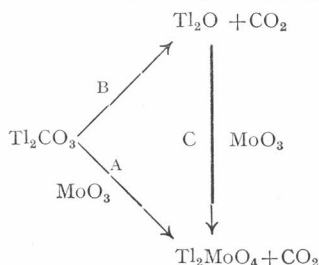
It is difficult to decide which of the above routes is actually operative. However, a comparison of TG plots of Tl_2CO_3 and an equimolar reaction mixture of Tl_2CO_3 and MoO_3 (Fig. 1) shows that Tl_2CO_3 starts decomposing at a lower temperature when MoO_3 is added as compared to the case of pure Tl_2CO_3. This shows that Tl_2CO_3 primarily reacts with MoO_3 to produce Tl_2MoO_4. However, a certain amount of Tl_2CO_3 not in immediate contact with MoO_3 can decompose into Tl_2O which may subsequently react with MoO_3. Further it has been found from the capillary experiment at 260° that thallous carbonate diffuses 0·064 cm into MoO_3. This is in agreement with the observations of Kononyuk et al.[14] that the lower melting species diffuses into species having higher melting point.
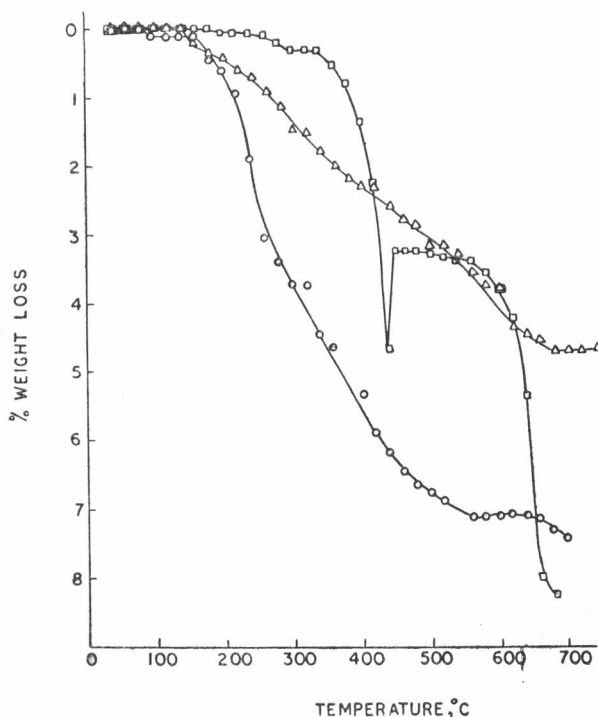

Fig. 1 — TG curves for thallous molybdate (△) an equimolar reaction mixture of thallous carbonate and molybdenum trioxide (⊙) and thallous carbonate (⊡)

The powder X-ray diffraction pattern of thallous molybdate indicated the formation of a single phased thallous molybdate, since the diffraction lines corresponding to Tl_2CO_3, Tl_2O and MoO_3 are absent. The X-ray diffraction studies show that (i) the crystal lattice belongs to hexagonal system; (ii) the unit cell dimensions are: $a = b = 6·526$ Å; $c = 15·417$ Å; $V = 5·68 \times 10^{-22}$ cm^{-3}; $z = 4$; and (iii) the X-ray density using four molecules of Tl_2MoO_4 in the unit cell is 6·65 g/ml which is in good agreement with the experimental value.
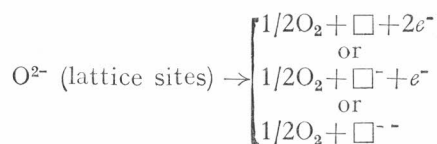
An examination of diffraction pattern shows broadening of diffraction lines. This may be either due to imperfections present in the crystal lattice[15] or due to crystallite size. The crystallite size of thallous molybdate, calculated by using Scherrer formula[16] (1)

$$t_{hkl} = \frac{0·9\,\lambda}{\beta \cos\theta_B} \cdot \frac{360}{2\pi} \text{ Å} \qquad \ldots(1)$$

where t_{hkl} = crystallite size perpendicular to the plane hkl, λ = wavelength, β = half maximum line breadth and θ = Bragg angle.

The crystallite size lies in the range 164-454 Å for different hkl planes. It is known that in the absence of lattice strains[16], the materials should give sharp lines at all angles if crystallite size >1000 Å. At crystallite size ≪ 100 Å, low angle lines become very wide and more diffuse. Thus, the broadening due to crystallite size may be a possibility. However, the broadening due to crystal imperfections may also not be ruled out.

During TG experiments of thallous molybdate, it is observed that there is a decrease in weight of the sample as the temperature is increased. This may be due to the escape of oxygen from lattice sites. The escape of oxygen from the lattice sites may create oxide ion vacancies as represented below:

$$O^{2-} \text{ (lattice sites)} \rightarrow \begin{cases} 1/2O_2 + \square + 2e^- \\ \text{or} \\ 1/2O_2 + \square^- + e^- \\ \text{or} \\ 1/2O_2 + \square^{--} \end{cases}$$

where $\square$ = oxide ion vacancy, $\square^-$, $\square^{--}$ = oxide ion vacancies with one and two trapped electrons respectively. The electrons trapped in the oxide ion vacancies may impart interesting properties to the crystal such as electrical conductivity.

The electrical conductivity of solid thallous molybdate measured at different temperatures provides information about the imperfection. The results indicate three distinct regions (Fig. 2) and the conductivity increases with the increase in temperature. The three temperature ranges and the corresponding energies of activation are given below:

Temp. range °C	Energy of activation eV
60-160	0·165
160-360	0·567
360-480	1·79

It has been observed that with decrease in temperature the magnitude of electrical conductivity decreases. This observation is consistent
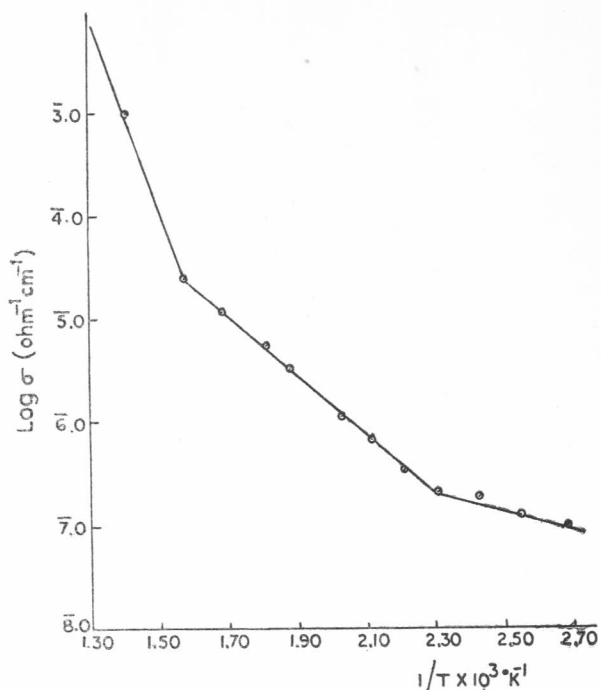
Fig. 2 — Electrical conductivity plot (log σ vs 1/T) for thallous molybdate

with the weight gain observed on cooling the sample obtained after TG. It has been confirmed by cooling in a desiccator that during cooling the sample takes up oxygen and not moisture. Thus the oxide ion vacancies in the crystal lattice are conserved resulting in the decrease of the current carriers and hence the conductivity.

IR spectrum of thallous molybdate exhibits a band at 825 cm^{-1} which on analogy with that of sodium molybdate[17] indicates that Mo^{6+} ions in thallous molybdate may also occupy tetrahedral sites[18,19].

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