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Short communication

Temperature dependence vapour pressure measurements of $Mg(tmhd)_2(tmeda)$ [(tmhd = 2,2,6,6-tetramethyl-3,5-heptanedione, tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine]

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ABSTRACT

The reaction between the magnesium β-diketonate complex $Mg(tmhd)_2(H_2O)_2$ and 1 equiv. of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda = $Me_2NCH_2CH_2NMe_2$) in hexane at room temperature yielded $Mg(tmhd)_2(tmeda)$. The standard enthalpy of sublimation ($83.2 \pm 2.3\ kJ\ mol^{-1}$) and entropy of sublimation ($263 \pm 6.3\ J\ mol^{-1}\ K^{-1}$) of $Mg(tmhd)_2(tmeda)$ were obtained from the temperature dependence vapour pressure, determined by adopting a horizontal dual arm single furnace thermogravimetric analyser as a transpiration apparatus. From the observed melting point depression DTA, the standard enthalpy of fusion ($58.3 \pm 5.2\ kJ\ mol^{-1}$) was evaluated, using the ideal eutectic behaviour of $Mg(tmhd)_2(tmeda)$ as a solvent with bis(2,4-pentanedionato)magnesium(II), $Mg(acac)_2$ as a non-volatile solute.

1. Introduction

Development of volatile compounds of magnesium has recently attracted much attention because they are needed for the preparation of MgO thin films by the chemical gas phase methods [1]. The controlled vapourisation and the subsequent transport of liquid and solid precursors are an essential part of gas phase process technology in CVD. It is imperative to know the vapour pressure, thermal stability and purity of the precursor in order to control the precursor feed rate with accuracy [2]. The thermal analysis made possible the estimation of $\Delta_{sub}H^\circ$ from $\Delta_{vap}H^\circ$ and $\Delta_{fus}H^\circ$ and was validated by direct equilibrium vapour pressure measurements on nickel complexes [3,4]. We hereby report the vapour pressure of $[Mg(tmhd)_2(tmeda)]$ as a function of temperature by a thermogravimetry (TG)-based transpiration method. The enthalpy of fusion is determined by melting point depression with a suitable solute, forming an ideal eutectic in an indirect but reliable estimation of vapourisation enthalpies ($\Delta_{vap}H^\circ$) of the liquid phase.

2. Experimental

$Mg(acac)_2(H_2O)_2$ and $Mg(tmhd)_2(H_2O)_2$ were prepared as reported [5]. *N*,*N*,*N*′*N*′-Tetramethylethylenediamine (Aldrich, 99%) and solvents were used without further purification.

2.1. *Preparation of $Mg(tmhd)_2(tmeda)$ [6]*

N,*N*,*N*′*N*′-Tetramethylethylenediamine (0.18 g, 1.55 mmol) was added to a solution of $Mg(tmhd)_2(H_2O)$ (0.325 g, 0.832 mmol) in hexane (20 ml). The resulting clear solution was stirred for 2 h at room temperature. Crystals were obtained after the partial evaporation of the solvent and the cooling of the solution. The crystals were washed with a small amount of solvent and dried in a vacuum desiccator. Yield: 78%.

The magnesium content in the complex was found to be 4.73 (4.92) by EDTA titration. FT-IR (KBr, cm^{-1}): 3447 (ν N—H), 2960 (ν C—H), 1592 (ν C═O), 1508 (ν C═C), 474 and (ν M—O).

2.2. *TG: dynamic mode*

The thermogravimetry of the complexes were carried out with PerkinElmer Pyris-Diamond TG–DTA. The purge gas was high purity nitrogen dried by passing through refrigerated molecular sieves

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(Linde 4A) at a flow rate of 12 dm^3 h^{-1}. The thermogravimetric analysis was performed at a linear heating rate of 0.17 K s^{-1} in ambient pressure at 320–550 K.

2.3. TG: transpiration mode

A horizontal thermal analyser was adopted as a transpiration setup for vapour pressure measurements. The block diagram of the thermal analyser, modified for its functioning in the transpiration mode is given elsewhere [7]. The details of precise flow calibration for the carrier gas, using a capillary glass flow meter and corrections for apparent weight losses in isothermal mode and experimental conditions, were described earlier [8,9]. The sample finely powdered by using a mortar and pestle was spread on a platinum crucible and was carefully flushed with nitrogen at a rate of 6 dm^3 h^{-1} at the ambient temperature. Vapour pressure measurements were done at 0.17 K s^{-1}. After the temperature stabilisation, subsequent changes in isothermal steps were done at a heating rate of 0.033 K s^{-1}.

2.4. DTA: fusion enthalpy studies

The different mole ratios of Mg(tmhd)$_2$(tmeda) with anhydrous Mg(acac)$_2$ were prepared by grinding each mixture in an agate mortar and pestle for an hour and compacting the mixture into thin pellets, using a hydraulic press. The compositions obtained were 0.82, 0.78, 0.66, and 0.62 for the mole fraction of xMg(tmhd)$_2$(tmeda) in the binary system of Mg(tmhd)$_2$(tmeda) + Mg(acac)$_2$. The same thermogravimetric analyser was used for recording the DTA curves on the mixtures and an equal weight of calcined α-alumina loaded in the reference pan. This model has the facility for base line correction, with the help of which the accurate inception temperatures for DTA endotherms could be identified with the required accuracy and precision, commensurate with the T-scale calibration. The accuracy of the temperature measurements was adjusted to be around ±0.05 K, using the recommended melting point standards namely indium, tin and aluminium.

3. Results and discussion

3.1. Dynamic thermogravimetry

The TG curve of Mg(acac)$_2$(H$_2$O)$_2$ in a dynamic (12 dm^3 h^{-1}) N$_2$ atmosphere at a linear heating rate of 0.17 K s^{-1} (Fig. 1a) showed a complete dehydration by 373 K followed by a plateau region up to the melting point of Mg(acac)$_2$ (532 K). The anhydrous magnesium complex (beyond 373 K) showed the loss of one ligand between 460 K and 540 K (Fig. 1a). The thermal behaviour of this complex revealed that magnesium was retained in the residue and could not be used as the precursor for the CVD applications. Anhydrous Mg(acac)$_2$ was obtained by heating the complex to 373 K, which has been used for eutectic studies. The TG traces of Mg(tmhd)$_2$(tmeda) showed (Fig. 1b) that a single sublimation starts at 375 K and ends at 525 K with 100% weight loss. The DTA curves recorded on different runs of Mg(tmhd)$_2$(tmeda) led to an average value of 418 K. The melting point reported by Hatanpaa et al. [5] for Mg(tmhd)$_2$(tmeda) was 425 K, making use of electrothermal melting point apparatus by using capillaries open to air without adequate facility for instrumental baseline correction and could be the cause of the larger scatter (±7 K). The temperature range over which the vapour pressure measurements need to be performed was chosen based on the TG–DTA results.

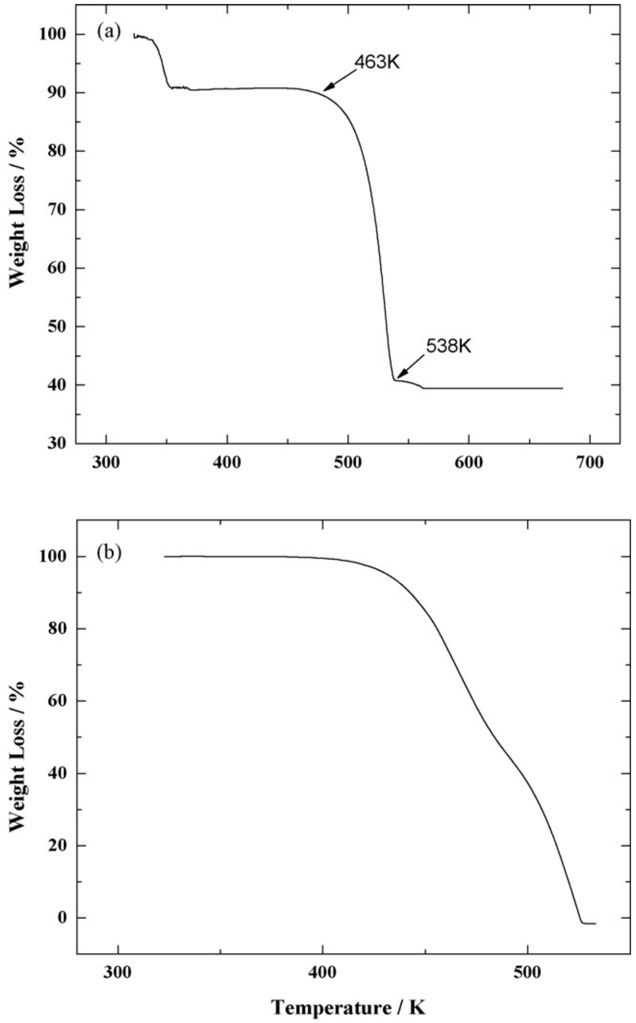

Fig. 1. TG curves of (a) Mg(acac)$_2$(H$_2$O)$_2$ and (b) Mg(tmhd)$_2$(tmeda) at a heating rate of 0.17 K s^{-1} in nitrogen atmosphere.

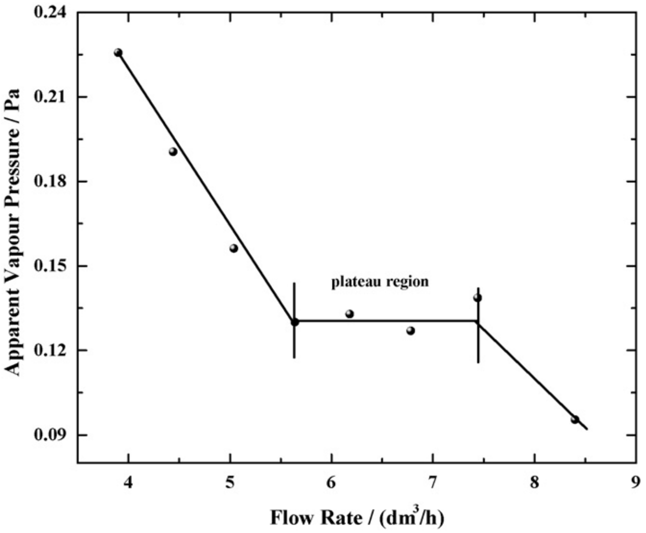

Fig. 2. Variation of apparent vapour pressure of Mg(tmhd)$_2$(tmeda) as a function flow rate of the carrier gas at 393 K.

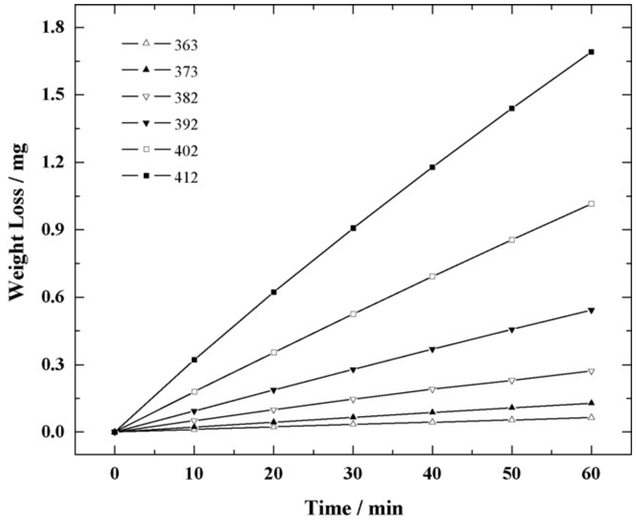

Fig. 3. Plot of isothermal time against weight loss of $Mg(tmhd)_2(tmeda)$.

3.2. TG: transpiration mode

The sample was heated to another isothermal temperature by heating at a rate of 0.033 $K\,s^{-1}$. The isothermal temperature was maintained up to 60 min to record the weight loss. The equilibrium vapour pressure (p_e) of $Mg(tmhd)_2(tmeda)$ could be calculated from the mass loss of the sample, using the relation $p_e = WRT/MV$ derived from Dalton's law of partial pressure. In order to establish the measured values of apparent vapour pressure (p') as the equilibrium vapour pressure data at the given isothermal temperature, the plot of apparent vapour pressure (p') against flow rate (Fig. 2) of the carrier gas N_2 at an isothermal temperature 393 K was carried out. The carrier gas is saturated with the vapour of the precursor in the flow rate region 5.5–7.5 $dm^3\,h^{-1}$ (plateau). Hence, the vapour pressure measurement was carried out at a carrier gas flow rate of 6 $dm^3\,h^{-1}$ at isothermal temperatures in the range of 360–415 K. As the measured vapour pressures satisfy the condition of equilibrium sublimation, these values are denoted by p_e. The isothermal steps are given by the straight line plots (Fig. 3), passing through the origin, indicating that the equal masses are vapourised in equal intervals of time. The Clausius–Clapeyron plot (Fig. 4) of log [p_e/Pa] against T^{-1}/KK^{-1} as a straight line ($R^2 = 0.9983$) gave the least square relation. The value of enthalpies of sublimation was calculated by multiplying the slope of relation with −2.303R. The enthalpy of sublimation ($\Delta_{sub}H^\circ$) and entropy of sublimation ($\Delta_{sub}S^\circ$) values are found to be 83.2 (±2.3) $kJ\,mol^{-1}$ and (263 ± 6.3 $J\,mol^{-1}\,K^{-1}$), respectively.

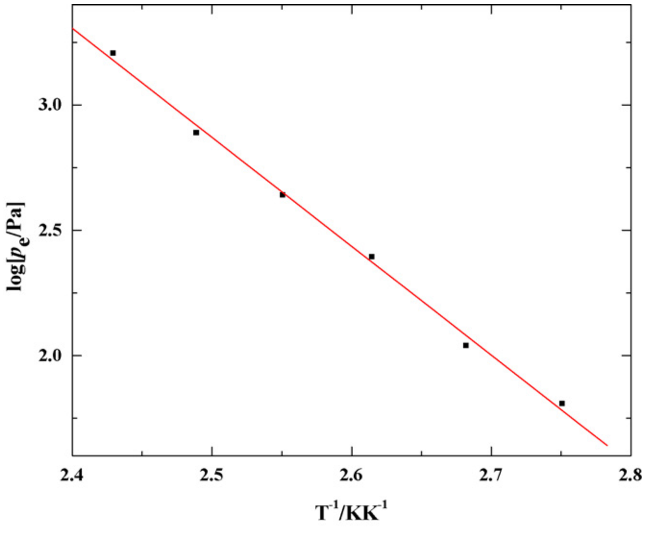

Fig. 4. Clausius–Clapeyron Plot of $Mg(tmhd)_2(tmeda)$ [log [p_e/Pa] = 13.7364 (± 0.3279) − 4.346 (± 0.12) K/T].

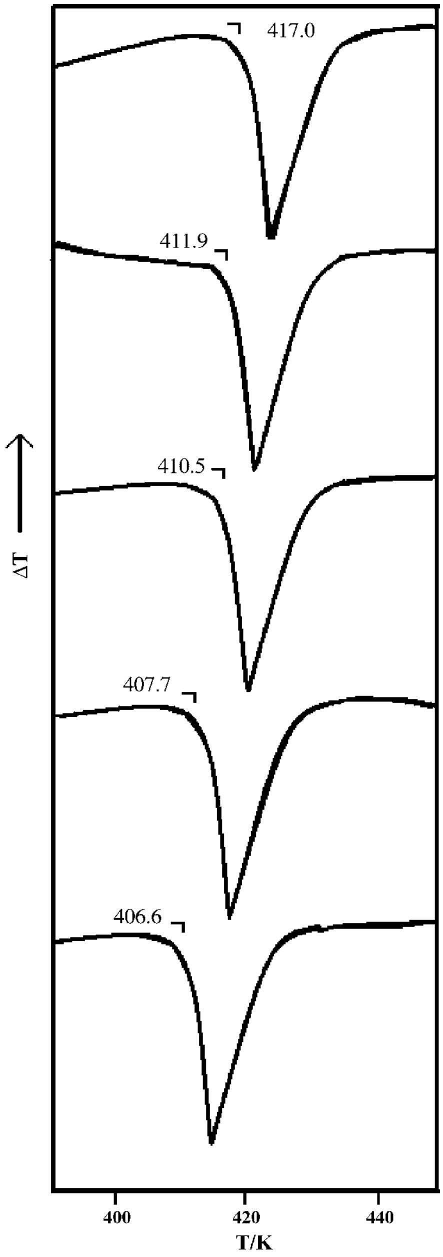

Fig. 5. DTA endotherms for the fusion of Mg′ + Mg″ compositions: Mg′ = $Mg(tmhd)_2(tmeda)$ and Mg″ = $Mg(acac)_2(H_2O)_2$.

Table 1
Liquidus temperatures of volatile $Mg(tmhd)_2(tmeda)$ with $Mg(acac)_2$

S. no	Mole ratio of Mg′/Mg″	$X_{Mg'}$	Liquidus (T/K)	$\Delta_{fus}H^o$ ($kJ\,mol^{-1}$)
1	1.00:0.00	1.00	417.0	0.0
2	1.00:0.22	0.82	411.9	54.1
3	1.00:0.28	0.78	410.5	53.6
4	1.00:0.52	0.66	407.6	62.3
5	1.00:0.61	0.62	406.5	63.4

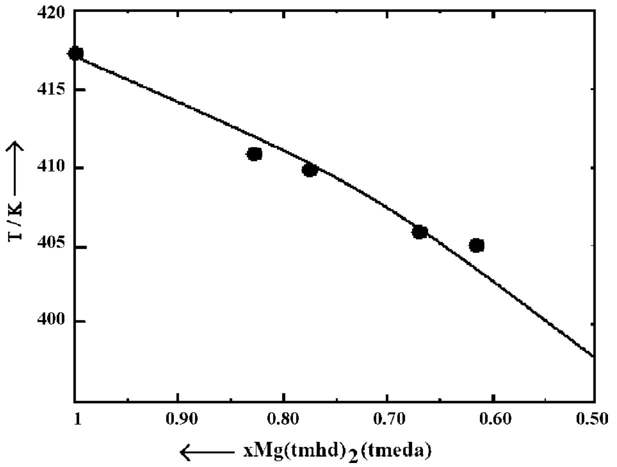

Fig. 6. Partial $T-x\mathrm{Mg}'$ diagram for the system $\mathrm{Mg(tmhd)_2(tmeda)}$ as a solvent and anhydrous $\mathrm{Mg(acac)_2}$ as a non-volatile solute.

3.3. DTA: fusion enthalpy studies

The rate of liquid evaporation was observed to be non-linear mass loss, precluding the direct determination of enthalpies of vapourisation since equilibrium (p_e) could not be achieved in its evaporation. DTA-based melting point depression technique (cryoscopic technique) was used for the evaluation of $\Delta_{\mathrm{fus}}H^\circ$ by employing the equation $\log x_{\mathrm{solvent,\,Mg(tmhd)2(tmeda)}} = [-\Delta_{\mathrm{fus}}H^\circ/2.303R]\ [1/T - 1/T_0]$ derived by Riesman for systems exhibiting ideal eutectic behaviour. The liquidus endotherms for the four compositions (Table 1) along with the melting endotherm for pure $\mathrm{Mg(tmhd)_2(tmeda)}$ are reproduced in Fig. 5. The instantaneous melting points for the four compositions of $\mathrm{Mg(tmhd)_2(tmeda)+Mg(acac)_2}$ along with the value of T_0 (418 K) facilitated the construction of partial $T-x\mathrm{Mg(tmhd)_2(tmeda)}$ (Fig. 6). From the thermodynamic correlation between the solvent mole fraction and the melting temperatures, $\Delta_{\mathrm{fus}}H^\circ$ the values (Table 1) were calculated for each binary system, using Riesman equation [10] with an average value of $58.3 \pm 5.2\ \mathrm{kJ\,mol^{-1}}$.

$\mathrm{Mg(tmhd)_2(tmeda)}$ was identified to be completely volatile at 525 K leaving no residue and recommended as an excellent precursor for CVD applications.

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