A thermoanalytical study of solid state reactions between tellurium oxide and the oxides of zirconium and hafnium

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Abstract

The solid state reactions of tellurium oxide with zirconium and hafnium oxides were investigated employing thermogravimetry (TG), differential thermal analysis (DTA) and X-ray diffraction (XRD) techniques. The only compounds reported in these two pseudo-binary systems are $ZrTe_3O_8$ and $HfTe_3O_8$, respectively. From the results obtained in these studies it is concluded that these compounds can be synthesized in the solid state in the pure form from their binary component oxides by heating the stoichiometric mixtures to temperatures as low as 900 to 950 K where the vaporization of the more volatile component TeO_2, is insignificant.

Keywords: DTA; Hafnium tellurate; Solid state reactions; Tellurate synthesis; TG; XRD; Zirconium tellurate

1. Introduction

The accuracy of thermochemical quantities like the standard enthalpy of formation, heat capacity, etc., derived from the calorimetric measurements depends largely on the purity and the stoichiometry (composition) of the compound being investigated. On several occasions the compound has to be synthesized by heating the mixture of its components to high temperature in some definite stoichiometry. It is often assumed that the proportion of the components in the mixture is retained in the resulting compound. Quite often, however, the components from which the compound is synthesized differ significantly in their volatility. Preparation of the compound by heating the mixture of such components to some arbitrary high temperature, therefore,

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could result in the contamination of the compound by a less volatile component. In some cases the quantity of the less volatile impurity may not exceed the limit of detection by X-ray diffraction, a technique generally employed to identify various phases, but this level of impurity could be quite significant and would introduce sizeable error into thermochemical quantities such as the heat of solution of the compound from which its standard enthalpy of formation could be derived.

In our recent study on the determination of the standard enthalpy of formation of zirconium and hafnium tellurates [1, 2] employing the isoperibol solution calorimeter, it was necessary to prepare these compounds in pure form. Heating mixtures of zirconium oxide and tellurium oxide and hafnium oxide and tellurium oxide arbitrarily to temperatures above 1000 K resulted in products contaminated with the less volatile components, namely ZrO_2 and HfO_2 respectively. It was, therefore, necessary to optimize the temperature at which the compounds would be formed in pure form at a reasonable rate without significant loss of the more volatile component, which in the present case was tellurium dioxide. In this paper we highlight the role of thermo- gravimetry (TG), differential thermal analysis (DTA) and X-ray diffraction (XRD) in arriving at the optimum temperature and time for obtaining these compounds in the pure form.

2. Experimental

$ZrTe_3O_8$ is the only ternary compound known to exist in the ZrO_2–TeO_2 pseudo-binary system [3,4]. The analogous $HfTe_3O_8$ isomorphous with the zirconium compound has also been reported [5]. The two compounds were prepared by heating the mixtures of their component oxides in a silica boat to a suitable temperature.

2.1. Chemicals

ZrO_2 used in the present work contained about 0.1% HfO_2 and was procured from the Nuclear Fuel Complex, Hyderabad. HfO_2 was prepared by heating hafnium oxychloride (Lieco Chemicals) in dry oxygen to 925 K. The total impurities in both these chemicals did not exceed 300 ppm. TeO_2 used in the synthesis was from Koch–Light Chemicals UK. The phase identification of all these chemicals was performed by X-ray diffraction.

2.2. Instrumentation

Thermogravimetric (TG) balance, differential thermal analyser (DTA) and X-ray diffractometer (XRD) were employed to follow the synthesis of these tellurates. A Shimadzu thermobalance (Model DT-30) was used to monitor the mass change at a sensitivity of 50 µg. The samples were heated at the constant heating rate of 5 K min^{-1}. The TG curves were recorded in argon at a flow rate of 2.5 l h^{-1}. Home built DTA apparatus was used to record the DTA curves for pure TeO_2 and the mixtures of $ZrO_2 + TeO_2$ and $HfO_2 + TeO_2$. The oxides were mixed in the ratio of 1:3. The samples and the inert calcined alumina powder used as reference contained in the silica

cups were heated and cooled at two different heating and cooling rates, 5 and 2 K min^{-1}. The heating was performed in purified argon employing the same flow rate as that used in the TG experiments. The differential and temperature-measuring thermocouples were made of chromel–alumel wires. The latter was calibrated against the melting points of Sn, Zn, Sb and Ag by recording their fusion and freezing temperatures. Only melting temperatures were considered for temperature calibration because of the observed undercooling of some of these metals during the cooling cycle. The TG and DTA curves were recorded on a strip chart recorder.

The starting chemicals and their reaction products were identified by X-ray diffraction. A Philips X-ray diffractometer (Model PW 1729/40) was used to record the X-ray patterns. The patterns were recorded employing CuKα radiation and a graphite monochromator.

The elemental analysis of pure compounds $ZrTe_3O_8$ and $HfTe_3O_8$ identified by X-ray diffraction was performed by gravimetric analysis and atomic absorption spectrometry. Zirconium and hafnium were estimated by precipitating them as mandelates and igniting them to the oxides [6] at temperatures between 1175 and 1275 K and weighing them as oxides.

The chemical analysis of tellurium in these compounds was carried out by atomic absorption spectrometry using a Varian Techtron atomic absorption spectrophotometer (Model AA-4 updatd to AA-6) having a 100 mm air–acetylene burner head with manual gas controls. A calibration curve was generated by measuring the absorbance of standard Te solutions. The amount of Te was estimated by interpolation from the calibration curve.

2.3. Procedure

The progress of the reaction between ZrO_2 and TeO_2 and between HfO_2 and TeO_2 was followed by heating the mixtures isothermally between 875 and 950 K. The mixtures heat-treated at these temperatures for different time intervals were taken out, ground thoroughly, and were reheated till the completion of the reaction. X-ray diffraction patterns were recorded every time to follow the progress of the reaction.

3. Results

Fig. 1 shows the thermogravimetric (TG) curves recorded for TeO_2, and the mixtures of $TeO_2 + ZrO_2$ and $TeO_2 + HfO_2$. The mixtures contained the oxides in the ratio 3:1 where 1 part was zirconium oxide. The TG curves were recorded in flowing argon at heating rates of 5 and 2 K min^{-1}. It can be seen from these curves that the vaporization temperature of TeO_2, indicated by the initiation of the mass loss, increased substantially on mixing it with ZrO_2. The rate of vaporization, however, decreased considerably, suggesting thereby the possibility of a reaction between TeO_2 and ZrO_2 resulting in the formation a compound decomposing at a much higher temperature. Mixing of HfO_2 with TeO_2 did not change the vaporization temperature noticeably, but the rate of vaporization decreased significantly. Moreover, the curve exhibited a peculiar
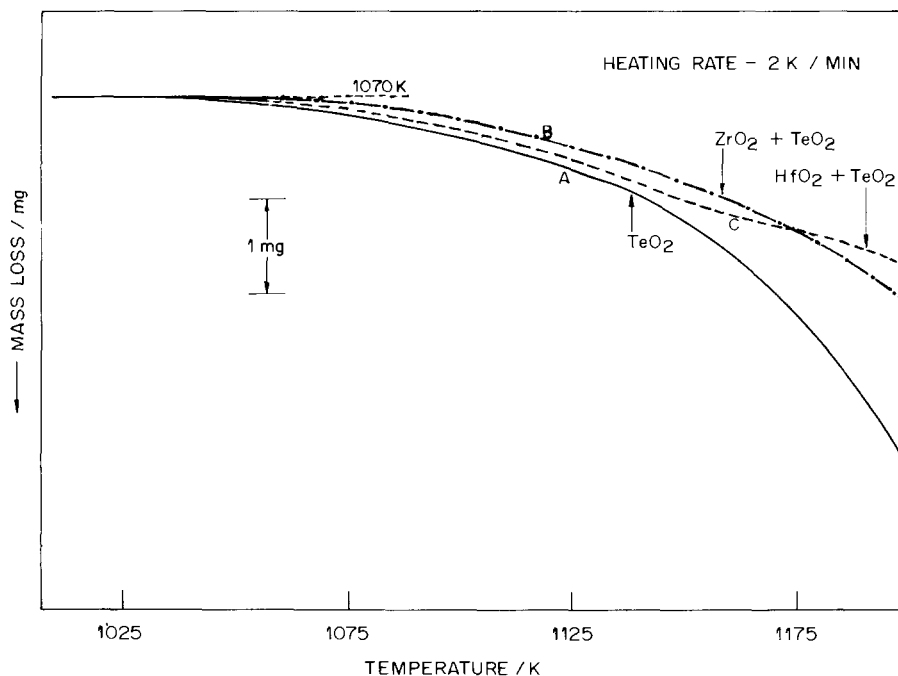
Fig. 1. Thermogravimetric curves for vaporization of (A) TeO_2, (B) mixture of $ZrO_2 + 3TeO_2$, and (C) mixture of $HfO_2 + 3TeO_2$.

change in slope unlike that in the $ZrO_2 + TeO_2$ mixture. The curves recorded for TeO_2 and the $TeO_2 + ZrO_2$ and $HfO_2 + TeO_2$ mixtures at $5 K min^{-1}$ are shown in Fig. 1. There was no change in the nature of the TG curve for the $HfO_2 + TeO_2$ mixture at the reduced heating rate of $2 K min^{-1}$.

Fig. 2 shows the DTA curves recorded for pure TeO_2 as well as the mixtures. The curve for TeO_2 was recorded at the heating rate of $5 K min^{-1}$. The curves for the mixtures were recorded at two heating rates, 5 and $2 K min^{-1}$. Fig. 2 shows the prominent endothermic peak (curve A) for melting of TeO_2 around 1005 K. The DTA recorded on the mixtures of $ZrO_2 + TeO_2$ and $HfO_2 + TeO_2$ containing 75 mol% of TeO_2 and an amount of TeO_2 the same as that used for recording the melting point (curve B), also showed the peaks around the same temperature at which the melting point of pure TeO_2 occurred, but of greatly reduced intensity. There was however total absence of the peak in the curve recorded for the $ZrO_2 + TeO_2$ mixture recorded at $2 K min^{-1}$ (curve D). The small peak observed for the $HfO_2 + TeO_2$ mixture around 1005 K at the heating rate of 5 K min, however, persisted even when the heating rate was reduced to $2 K min^{-1}$.

Figs. 3 and 4 indicate, respectively, the progress of the reaction between ZrO_2 and TeO_2 and between HfO_2 and TeO_2 as followed by X-ray diffraction. It can be seen from these figures that the reaction in the former mixture was complete on heating for about 3 h at 900 K with one intermediate grinding after 90 min. The mixture of HfO_2 and
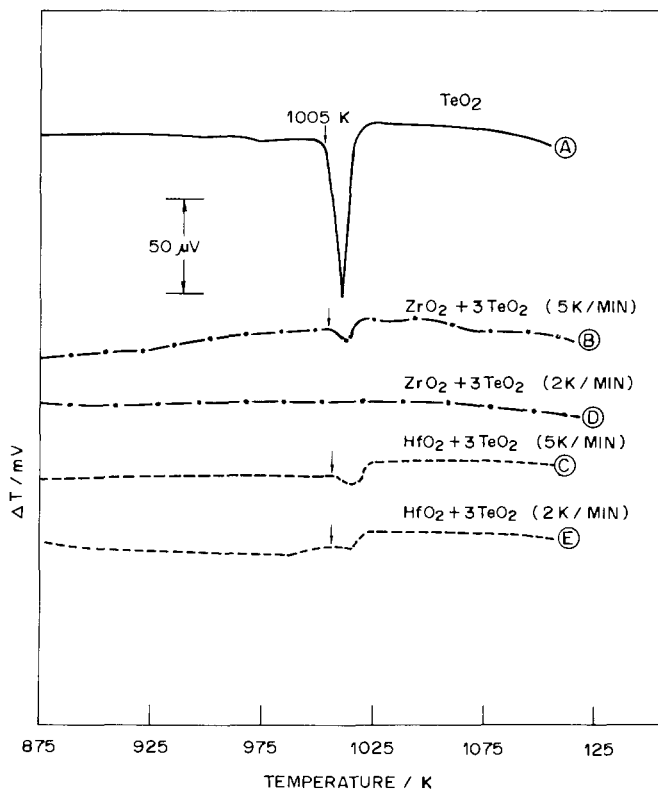
Fig. 2. Differential thermal analysis curves for TeO_2, $ZrO_2 + 3TeO_2$ and $HfO_2 + 3TeO_2$.

TeO_2, however, had to be heated by at least 50 K more for the same time interval to yield the pure stoichiometric compound.

The chemical analysis data for zirconium and hafnium tellurates are listed in Table 1.

It can be seen that the composition of these compounds was in good agreement with their expected stoichiometries.

Table 1
Analytical results; molar mass M and mass fraction w

Compound	$M/(\text{g mol}^{-1})$	$w(\text{Zr}) \times 10^2$		$w(\text{Hf}) \times 10^2$		$w(\text{Hf}) \times 10^2$	
		Found	Calc	Found	Calc	Found	Calc
$ZrTe_3O_8$	602.0192	15.02 ± 0.15	15.15			63.40 ± 0.50	63.59
$HfTe_3O_8$	689.2585			25.63 ± 0.20	25.89	55.17 ± 0.50	55.54

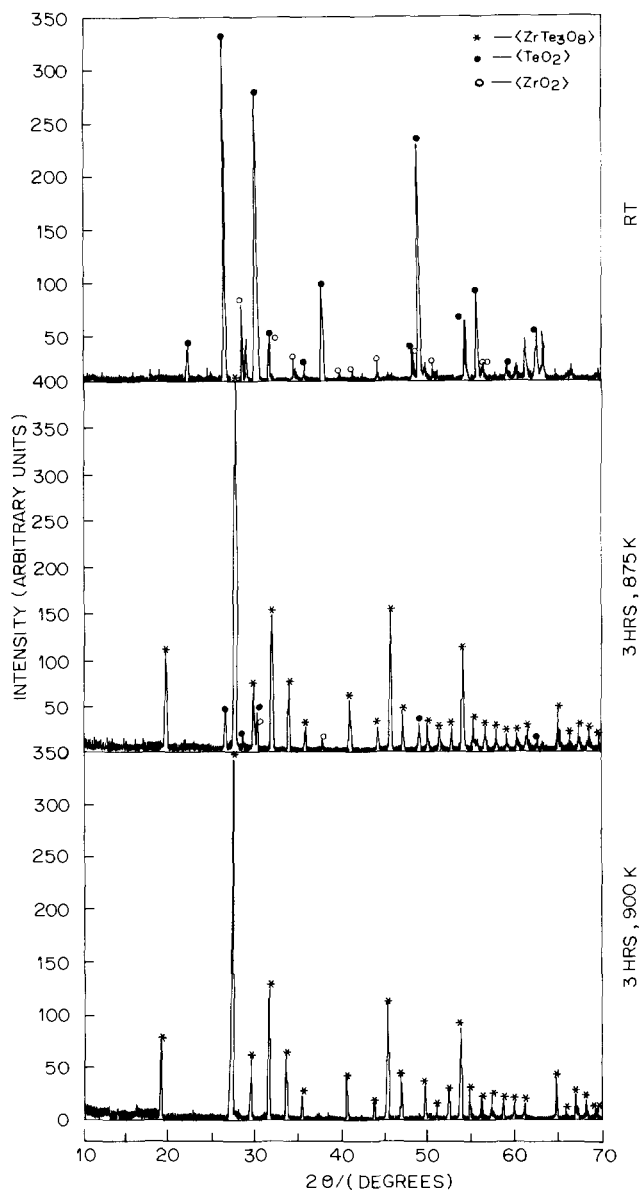Fig. 3. X-ray diffraction patterns for the mixture $ZrO_2 + 3TeO_2$ heated at various temperatures.

4. Discussion

The drastic reduction in the magnitude of the melting peak for TeO_2 on mixing intimately with ZrO_2 or HfO_2 suggests that the formation of the tellurates has progressed sufficiently during the course of heating of the mixture in the DTA
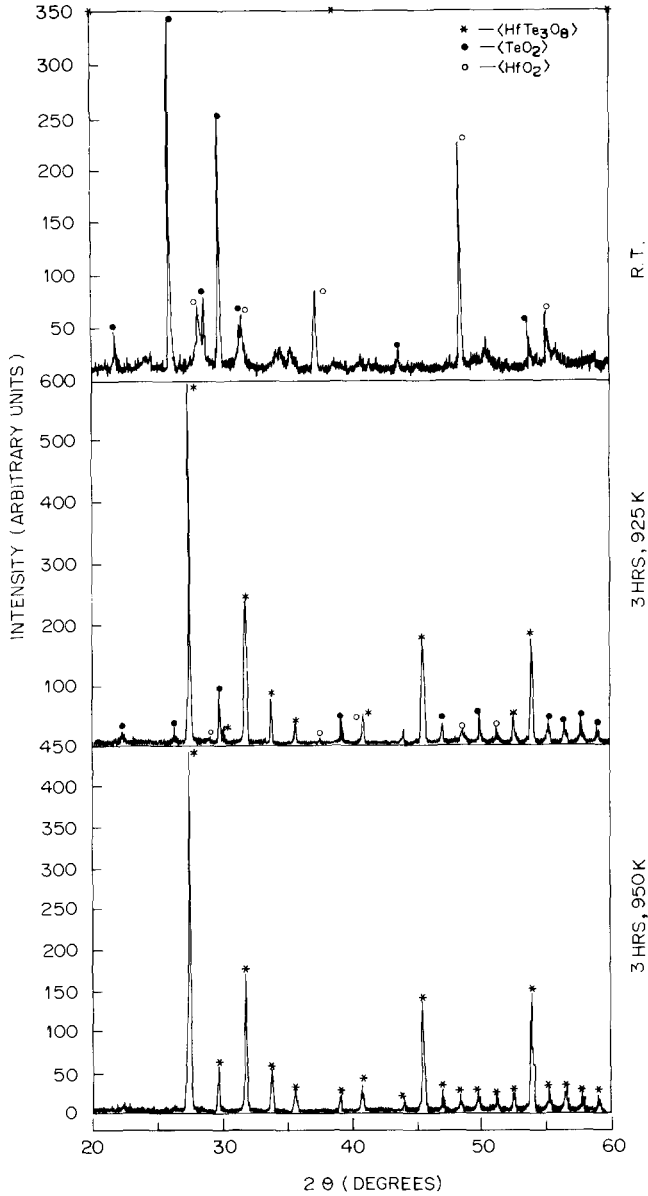
Fig. 4. X-ray diffraction pattern for the mixture $HfO_2 + 3TeO_2$ heated at various temperatures.

apparatus. The complete disappearance of the peak for the $ZrO_2 + TeO_2$ mixture on reduction of the heating rate from 5 to $2\,K\,min^{-1}$ indicates that the formation of $ZrTe_3O_8$ from the mixture was total before the melting point of TeO_2 was attained. Persistence of the peak for the $HfO_2 + TeO_2$ mixture, even at the reduced rate of

$2\,K\,min^{-1}$ suggests that the rate of reaction between HfO_2 and TeO_2 was significantly lower than that between ZrO_2 and TeO_2 as was borne out by the X-ray diffraction and the TG studies carried out on the two mixtures.

The X-ray patterns of the mixtures of $ZrO_2 + TeO_2$ and $HfO_2 + TeO_2$ heated between 875 and 950 K indicated that the reaction in the former mixture was complete on heating it for 3 h at 900 K with one intermediate grinding. The temperature of $HfO_2 + TeO_2$ mixture, however, had to be increased to 950 K in order to obtain the pure product on heating for the same length of time. The progress of reaction at various temperatures for the two mixtures followed by X-ray diffraction is shown in Figs. 3 and 4.

The TG curves recorded for TeO_2 and the mixtures are presented in Fig. 1. A significant change occurred in the TG curve recorded for TeO_2 on addition of ZrO_2 and HfO_2. Addition of ZrO_2 to TeO_2 increased the vaporization temperature by about 50 K. The rate of vaporization was also significantly reduced. The vaporization curve was smooth and continuous. For the HfO_2 mixture, the rate of vaporization was lower than that for TeO_2, but the curve showed the beginning of the loss starting around the same temperature as that for pure TeO_2. The curve, however, showed a significant change in slope as the reaction progressed. This is probably because in the beginning free TeO_2 might be getting lost from the mixture, due to the poorer reactivity of the constituents in the mixture. At higher temperatures the progressively increasing reaction rate between HfO_2 and TeO_2 would reduce the rate of vaporization. This, in fact, is observed from the TG curves.

5. Conclusion

It can be concluded from the present study that in the solid state synthesis of the ternary oxides from the binary components in which a, significant difference in volatility exists between the component oxides, thermal techniques like TG and DTA coupled with X-ray diffraction can be extremely useful for optimizing the experimental conditions for the solid state synthesis of pure phase free from contamination by the less volatile component. The present study indicated that the mixtures of $ZrO_2 + TeO_2$ need not be heated above 900 K and that of $HfO_2 + TeO_2$ above 950 K at which the vaporization of TeO_2 becomes significant. For acquisition of accurate thermochemical data for the compounds in such pseudo-binary systems, the method adopted for the preparation of the compound based on the present studies will yield much more reliable results free from uncertainty introduced by impurity phases.

The observations made in the present work suggest that the formation of the ternary oxide from its binary components is complete at a temperature significantly below the melting point of the lower melting oxide, where its vaporization is also insignificant. These observations concur with our earlier studies on $ZrO_2 + MoO_3$ [7] and $HfO_2 + MoO_3$ [8] systems, where the compounds $ZrMo_2O_8$ and $HfMo_2O_8$ were formed much below the melting point of MoO_3, where its vapour pressure was insignificant.

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