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PREPARATION OF Cs_2ZrO_3 AND Cs_2ThO_3 THROUGH SOL-GEL METHOD AND THEIR CHARACTERIZATION

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Abstract

Cesium zirconate and cesium thorate were prepared by sol-gel method following citrate-nitrate route. The compounds were characterized by X-ray diffraction, chemical analysis and simultaneous TG-DTA. The methods of preparation of Cs_2ZrO_3 and Cs_2ThO_3 reported in literature involve difficult steps and require stringent experimental conditions for obtaining the compounds. In this work we report an easier method for the preparation of these compounds at relatively low temperature.

Keywords: cesium thorate, cesium zirconate, simultaneous TG-DTA, sol-gel method, X-ray powder diffraction

Introduction

Thermochemistry of the compounds of cesium plays an important role in nuclear applications. The fission product iodine formed in fuel pin during burn up inside a nuclear reactor combines with another fission product cesium giving a significant amount of CsI [1]. Even at a low oxygen potential of about –400 kJ mol^{-1}, CsI reacts with the fuel-matrix UO_2 or, with ZrO_2 layer on zircaloy to form ternary compounds of cesium such as Cs_2UO_4, Cs_2ZrO_3 etc. and releases elemental iodine [2]. The migration of the released iodine to the clad surface and its subsequent reaction with clad material (e.g. zircaloy) causes stress corrosion cracking [2, 3] which is detrimental to the long term stability of the nuclear fuel pins. In this context the data of thermodynamic stability of the compounds of Cs with the other fission products, fuel matrix and the clad materials are important. Recently, Scharm *et al.* [4] reported the thermodynamic properties of Cs_2ZrO_3 from the standard enthalpy of formation and heat capacity measurements. Thermodynamic investigation on Cs_2ThO_3 has not been reported so far. Considering the importance of thermodynamic data for these compounds, we initiated the program of their thermodynamic investigations and worked

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out the sol-gel method for the preparation of Cs_2ZrO_3 and Cs_2ThO_3 presented in this paper.

The reported method for the preparation of Cs_2ZrO_3 or Cs_2ThO_3 [5–7], uses cesium metal or its oxide and therefore, involves stringent experimental conditions to get the product in the pure form. In this work we report an easier method of preparation of the compounds at relatively low temperature. The compounds prepared by this new method were subsequently used for the thermodynamic investigations [8, 9].

Experimental

Cs_2ZrO_3 and Cs_2ThO_3 were prepared by sol-gel method through citrate-nitrate route. The chemicals used for the preparation of the compound are Cs_2CO_3 (99.99% purity, Aldrich, USA), CsI (99.99% purity, Aldrich, USA), $ZrOCl_2{\cdot}xH_2O$, $Th(NO_3)_4{\cdot}xH_2O$, citric acid, HNO_3 and NH_4OH solutions (all AR Grade).

Preparation of Cs_2ZrO_3

The aqueous solution of cesium nitrate of known concentration was prepared from either cesium carbonate or cesium iodide by their dissolution in nitric acid. Carbon dioxide or iodine evolved was removed thoroughly before use. Aqueous solution of zirconium nitrate was prepared from its oxychloride by precipitating zirconium hydroxide in ammoniacal medium followed by dissolving the thoroughly washed precipitate with nitric acid. Aqueous solutions of cesium nitrate and zirconium nitrate were mixed in 2:1 molar ratio. Citric acid amounting to 2.5 times the number of moles of total metal content was added to the above resulting solution. pH of the solution was adjusted by adding ammonia or nitric acid so as to maintain a homogenous solution.

The solution was slowly heated in an open beaker at 80°C in a fume hood till it formed a gel, which was transformed into fine powder on prolonged heating. The solid powder was vacuum dried and transferred to a platinum boat placed in a furnace under dry flowing oxygen gas and ignited at 400°C for 1 h. The material thus formed during the ignition process was heated at 600°C for 6 h under similar conditions to increase the crystallinity of the product. The compound was cooled to room temperature in gas flow condition and was immediately transferred to a vacuum desiccator.

Preparation of Cs_2ThO_3

Aqueous solutions of cesium nitrate and thorium nitrate were mixed in the molar ratio 2:1 and citric acid amounting to 2.5 times the total number of moles of total metal content was added to this mixture. pH of the solution was adjusted so as to maintain a homogenous solution. Further preparation of the compound Cs_2ThO_3 from this solution is the same as given under preparation of Cs_2ZrO_3.

Characterization of Cs_2ZrO_3 and Cs_2ThO_3

The compounds were characterized by X-ray diffraction and chemical analysis followed by their thermogravimetry, differential thermal analysis (simultaneous TG-DTA). Thermogravimetry and differential thermal analysis runs were taken using a SETARAM simultaneous TG-DTA instrument (Model No. 92-16.18) at a heating rate of 10°C min^{-1} up to 1000°C in a completely dry flowing argon atmosphere. X-ray diffraction pattern of the compound covered with a paraffin paper, was recorded in a Philips X-ray Diffractometer (Model No. 1729) in the 2θ angle range 20–60° at a scan speed of 1°C min^{-1} using silicon powder as an internal standard and CuK_α radiation. Chemical analysis of the completely dry compound was done to determine the cesium, zirconium, thorium and carbon contents.

Results and discussion

Table 1 gives the typical results of chemical analysis for these two compounds. It is seen that the total carbon contents in the samples prepared through the citrate precursor are very small. In the sample of Cs_2ZrO_3 the results of chemical analysis indicate the presence of an excess zirconium over the stoichiometric compound. The excess Zr was found to be present as ZrO_2. X-ray diffraction pattern for the product (Fig. 1) obtained after annealing at 600°C for 6 h showed the broadened lines of Cs_2ZrO_3 and also, of ZrO_2. XRD peaks corroborated to reported data of the compounds (JPCDS file Nos 41-513 (Cs_2ZrO_3) and 37-1484 (ZrO_2) respectively). The observed line broadening corresponded to an average crystallite size of 25 nanometers. Similarly, Cs_2ThO_3 was characterized by XRD. Figure 2 gives the XRD pattern of Cs_2ThO_3, which matches with the reported JCPDS File No. 31-385. No thoria lines are seen in the pattern corroborating to the result of the chemical analysis.

Table 1 Results of chemical analysis

Compound	Mass percentages of the elements analyzed/%, obs. (calc.)			
	Zirconium	Thorium	Cesium	Carbon
Cs_2ZrO_3	25.8 (22.5)		56.4 (65.6)	1.04
Cs_2ThO_3		42.7 (42.6)	48.7 (48.6)	0.08

The reason for the observed excess of zirconia in the preparation of cesium zirconate was due to the loss of Cs as $Cs_2O(g)$ and $CsOH(g)$ during autoignition of the dried gel. The steam coming from citrate-nitrate burning leads to the formation of the hydroxide species. The exothermic step of ignition of gel is common to the preparation of both cesium zirconate and cesium thorate. In the ignition process, the oxides of cesium and zirconium or thorium formed in situ combine to yield the respective double oxides. The chemical combinations of the oxides being again exothermic release extra heats. However, it has been seen by our thermodynamic study of the compounds [8, 9] that the respective values of their enthalpies of formation from the con-

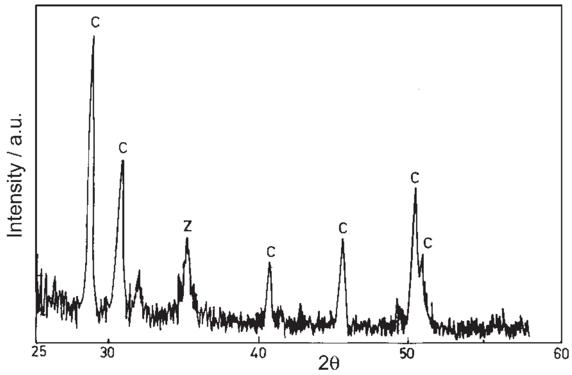

Fig. 1 X-ray diffraction pattern for the compound Cs_2ZrO_3. C – peaks due to the compound and Z – peak due to zirconia

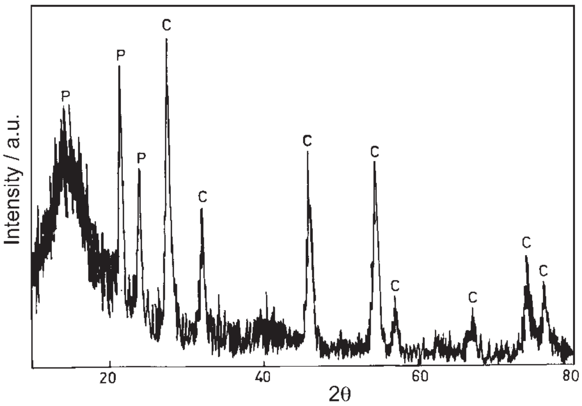

Fig. 2 X-ray diffraction pattern for the compound Cs_2ThO_3. C – peaks due to the compound and P – peaks due to paraffin paper

stituent oxides are quite different for the two double oxides; cesium zirconate formation releases much more heat than cesium thorate. As a result, in the preparation of cesium zirconate the exothermic step of autoignition of gel and formation of the double oxide evolves comparatively larger heat and results in higher local temperature. During the progress of the process, a portion of freshly formed cesium oxide volatilizes out as its oxide and hydroxide by the elevated temperature. The sacrificial aspect of cesium in the preparation of cesium zirconate by gel ignition is an inherent limitation of the technique.

Though the presence of ZrO_2 phase in the prepared Cs_2ZrO_3 was a necessity in defining thermodynamic univariancy of the system in volatilization study of the zirconate [8], attempt was made to make a stoichiometric compound by the present method of preparation. Later findings showed that taking an excess amount of $CsNO_3$ in the initial ingredient of the gel preparation could make up for the cesium loss in attaining stoichiometry. The sacrifice of cesium in the process of preparation was seen to be as high as 25% of the stoichiometric requirement.

TG curve for the compound showed initial mass loss near 100°C due to the loss of adsorbed moisture, followed by the decomposition of the compound at 830°C in a single step. The mass loss at 830°C corresponded to the stoichiometric loss of Cs_2O from Cs_2ZrO_3. The simultaneous TG-DTA runs gave one small endothermic peak at 780°C, which could be due to solid-solid phase transition in the compound. Similarly, Cs_2ThO_3 was characterized by simultaneous TG-DTA. Mass loss at 700°C corresponding to the loss of Cs_2O was observed.

With partial decompositions of Cs_2ZrO_3 and Cs_2ThO_3 the X-ray diffraction patterns of the respective products showed the built up of ZrO_2 and ThO_2 lines. The literature data for the gaseous cesium oxides [10] indicates that at an oxygen partial pressure of 10^{-13} Pa the predominant gaseous species is $Cs_2O(g)$. From the above observations it is concluded that Cs_2ZrO_3 and Cs_2ThO_3 vaporize incongruently to $Cs_2O(g)$ and $ZrO_2(s)$ or $ThO_2(s)$ as the case may be. The vaporization reactions can be given by the equations

$$Cs_2ZrO_3(s)=ZrO_2(s)+Cs_2O(g) \tag{1}$$

$$Cs_2ThO_3(s)=ThO_2(s)+Cs_2O(g) \tag{2}$$

These reactions were used to derive the thermodynamic properties of Cs_2ZrO_3 and Cs_2ThO_3 by monitoring their mass losses in a Knudsen effusion apparatus [8, 9].

Conclusions

The compounds Cs_2ZrO_3 and Cs_2ThO_3 could be prepared by sol-gel method. In this method handling of hygroscopic and hazardous cesium metal is avoided. Pure and crystalline samples suitable for thermodynamic measurements could be obtained. The method, however, has an inherent limitation in the preparation of some double oxides that have a high enthalpic stability with respect to the constituent oxides, one of which has a significant volatility. In such cases as seen in cesium zirconate, the method demands an excess of the volatile component in the initial ingredient for attaining stoichiometry in the final product, as there is a sacrificial loss of the component at the autoignition stage of gel.

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