

## PREPARATION, SPECTRAL AND THERMAL STUDIES OF NEODYMIUM ZIRCONYL OXALATE HEXAHYDRATE

*V. B. Reddy and P. N. Mehrotra*

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROORKEE, ROORKEE-247 667, INDIA

(Received August 21, 1982; in revised form May 16, 1983)

Neodymium zirconyl oxalate (NdZrOX) is prepared and characterized by chemical analysis and ir spectral studies. Its thermal decomposition has been investigated by using DTA, TG, DTG, X-ray diffraction and ir spectroscopy. On the basis of thermogravimetry and isothermal studies a probable mechanism for the decomposition is proposed. The decomposition proceeds mainly through three stages: i) dehydration between RT–413 K, ii) decomposition of oxalate between 413–943 K and iii) decomposition of the carbonate between 1028–1235 K to give a mixed oxide. The ir spectra and X-ray diffraction studies are made for identification of the intermediates. X-ray diffraction studies of the end product indicates that it belongs to cubic crystal system with  $a = 11.520 \text{ \AA}$ .

In recent times the quest for high purity ceramic materials of controlled particle size, particularly for electronic industry, has led the chemists to search for different techniques for the preparation of various mixed oxide ceramics. It has been demonstrated by several workers that high purity titanates, stannates, ferrites, zirconates of perfect stoichiometry can be prepared from pyrolysis of mixed metal oxalate systems [1–4]. Zirconium is reported to form anionic oxalato zirconates [5] and thermal decomposition of such complex salts make up an interesting study. The lack of literature on oxalato zirconates of trivalent cations led us to prepare and study the thermal decomposition of neodymium zirconyl oxalate whose end product is expected to be a mixed oxide.

### Experimental

All the materials used in the present work were of BDH AnalaR quality. Neodymium oxide was of 99.99% purity obtained from Indian Rare earths Ltd. The zirconium oxychloride octahydrate was of Fluk AG, Switzerland. Neodymium zirconyl oxalate hydrate (NdZrOX) was prepared by adding equimolar (0.1 M) aqueous solutions of zirconyl oxychloride and neodymium oxide (dissolved in  $\text{HNO}_3$ ) to warm oxalic acid (0.3 M). On vigorous stirring the precipitation started. An excess of acetone was added to facilitate the precipitation. After keeping for overnight the light violet

coloured precipitate was filtered washed with acetone and air dried. The product was amorphous to X-ray. Such a sample was subjected for chemical analysis and the results were: Nd: 27.35%, ZrO: 21.0%, C<sub>2</sub>O<sub>4</sub>: 41.8%, H<sub>2</sub>O: 10.3%; the calculated values for Nd<sub>2</sub>(ZrO)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>5</sub> · 6 H<sub>2</sub>O are Nd: 27.45%, ZrO: 20.40%, C<sub>2</sub>O<sub>4</sub>: 41.86%, H<sub>2</sub>O: 10.27%. Thus a good agreement between the two sets of values is seen. Thermogravimetry was carried out using Stanton Redcroft TG-770 thermobalance with 5–10 mg samples in platinum crucibles. The heating rate used was 5 deg min<sup>-1</sup>. Differential thermal analysis was carried out by employing Fisher differential thermalyser model 260P with 100–150 mg samples in quartz crucibles. The heating rate was 10 deg min<sup>-1</sup> and α-alumina was used as reference material.

Infrared spectra were recorded on Beckman IR-20 in 4000–250 cm<sup>-1</sup> region, with samples in KBr pellets. The X-ray diffraction studies were carried out on a Phillips diffractometer using CuK<sub>α</sub> radiation.

### Results and discussion

Figure 1 gives the DTA, TG and DTG of neodymium zirconyl oxalate in air and it indicates that the decomposition of this system is complex. The decomposition broadly takes place in three steps. It can be seen that 1:1 correlation exists between

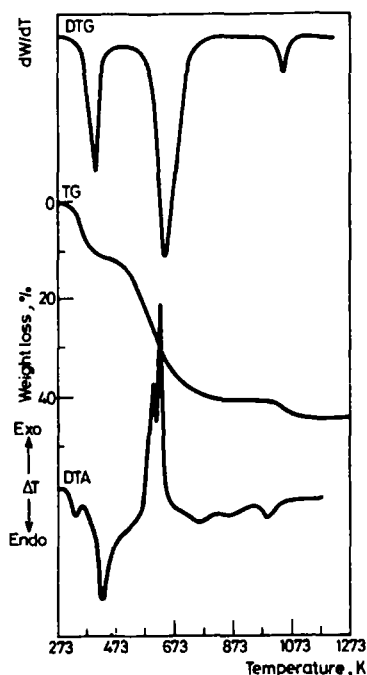


Fig. 1 DTA, TG and DTG curves for NdZrOX

DTA and DTG indicating that all the heat effects are accompanied by weight losses. The detailed data of various thermal changes and corresponding temperature ranges are given in Table 1. Characterization of intermediate products has been made by ir spectroscopy and X-ray diffraction studies. The detailed discussion is given below.

**Table 1** Thermogravimetric data of NdZrOX

Thermal change	Weight loss, %		Temperature range, K
	Calculated	Observed	
Dehydration	10.28	11.47	333–423
Decomposition of oxalate	31.56	29.20	413–943
Decomposition of the carbonate	1.52	2.00	943–1235

### *Dehydration*

The dehydration of NdZrOX is a single step process which occurs between room temperature and 413 K. Weight loss in TG experiments suggests that all the six moles of water associated with NdZrOX is lost in one step. However in DTA there are two peaks around 333 K and 423 K. The peak at 333 K may be due to absorbed moisture which can also be supported with the calculated and observed weight loss values for H<sub>2</sub>O in Table 1 and that at 423 K is due to the dehydration of NdZrOX.

### *Decomposition of oxalate*

The decomposition of oxalate is a multistep process. It occurs between 413–943 K with 29.2 percent weight loss against the calculated value of 31.56 percent. This step corresponds to the loss of five moles of carbon monoxide and four moles of carbon dioxide with the formation of an intermediate carbonate. In DTA the entire process shows a complex behaviour unlike other similar systems studied earlier. Soon after the endothermic peak due to dehydration, a sharp exothermic peak (doublet) due to oxalate decomposition is observed. This may be due to the domination of oxidation of carbon monoxide in air over the endothermic oxalate decomposition. The nature of this exothermic peak is just similar to the DTA peak reported for the decomposition of neodymium oxalate [6]. The results of TG and isothermal studies indicate the formation of an intermediate carbonate.

### *Decomposition of the carbonate*

The decomposition of carbonate takes place between 943–1235 K with a weight loss of 2.0 percent that corresponds to the loss of one mole of carbon dioxide. This change is clearly indicated as an endothermic peak in DTA around 973 K and a mixed oxide, Nd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> is formed.

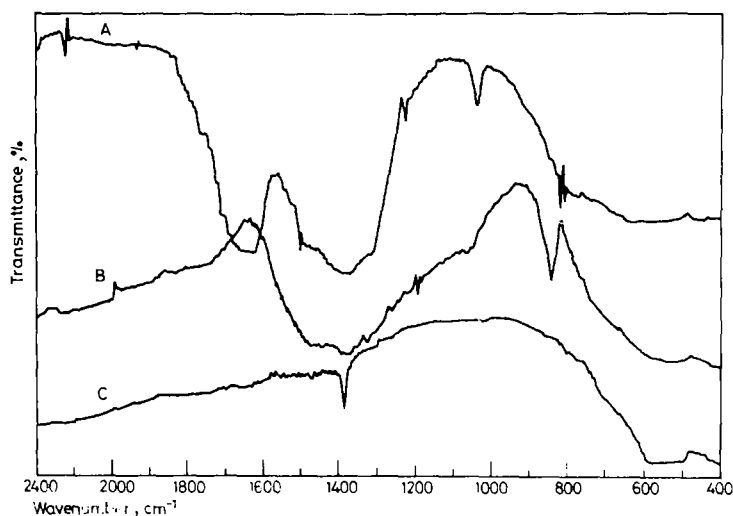
X-ray diffraction studies of the end product heated at 1235 K for six hours show the presence of neodymium zirconate as the only phase which belongs to cubic (Pyro-

chlore) system with  $a = 11.520 \text{ \AA}$ . All the lines could be indexed successfully into a cubic system. The value of cell parameter,  $a$  is slightly higher than the earlier reported [7] value. The detailed data is given in Table 2.

**Table 2** X-ray diffraction data of end product,  $\text{Nd}_2\text{Zr}_2\text{O}_7$

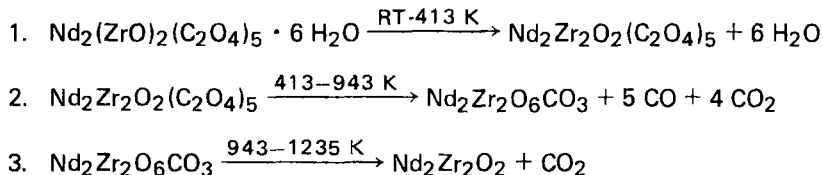
$\text{Sin}^2\theta$		$hkl$	Relative intensity, $I/I_1$
calculated	observed		
0.0574	0.0573	311	4
0.0636	0.0627	322	100
0.0730	0.0714	321	16
	0.0741		
0.0835	0.0835	400	45
0.0992	0.0996	331	6
0.1670	0.1661	440	60
0.2297	0.2291	622	50
0.2505	0.2500	444	18

Figure 2 gives the ir spectra of  $\text{NdZrOX}$  and various products obtained from its decomposition. The  $\nu_{\text{as}}(\text{C}=\text{O})$ , principal band of  $\text{NdZrOX}$  appears at  $1650 \text{ cm}^{-1}$ , and all other bands can be assigned for different normal modes of vibration of oxalate group [8]. And the bands in the region  $1500\text{--}1200 \text{ cm}^{-1}$  are not well resolved. Spectrum (B) of a sample heated at  $873 \text{ K}$  indicates the presence of carbonate [9]. Spectrum (C) is of the end product, identified as pyrochlore type  $\text{Nd}_2\text{Zr}_2\text{O}_7$  by X-ray studies. It shows two bands between  $500\text{--}600 \text{ cm}^{-1}$  and  $400\text{--}500 \text{ cm}^{-1}$  that can be attributed to Pyrochlore [10]  $\text{Nd}_2\text{Zr}_2\text{O}_7$ . On the basis of TG and other



**Fig. 2** Infrared spectra of (A)  $\text{NdZrOX}$ , (B)  $\text{NdZrOX}$  heated at  $873 \text{ K}$  and (C) the end product neodymium zirconate

studies the following tentative scheme for the thermal decomposition of NdZrOX is proposed.



The present work elucidates some of the intermediates which form during dynamic thermal decomposition of neodymium zirconyl oxalate.

\* \* \*

One of the authors (VBR) is grateful to CSIR (India) for the senior research fellowship.

## References

- 1 W. S. Clabaugh, E. M. Swiggard and R. Gilchrist, *J. Res. Natl. Bur. Stds.*, 56 (1956) 289.
- 2 P. K. Gallagher, in *Thermal Analysis Comparative studies of materials*, Ed. H. Kambe and P. D. Garn. John Wiley, New York, 1974, p. 17.
- 3 P. K. Gallagher, *Inorg. Chem.*, 4 (1965) 965.
- 4 V. B. Reddy and P. N. Mehrotra, *J. Thermal Anal.*, 21 (1981) 21.
- 5 A. A. Grinberg and V. I. Astapovich, *Russ. J. Inorg. Chem.*, 6 (1961) 164.
- 6 R. C. Ropp and E. E. Gritz, *Rareearth Research III*, Ed. Eyring, Gordon and Breach, New York, 1965, p. 736.
- 7 R. Roth, *J. Res. Natl. Bur. Stds.*, 56 (1956) 17.
- 8 K. Nakamoto, *Infrared spectra of Inorganic and Co-ordination Compounds*, John Wiley, New York, 1963, p. 210.
- 9 C. N. R. Rao, *Chemical application IR Spectroscopy*, Academic Press, New York, 1963, p. 342.
- 10 N. V. Gudanouin, F. M. Spiridonov, L. N. Komissarova and K. I. Petrov, *Russ. J. Inorg. Chem.*, 20 (1975) 325.

**Zusammenfassung** – Neodymzirkonyloxalat (NdZrOX) wurde dargestellt und durch chemische Analyse und IR-spektroskopische Untersuchungen charakterisiert. Die thermische Zersetzung dieser Verbindung wurde mittels DTA, TG, DTG, Röntgendiffraktometrie und IR-Spektroskopie untersucht. Basierend auf Ergebnisse der Thermogravimetrie und isothermer Methoden wird ein möglicher Zersetzungsmechanismus vorgeschlagen. Die Zersetzung verläuft im wesentlichen über drei Stufen: i) Dehydratisierung zwischen Zimmertemperatur und 413 K, ii) Zersetzung des Oxalats zwischen 413 und 943 K und iii) Zersetzung des Carbonats zwischen 1028 und 1235 K unter Bildung eines Mischoxides. IR-spektroskopische und röntgendiffraktometrische Untersuchungen wurden zur Identifizierung der Zwischenprodukte ausgeführt. Die röntgendiffraktometrische Untersuchung des Endproduktes ergibt eine kubische Zelle mit  $a = 11.520 \text{ \AA}$ .

**Резюме** – Полученный цирконилоксалат неодимия охарактеризован химическим анализом и ИК-спектроскопией. Термическое разложение его было исследовано методами ДТА, ТГ, ДТГ, дифракцией рентгеновский лучей и инфракрасной спектроскопией. На основе

термогравиметрии и изотермических исследований предложен возможный механизм разложения. Разложение, главным образом, протекает в три стадии: а/ дегидратация в области температур от комнатной до 413 К, б/ разложение оксалата в области температур 413–943 К и в/ разложение карбоната в интервале 1028–1235 К с образованием смешанного окисла. Рентгенография и ИК-спектроскопия были использованы для идентификации промежуточных продуктов. Рентгено-дифракционные измерения показали, что конечный продукт реакции относится к кубической кристаллической структуре с параметром решетки  $a = 11,520 \text{ \AA}$ .