Journal of Thermal Analysis, Vol. 21 (1981) 21–26

IR AND THERMAL STUDIES ON LANTHANUM ZIRCONYL OXALATE

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(Received May 7, 1980; in revised form October 21, 1980)

Lanthanum zirconyl oxalate hydrate (LaZO) was prepared and characterized by chemical analysis and i.r. spectral studies. Its thermal decomposition was investigated by using DTA, TG, X-ray diffraction and i.r. spectral studies. On the basis of the TG and isothermal results, a tentative decomposition scheme was proposed. In the first step the dehydration of LaZO takes place in two steps between room temperature and 498 K, to give the anhydrous compound. The anhydrous oxalate decomposes in a series of steps (498–548 K, 548–673 K and 673–773 K). Finally the decomposition of the carbonate takes place (773–1073 K) to give lanthanum zirconate ($La_2Zr_2O_7$).

In view of the wide variety of applications in technology, the preparation of perovskite and pyrochlore type mixed oxides has attracted the attention of chemists and ceramists, with a view to obtaining them in high purity by simpler methods. The zirconates of the alkaline earths and rare earths have found considerable importance in ceramics. The preparation of various mixed oxides in pure and homogeneous form could be achieved by thermal decomposition of mixed metal oxalate salts [1, 2]. Zirconium is reported to form anionic oxalato zirconates with bivalent metal cations [3], and the thermal decomposition of such complex salts makes an interesting study. The lack of literature on zirconyl oxalates of trivalent cations led us to prepare and study the thermal decomposition of lanthanum zirconyl oxalate hydrate (LaZO). In its decomposition behaviour, this may show some interesting features different from those of the systems studied earlier [4–8], since the decomposition of the simple lanthanum oxalate is of a complex nature [9].

Experimental

All the materials used in the present study were of analytical grade. Lanthanum oxide of 99.99% purity was obtained from Indian Rare Earths, Ltd. The zirconium oxychloride octahydrate was a product of Fluka AG, Switzerland. Lanthanum zirconyl oxalate hydrate (LaZO) was prepared by adding equimolar ($0.1M$) solutions of zirconyl chloride and lanthanum oxide (dissolved in HNO_3) to warm oxalic acid solution ($0.3M$). The clear solution so obtained was left in a refrigerator for five to six days, whereupon a white, fine powder solid settled out. The product was filtered, washed with distilled water and acetone, and air-dried. Such a sample was analyzed for various constituents. Wet chemical analysis indicated that the ratio La : Zr was approximately unity. The complete analysis of the product gave ZrO: 19.30, La: 25.00, C_2O_4: 39.50, and H_2O: 16.50%, which corresponds to $La_2(ZrO)_2(C_2O_4)_5 \cdot 10H_2O$. The calculated values for the above formula are ZrO: 19.27, La: 24.99, C_2O_4: 39.55, and H_2O: 16.18%. The X-ray powder diffraction pattern of this product indicated that it was a crystalline compound.

Thermogravimetry was carried out using a Stanton thermobalance (HT-D), with 500–600 mg samples in platinum crucibles. The heating rate was 3°/min. Differential thermal analysis was carried out on a Fischer differential thermalyser model 260P, fitted with an automatic voltage stabilizer, amplifier and recorder. 100–150 mg samples were taken in quartz crucibles for DTA, and the heating rate was 10°/min. IR spectra were recorded on, a Beckman IR-20, double-beam instrument in the 4000–250 cm^{-1} region, with samples in KBr pellets. X-ray diffraction studies were carried out on a Philips diffractometer, using Cu K_α radiation.

Results and discussion

The results of the i.r. spectra (Fig. 1a) of LaZO are summarized in Table 1; the band assignments are based on the available literature information [10–14]. Comparison of the spectrum of LaZO with those of lanthanum oxalate hydrate and zirconyl oxalate hydrate revealed that it is not a superimposition of these two spectra, which rules out the possibility of LaZO being a mixture of the two oxalates. The bands in the 1750–900 cm^{-1} region also indicate the bidentate nature of the oxalate group [11]. Thermal studies (Fig. 2) on LaZO indicate that it de-

Table 1

IR data on $La(ZrO)_2(C_2O_4)_5 \cdot 10\ H_2O$

Band position	Assignment
3400 vs, b	ν_{OH} of H_2O
1650 vs	ν_a (C=O)
1470 s, sh	ν_a (C–O) + ν(C–C)
1390 s, sh	ν_s (C–O) + (O–C=O)
1340 m, sh	
1300 m, sh	
980 m	M=O
910 m, b	ν(C–O) + ν(Zr–O) + δ(O–C=O)
800 vs, sh	δ(O–C=O) + (MO)
560 m	ν(MO) + δ ring def.
520 m	

vs = very strong, s = strong, sh = sharp, m = medium, b = broad.

composes in a complex manner, forming various intermediates. The decomposition takes place in five steps. The intermediates obtained in isothermal studies were characterized by spectral and chemical analysis.

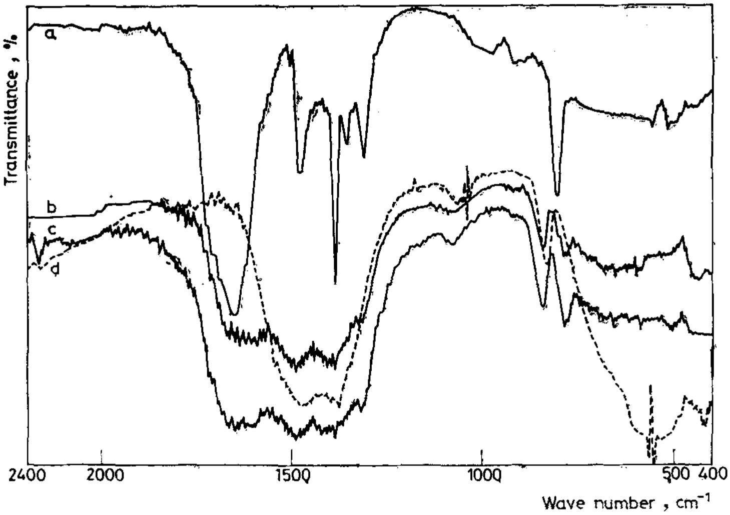

Fig. 1. IR spectra of a) LaZO and the products heated at b) 523 K, c) 623 K, d) 723 K

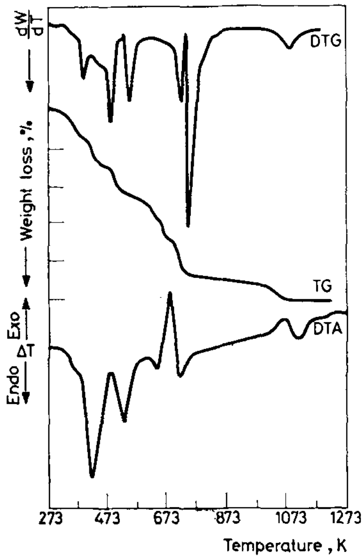

Fig. 2. TG, DTG and DTA of LaZO in air

Dehydration

The dehydration of LaZO takes place in two steps between room temperature and 498 K, giving the anhydrous oxalate. This reaction is shown as one endotherm in the DTA curve (Fig. 2). However, in TG and DTG this change appears in two steps. The different nature of this change in DTA and DTG may be attributed to the different heating rates used (10^0 min^{-1} in DTA and 3^0 min^{-1} in TG) and the large difference in sample size in the two cases. The calculated and observed weight losses are in good agreement (Table 2).

Table 2

Thermal change	Wt. loss Observed, %	Wt. loss Calculated, %	Temp. range
1. a) Partial dehydration	9.50	9.70	RT-423 K
b) Dehydration	6.30	6.48	423–498 K
2. 1st step of oxalate decomposition	6.5	5.05	498–548 K
3. 2nd step of oxalate decomposition	10.5	10.42	548–673 K
4. Decomposition of intermediate oxalate carbonate	10.60	10.43	673–773 K
5. Decomposition of the carbonate	6.0	6.47	773–1073 K

Decomposition of oxalate

The first step in the oxalate decomposition occurs at 498–548 K and the weight loss corresponds to the loss of two moles of carbon monoxide. This is shown in DTG and DTA at 503 K and 518 K, respectively. The i.r. spectrum of the solid obtained isothermally at 523 K (Fig. 1b) indicates the presence of oxalate. Decomposition of the intermediate oxalate carbonate occurs at 548–673 K and is shown in DTG. The i.r. spectrum of the solid obtained isothermally at 623 K (Fig. 1c) also indicates the presence of oxalate. The band at 2340 cm^{-1} is attributed to the presence of carbon dioxide adsorbed on the solid [6]. However, the sample heated at around 623 K for a few hours and then air-quenched does not show any band in this region, indicating the adsorption of CO_2 on the solid when the heated sample is furnace-cooled. The final decomposition of the oxalate occurs at 673–773 K, giving an intermediate carbonate. DTA suggests that these two changes are of a complex nature. There is an endothermic peak around 643 K, immediately followed by an exothermic peak. The latter peak may be due to domination of the oxidation of the CO evolved in air over the oxalate decomposition. The weight losses of 6.5, 10.5 and 10.6% agree with the values calculated for the different reactions (Table 2). The i.r. spectrum (Fig. 1d) of the solid obtained isothermally at 673 K for 4 h indicates the presence of carbonate.

Decomposition of the carbonate

Decomposition of the carbonate occurs at 773–1073 K, liberating one mole each of carbon monoxide and carbon dioxide. This change occurs in DTA at around 1133 K, which is higher than the position of the peak in DTG. This may again be due to the fast heating rate used in DTA. The end-product corresponds to $La_2Zr_2O_7$. The X-ray powder diffraction pattern data of the end-product heated at 1273 K for several hours indicates that it belongs to the cubic system with $a = 10.680$ Å. This is slightly less than the earlier reported [16] value ($a = 10.793$ Å). No other phase is found except lanthanum zirconate.

On the basis of the TG and other studies, the following tentative scheme is proposed for the thermal decomposition of LaZO:

1.a) $La_2(ZrO)_2(C_2O_4)_5 \cdot 10\,H_2O \xrightarrow{RT-423\,K} La_2(ZrO)_2(C_2O_4)_5 \cdot 4\,H_2O + 6\,H_2O$

b) $La_2(ZrO)_2(C_2O_4)_5 \cdot 4\,H_2O \xrightarrow{423-498\,K} La_2(ZrO)_2(C_2O_4)_5 + 4\,H_2O$

2. $La_2(ZrO)_2(C_2O_4)_5 \xrightarrow{498-548\,K} La_2(ZrO)_2(C_2O_4)_3(CO_3)_2 + 2\,CO$

3. $La_2(ZrO)_2(C_2O_4)_3(CO_3)_2 \xrightarrow{548-673\,K} La_2Zr_2O_4(C_2O_4)_2CO_3 + 2\,CO_2 + CO$

4. $La_2Zr_2O_4(C_2O_4)_2CO_3 \xrightarrow{673-773\,K} La_2Zr_2O_6CO_3 \cdot CO + 2\,CO_2 + CO$

5. $La_2Zr_2O_6CO_3 \cdot CO \xrightarrow{773-1073\,K} La_2Zr_2O_7 + CO_2 + CO$

From the above results and the discussion it is clear that the weight loss steps in dynamic thermogravimetry and the explanations based on them are limited in scope, and the compositions of the residues obtained isothermally may not tally with the exact compositions assigned from weight loss measurements.

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The authors are grateful to Dr. W. U. Malik, Prof. & Head of Chemistry Department, Roorkee University, for providing the research facilities. V. B. R. is also grateful to the CSIR (India) for the award of a senior research fellowship.

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Résumé — L'oxalate hydraté de lanthane-zirconyle (LaZO) a été préparé et caractérisé par analyse chimique et spectrométrie infrarouge. La décomposition thermique de ce composé a été examinée par ATD, TG, diffraction des rayons X et spectrométrie infrarouge. Un mécanisme de décomposition est proposé, d'après les résultats TG, obtenus en régimes dynamique et isotherme. Dans un premier temps la déshydratation de LaZO a lieu en deux étapes (température ambiante — 498 K) pour fournir le composé anhydre. L'oxalate anhydre se décompose en plusieurs étapes et plusieurs composés intermédiaires contenant l'oxalate ainsi que du carbonate (498—548 K, 548—673 K, 673—773 K). Finalement, la décomposition du carbonate (773—1073 K) fournit du zirconate de lanthane ($La_2Zr_2O_7$).

Zusammenfassung — Lanthanzirkonyloxalathydrat (LaZO) wurde hergestellt und durch chemische Analyse sowie durch Infrarotspektroskopie charakterisiert. Seine thermische Zersetzung wurde unter Einsatz von DTA, TG, Röntgendiffraktion und Infrarotspektroskopie untersucht. Aufgrund der TG und isothermen Ergebnisse wurde ein Zersetzungsschema vorgeschlagen. In der ersten Stufe erfolgt die Dehydratisierung von LaZO in zwei Schritten zwischen (RT-498 K) um die Anhydroverbindung zu ergeben. Das wasserfreie Oxalat wird in einer Serie von Stufen zersetzt und verschiedene Zwischenprodukte enthalten sowohl Oxalat als auch Carbonat (498—548 K, 548—673 K und 673—773 K). Abschließend findet die Zersetzung des Carbonats statt (773—1073 K) unter Bildung von Lanthazirkonat ($La_2Zr_2O_7$).

Резюме — Получена двойная соль гидрат лантан цирконил оксалата, которая охарак теризована химическим анализом и ИК спектрами. Термическое разложение этой соли исследовано с помощью ДТА, ТГ, рентгенографии и ИК спектроскопии. На основании ТГ результатов изотермического исследования, предложена экспериментальная схема реакции разложения этой соли. На первой стадии имеет место двухступенчатая дегидратация, протекающая между комнатной температурой и 498 К с образованием безводного соединения. Разложение безводного оксалата протекает многоступенчато с образованием промежуточных продуктов, содержащих как оксалат, так и карбонат в температурных интервалах 498—548 К, 548—673 К и 673—773 К. В интервале 773—1073 К имеет место конечное разложение карбоната с образованием цирконата — $La_2Zr_2O_7$.