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The thermal behaviour of ceric ammonium nitrate studied by temperature-dependent X-ray powder diffraction

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Abstract

The thermal decomposition process of Ce(IV) $(NH_4)_2(NO_3)_6$ has been determined by means of temperature-dependent X-ray diffraction and TG–DSC. The first stage is characterised by the simultaneous formation of CeO_2 and the cerous compound $Ce(III)_2(NH_4)_3(NO_3)_9$, isostructural with the compounds $Ce(III)_2M(I)_3(NO_3)_9(M = K, Rb)$, which decomposes into CeO_2 in the second stage. The process of the reduction of Ce(IV), induced by thermal decomposition, is discussed

Keywords: Ceric ammonium nitrate, $Ce(IV)(NH_4)_2(NO_3)_6$; DSC; Temperature-dependent X-ray powder diffraction (TDXD); TG; Thermal decomposition

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1. Introduction

In recent studies [1–3], it was demonstrated by temperature-dependent X-ray powder diffraction (TDXD) that the thermal decomposition of the mixed salts $Ce(IV)M(I)_2(NO_3)_6(M(I) = K,Rb)$ proceeds through the formation of the intermediate cerous phases $Ce(III)_2M(I)_3(NO_3)_9$, which provide the final product CeO_2. This sequence involves two successive changes of cerium oxidation state, Ce(IV)→ Ce(III)→Ce(IV). This feature has also been reported by Pokol et al. [4] for the decomposition of the ammonium analogue, $Ce(IV)(NH_4)_2(NO_3)_6$, from magnetic susceptibility and XPS measurements. On the basis of TG analysis, they suggested the

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formation of cerous nitrate $Ce(NO_3)_3$ as the intermediate phase. The purpose of the present study is the investigation of the thermal behaviour of the ceric ammonium nitrate by means of TDXD which is an efficient tool for tracing in situ the structural changes occurring in a precursor submitted to a thermal treatment.

2. Experimental

Analytical grade ammonium cerium nitrate $Ce(IV)(NH_4)_2(NO_3)_6$(Merck) was used as supplied. In order to avoid preferential orientation effects of the crystallites in the powder diffraction study, the salt was ground in cyclohexane for 3 min using a McCrone micronising mill.

TDXD measurements were carried out by means of an INEL (CPS 120) curved position-sensitive detector, used with a monochromatic $CuK\alpha_1$ radiation and a diffraction geometry described elsewhere [5]. The sample was located in a monitored high-temperature X-ray diffractometer attachment (Rigaku) designed to maintain the specimen in a controlled atmosphere. Acquisition time for each pattern was 3000 s.

Simultaneous TG and DSC analyses were carried out using a Rigaku Thermoflex TG–DSC instrument. Sample mass was about 50 mg. When only the TG curve was recorded, the sample was spread evenly in a large sample holder to avoid mass effects and to reproduce as much as possible the experimental conditions used in TDXD.

3. Results and discussion

Fig. 1 shows the 3D representation of the successive powder diffraction patterns recorded during the decomposition performed in flowing nitrogen, in the temperature range 20–500°C. It clearly demonstrates that the decomposition takes place in two stages. The first stage occurs in the range 110–150°C. It corresponds to the simultaneous formation of CeO_2 and a new phase which further transforms into CeO_2 in a second stage, between 155 and 190°C.

3.1. Indexing of the powder diffraction pattern and identification of the intermediate phase

A powder diffraction pattern of the mixture of CeO_2 and the new phase, at 155°C, was selected from the 3D plot. After elimination of the broad diffraction lines of CeO_2, the peak positions of the lines of the additional phase were obtained from profile fitting techniques. The diffraction pattern was indexed with the program DICVOL91 [6] and the complete data set was reviewed by means of the computer program NBS*AIDS83 [7]. From this evaluation a cubic solution with the cell parameter $a = 13.890(3)$ Å [$M_{20} = 22$ and $F_{24} = 30(0.026, 31)$] was obtained. This result is in complete agreement with the indexing of the diffraction pattern of $Ce(III)_2(NH_4)_3(NO_3)_9$, [$a = 13{,}8358(5)$ Å] recently observed during the decomposition of $Ce(III)(NH_4)_2(NO_3)_5 \cdot 4H_2O$ [8], and for which the powder diffraction data have been

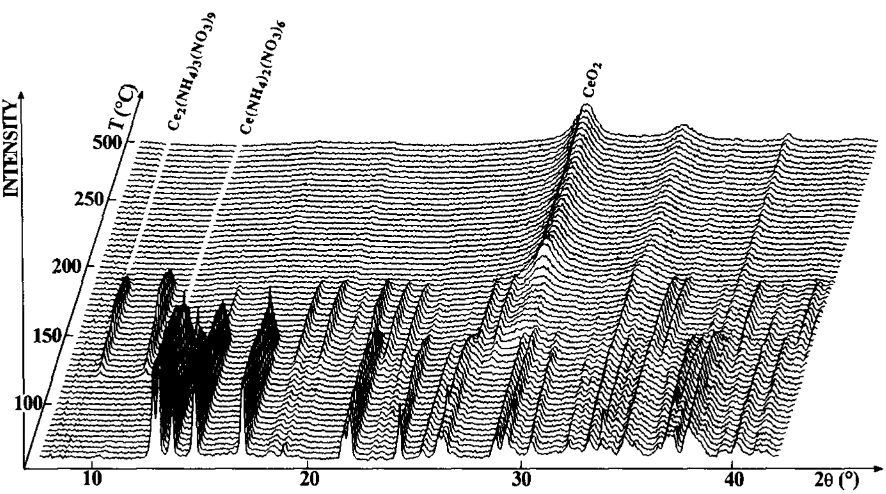

Fig. 1. TDXD plot for Ce(IV)$(NH_4)_2(NO_3)_6$, in nitrogen atmosphere (heating rate: 10°C h^{-1} between room temperature and 100°C, 5°C h^{-1} in the range 100–250°C, 20°C h^{-1} in the range 250–280°C and 30°C h^{-1} in the range 280–500°C).

deposited with the International Centre for Diffraction Data [9]. The cubic solution obtained in the present study compares well with the cubic unit cell parameter reported by Guillou et al. for $Ce_2K_3(NO_3)_9$[a = 13.5840(3) Å] [2] and for $Ce_2Rb_3(NO_3)_9$ [a = 13.8411(4)Å] [3]. This demonstrates that the intermediate phase, formed during the first stage of the decomposition of the ammonium compound, is Ce(III)$_2(NH_4)_3(NO_3)_9$ isostructural with the two last cerous compounds. The crystal structure of the cubic phase has been described for the potassium [10] and rubidium [3] compounds. It is built from a three-dimensional anionic network, $[Ce_2(NO_3)_9]^{3-}$, in which cerium polyhedra are linked together by bridging nitrate groups. Therefore, the result reported here supports the study by Pokol et al. [4] who, from ex situ magnetic susceptibility measurements, observed the presence of paramagnetic cerium (III) in the course of the thermal decomposition.

3.2. Decomposition scheme of Ce(IV)$(NH_4)_2(NO_3)_6$ under nitrogen

In Fig. 2 are displayed the changes of the relative integrated intensities with temperature, of selected diffraction lines for the precursor and Ce(III)$_2(NH_4)_3(NO_3)_9$, as well as the corresponding TG curve. Due to the serious broadening of the diffraction lines of CeO_2 arising from the very small size of the crystallites formed, the corresponding integrated intensities could not be measured with high accuracy. However, it has been roughly estimated that about the third of the total amount of CeO_2 is formed at the end of the first stage. It can be seen that Ce(III)$_2(NH_4)_3(NO_3)_9$ decomposes just after the end of the first stage from 155°C. This can explain the absence of any peculiar point on the TG curve between 110 and 180°C. In other respects, the inflection observed on the TG curve at 180°C can be due to the slow release of the gaseous

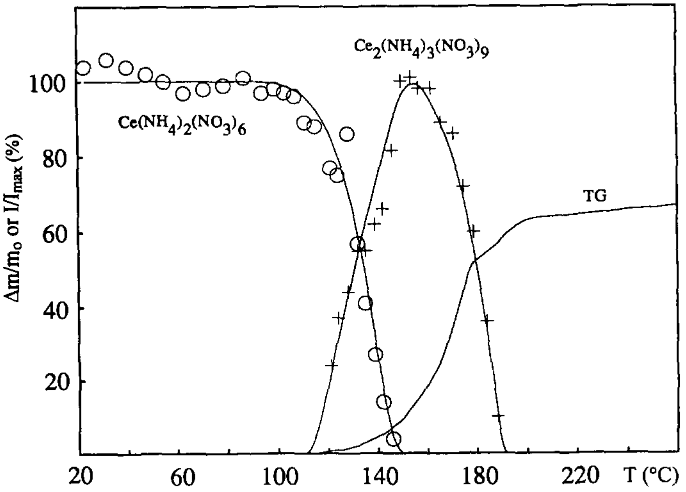

Fig. 2. TG curve and integrated intensities of selected diffraction lines vs temperature from the TDXD plot. o:line 200 for $Ce(IV)(NH_4)_2(NO_3)_6$; + :lines 110 and 111 for $Ce(III)_2(NH_4)_3(NO_3)_9$.

decomposition products adsorbed on the finely divided CeO_2. Indeed a total weight loss of 58% was only obtained at 190°C and it was necessary to heat the final product up to 800°C to achieve the theoretical weight loss of 68.6%.

On the other hand, from the TDXD plot (Fig. 1) it can be deduced that NH_4NO_3 is not formed during the decomposition process. This was confirmed by DSC measurements which did not exhibit endothermic peaks which could correspond either to the phase transformation of NH_4NO_3 at 125°C or to its melting at 170°C [11]. Therefore, the gases NH_3, NO, NO_2 and O_2 are released during the two stages of the decomposition.

From these results, the following reaction sequence can be proposed:

$$Ce(IV)(NH_4)_2(NO_3)_6 \rightarrow \tfrac{1}{3}Ce(III)_2(NH_4)_3(NO_3)_9 + \tfrac{1}{3}CeO_2 + (NH_3,NO,NO_2,O_2)(110\text{–}150°C) \quad (1)$$

$$\tfrac{1}{3}Ce(III)_2(NH_4)_3(NO_3)_9 \rightarrow \tfrac{2}{3}CeO_2 + (NH_3,NO,NO_2,O_2)(155\text{–}190°C) \quad (2)$$

The difference between the experimental weight loss (about 10%) observed at 150°C and the theoretical value (35.3%) may be due to the adsorption phenomena of gaseous products on CeO_2 as mentioned above.

To conclude, the use of TDXD has clearly demonstrated the formation of the cerous compound $Ce(III)_2(NH_4)_3(NO_3)_9$ and consequently the occurrence of the double valence change of cerium Ce(IV)→Ce(III)→Ce(IV) during the thermal decomposition of $Ce(IV)(NH_4)_2(NO_3)_6$. The reducing effect of the ammonium ions was put forward by Pokol et al. [4] to explain this change of the cerium oxidation state, but it is probably not the sole reducing agent since this phenomenon is also observed for the two others precursors $Ce(IV)K_2(NO_3)_6$ and $Ce(IV)Rb_2(NO_3)_6$. To explain the redox reaction occurring at the first stage of the decomposition, another competitive reaction has also been proposed [2]:

$$2Ce^{4+} + O^{2-} \rightarrow 2Ce^{3+} + \tfrac{1}{2}O_2$$

where the O^{2-} arise from the breakdown of N–O bonds in nitrate groups.

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