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Preparation and thermal decomposition of $Y_2(OH)_5NO_3 \cdot 1.5H_2O$

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Abstract

The composition of the basic nitrate salt of Y^{3+} has been investigated by Gran plots, ion chromatography (IC), atomic absorption spectroscopy (AAS) and X-ray diffraction (XRD). The salt seems to be stoichiometric with formula $Y_2(OH)_5NO_3 \cdot 1.5H_2O$. The decomposition is studied using TG–FTIR (heating rate, 10°C min^{-1}). The product decomposes between 200 and 600°C. The solid residue is Y_2O_3 and the gases evolved stepwise during decomposition are H_2O, NO_2 and O_2.

INTRODUCTION

There has been great interest in superconductors since the discovery of high T_c superconductors, such as YBaCu. Several techniques to synthesize the superconducting material $YBa_2Cu_3O_{7-\delta}$ have been described. A common route is the solid state reaction of mixed oxides and carbonates. A number of disadvantages of this method have been mentioned, such as inhomogeneities at atomic level [1] resulting in long calcination and sintering times. Therefore the preference is given to other techniques such as the precipitation-filtration technique [2].

It is generally believed that precursors can be synthesized yielding very homogeneous starting material which can lead to reduction of the reaction times. Although the oxalate ion [3, 4] is mostly used as precipitating agent, the hydroxide ion yields the advantage of the formation of $Ba(OH)_2$ instead of the thermally very stable $BaCO_3$ and low cost materials. Another advantage is the transformation of the metal hydroxides through sols into gels. Increased chemical homogeneity in a multicomponent system and a high surface area of the gels are obtained [5].

In this paper we describe the reaction of a sodium hydroxide solution with a yttrium nitrate solution, which fits into a systematic study of the

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preparation of hydroxide precursors. The solids obtained are examined by potentiometry, atomic absorption spectroscopy (AAS), ion chromatography (IC), X-ray diffraction (XRD) and TGA coupled with FTIR spectroscopy (TG–FTIR).

EXPERIMENTAL

The following products were used: $Y(NO_3)_3 \cdot 5H_2O$ (Merck p.a.) and NaOH (Titrisol, Merck). The solutions were made with CO_2-free water, which had been obtained by boiling deionized and twice-distilled water for 1 h and cooling under a dynamic N_2 gas atmosphere.

The precipitate was prepared in a thermostated cage (25.0 ± 0.2°C) by mixing the sodium hydroxide solution (0.1 M) with the yttrium nitrate solution (0.1 M) using two motor driven burettes (Schott Geräte T100) at the same speed and under continuous stirring. The precipitate obtained was filtered off and then washed and dried over P_2O_5 in a desiccator.

The analysis of the metal ion in the starting material and precursor has been performed with a Perkin-Elmer 703 atomic absorption spectrometer. The absorption is measured at 410.2 nm. As gas we used a mixture of N_2O and acetylene, which gave a flame of 2700°C. The hydroxide and nitrate content in the precipitate have been examined by potentiometry and IC (Dionex 2000i/SP) respectively. The columns used in IC are an AS4A guard column, an AS4A separator column and a micro-membrane-surpressor column. The eluent used was a mixture of $NaHCO_3$ and Na_2CO_3. Instead of conductivity measurements UV absorption at 215 nm was used to detect NO_3^-. The TGA experiments were performed with a TA Instruments (formerly Du Pont) model 2000–951. The evolved gases were examined by a Bruker FTIR IFS 48 coupled to the TGA unit [6]. The FTIR spectrometer had a resolution of 8 cm^{-1}. XRD data were obtained by measurements on a Philips PW 1050/70 instrument.

RESULTS

The basic yttrium nitrate salt was prepared as follows: 25 ml portions of yttrium nitrate (0.1 M) were titrated with exactly 0.1 M carbonate-free sodium hydroxide in a thermostat controlled at 25°C ± 0.2°C. The changes in pH were followed with a Microprocessor pH meter 537. The solution was stirred continuously and atmospheric carbon dioxide was excluded by bubbling nitrogen through the solution. The titration curve rose steeply before the theoretical $3OH^-$ to $1Y^{3+}$ mole ratio was attained, namely at a ratio of ±2.5/1. The chemical composition of this salt was not quite clear. Chou and Burkhart [7] found $Y_2(OH)_{5.46}(NO_3)_{0.54} \cdot 1.6H_2O$; Holcombe [8] found $Y_2(OH)_{5.14}(NO_3)_{0.86}$ and Mzareulishvili [9] found $Y(OH)_{2.6}(NO_3)_{0.4}$.

The general formula of the basic salt is given by $Y_2(OH)_{6-u}(NO_3)_u \cdot vH_2O$. The composition of the precipitate, obtained by mixing 200 ml NaOH and 100 ml $Y(NO_3)_3$, has been determined using two techniques. In the first one the Y^{3+} and OH^- content has been examined, while the second one is based on the determination of the Y^{3+} and, instead of OH^-, the NO_3^- content.

OH^- and Y^{3+} content

The OH^- concentration was determined by means of potentiometric titrations in a thermostated cage (25.0 ± 0.2°C). Solution 1 held 0.05929 g of the precipitate dissolved in 25 ml HNO_3 (0.1 M, Titrisol Merck) and 25.2778 g KNO_3 (Merck p.a.) in a 250 ml graduated retort. 20 ml of solution 1 was titrated with solution 2 containing 0.1 M NaOH and 1 M KNO_3. The solution was stirred continuously and carbon dioxide was excluded by bubbling nitrogen through the solution. This tritation is based on back titration. The OH^- ions from the precipitate were neutralized by H^+ ions of the acid. The excess of the H^+ ions was then back-titrated with NaOH. During the titration the potential differences, between the glass electrode and the argental reference electrode, and the corresponding volumes of added solution 2 were measured.

By means of the Gran function [10, 11] the plot was made linear and the volume of equivalence was calculated ($V_{eq} = 1.335$ ml). Because a mixture of a strong acid (HNO_3) and a weak acid (Y^{3+}) was obtained and we are only interested in the concentration of the strong acid, only the potential differences until 8 ml are used in the calculation. The H^+ concentration is 6.675×10^{-3} M, which corresponds to a OH^- concentration of 3.225×10^{-3} M.

The Y^{3+}-concentration in solution 1 was determined by AAS. KNO_3 was added to the standards, taking into account the amount present in solution 1. The yttrium concentration calculated was 1.284×10^{-3} M.

The ratio of $[Y^{3+}]$ to $[OH^-]$ is 2.51. The formula of this basic salt is then given by $Y_2(OH)_{5.02}(NO_3)_{0.98}$.

NO_3^- and Y^{3+} content

0.25 g precipitant and 0.5 ml HCl (37%) were diluted to 100 ml. This solution was used to determine the NO_3^- and Y^{3+} content of the basic salt. The Y^{3+} concentration was measured by AAS. This time no KNO_3 was added to the standards, because there was no indifferent electrolyte in the solution. The yttrium concentration was calculated as 0.01426 M. The chemical analysis of NO_3^- was carried out by IC. The standards used to calculate the concentration were between 2 and 5 ppm. The nitrate concentration was 0.007185 M. The chemical analysis of the precipitant showed that the Y^{3+}/NO_3^- ratio is 1.98. Thus the empirical formula for this basic salt will be $Y_2(OH)_{4.99}(NO_3)_{1.01}$.

DISCUSSION

Taking into account the experimental errors we can conclude from the above results that a stoichiometric product with empirical formula $Y_2(OH)_5NO_3 \cdot vH_2O$ is formed.

The value of v can be calculated by means of TGA. TGA experiments were carried out in flowing nitrogen (60 ml min^{-1}) at a heating rate of 10°C min^{-1}. The inert working conditions of the TGA were checked as described elsewhere [12]. The TGA plot is given in Fig. 1. The weight loss occurs in three steps. The common decomposition reaction can be represented by following equation with its onset and terminal temperatures

$$Y_2(OH)_5NO_3 \cdot 1.5H_2O \xrightarrow{25-575°C} Y_2O_3 + \text{gases} \qquad 35.8\%$$

This theoretical value corresponds very well with the experimental value of 35.7%. The first loss can be ascribed to H_2O and amounted to a weight loss of 7.7%.

$$Y_2(OH)_5NO_3 \cdot vH_2O \rightarrow Y_2(OH)_5NO_3 + vH_2O \qquad 7.7\%$$

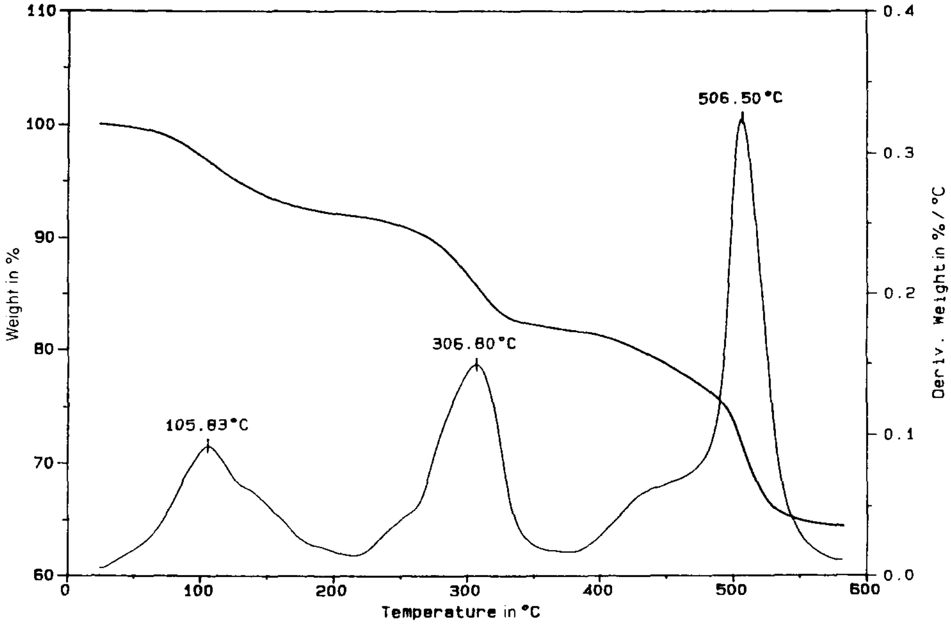

Fig. 1. TGA plot for the basic salt.

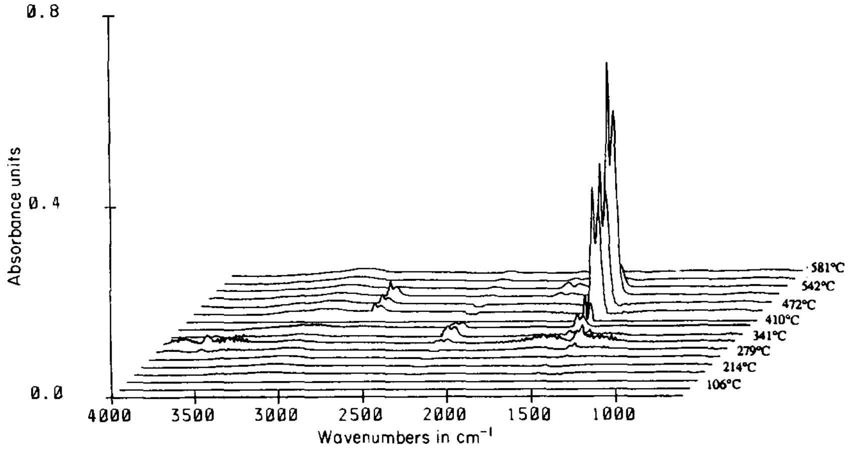

Fig. 2. A three dimensional FTIR plot for the basic yttrium nitrate salt.

From those two results we can conclude that $v = 1.5$. The general formula of the basic salt is then given by $Y_2(OH)_5NO_3 \cdot 1.5H_2O$.

The evolved gases from the TGA experiment are conveyed with nitrogen to the FTIR spectrometer. A three dimensional IR spectrum of the gases is given in Fig. 2. The different gases are liberated at different times. The decomposition is thus not the same as the decomposition of the basic nitrate salt of copper [13], where the gases are set free at the same time in a broad temperature interval.

In the temperature domain 25–341°C water (3800–3600 cm^{-1} and 1600–1500 cm^{-1}) is the only gas evolved. The spectrum shows a large rotation–vibration fine structure.

From 375°C another gas is evolved. The FTIR plot from 4000 cm^{-1} to 500 cm^{-1} at 518°C is shown in Fig. 3. The peak at 1613 cm^{-1} can be

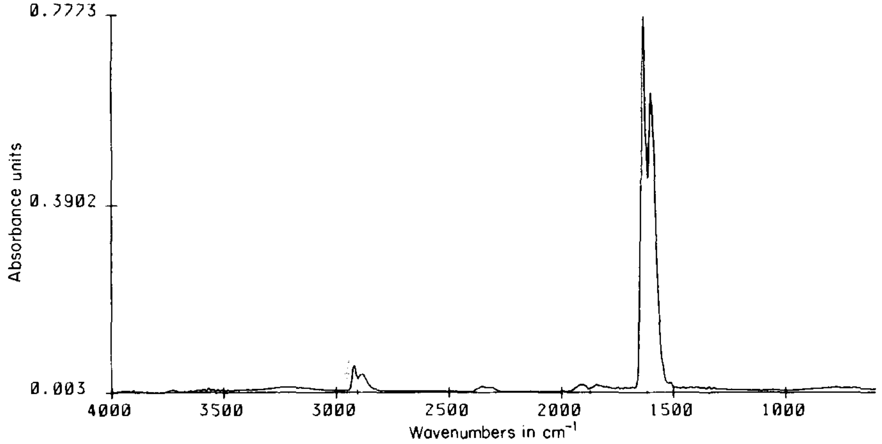

Fig. 3. FTIR plot of the gases evolved upon heating the basic yttrium nitrate salt.

attributed to NO_2 (1610 cm^{-1} [14]). Absorption frequencies typical for HNO_3 [15] are not found. Besides NO_2, H_2O is also released in this temperature region.

According to the FTIR and TGA results it can be concluded that the formula of the basic yttrium nitrate compound must be $Y_2(OH)_5NO_3 \cdot 1.5H_2O$, which decomposes as follows:

$Y_2(OH)_5NO_3 \cdot 1.5H_2O$

$$Y_2(OH)_5NO_3 \cdot 1.5H_2O \xrightarrow{25-175°C} Y_2(OH)_5NO_3 + 1.5H_2O \qquad 7.7\% \text{ (Exp.: 7.7\%)}$$

$$Y_2(OH)_5NO_3 \xrightarrow{225-350°C} Y_2O_2(OH)NO_3 + 2H_2O \qquad 11.1\% \text{ (Exp: 11.2\%)}$$

$$Y_2O_2(OH)NO_3 \xrightarrow{375-600°C} Y_2O_3 + 0.5H_2O + NO_2 + 0.25O_2 \qquad 21.8\% \text{ (Exp: 21.4\%)}$$

This mechanism is also proposed by Haschke [16] and Holcombe [8] but instead of only NO_2 they proposed a mixture of NO_2, NO, N_2O and N_2O_5 gases that are released, which cannot be confirmed by our TG-FTIR experiment.

The XRD results of $Y_2(OH)_5NO_3 \cdot 1.5H_2O$ are represented in Fig. 4. In

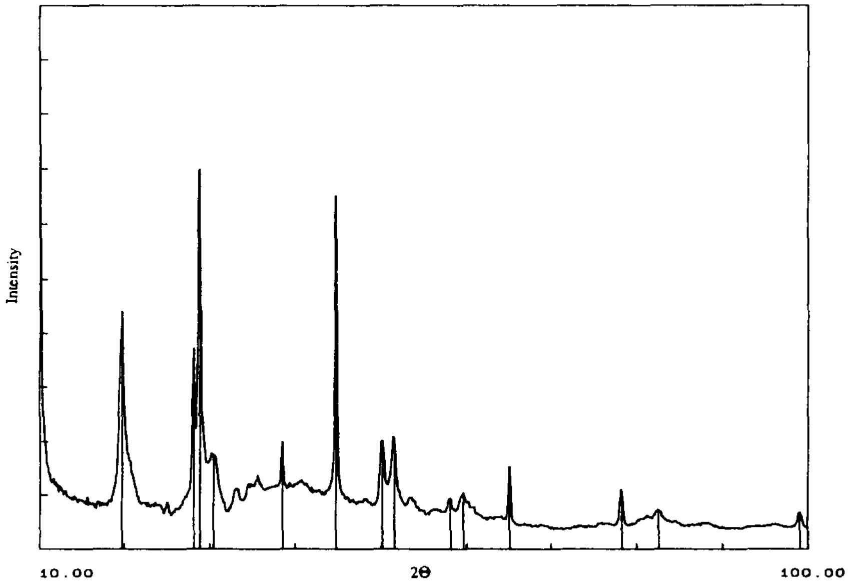

Fig. 4. XRD spectrum of $Y_2(OH)_5NO_3 \cdot 1.5H_2O$.

TABLE 1

XRD data for the basic nitrate salt

d Å	Intensity %	*d* Å	Intensity %
4.5063	63.1	1.7744	29.3
3.1754	53.7	1.5876	13.4
3.0998	100.0	1.5512	14.9
2.9402	25.1	1.4328	21.9
2.3382	28.9	1.2217	12.9
2.0273	93.5	1.1686	10.5
1.8207	28.9	1.0134	9.5

Table 1 the *d* values and their relative intensities are given. These results cannot be found in the library of the Philips PW 1050/70 and are therefore added as a new reference.

CONCLUSION

Our results all lead to one composition of the basic salt, namely $Y_2(OH)_5NO_3 \cdot 1.5H_2O$. The product decomposes completely on heating above 600°C into NO_2, H_2O and O_2. The basic yttrium nitrate is a typical sample for which advanced evolved gas analysis is indispensable for a complete description of the decomposition process.

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