

## PREPARATION AND THERMAL DECOMPOSITION OF INDIUM HYDROXIDE

T. Sato\*

Faculty of Engineering, Shizuoka University, Hamamatsu, 432-8011 Japan and Queen's University, Department of Materials and Metallurgical Engineering, Kingston, Ontario K7L 3N6, Canada

Indium hydroxides were prepared by the mixing of aqueous indium nitrate solution with sodium or ammonium hydroxide solutions under various conditions. The thermal decomposition of the resulting materials was examined by thermogravimetry, differential thermal analysis, X-ray diffraction study and infrared spectroscopy. It has been found that sodium hydroxide solution is more suitable than the addition of ammonium hydroxide solution to prepare indium hydroxide in well crystallization; the thermal decomposition of indium hydroxide, in which the composition is  $\text{In}(\text{OH})_3 \cdot x\text{H}_2\text{O}$  where  $x \leq 2$ , proceeds according to the following process:  $\text{In}(\text{OH})_3 \cdot x\text{H}_2\text{O} \rightarrow \text{cubic In}(\text{OH})_3 \rightarrow \text{cubic In}_2\text{O}_3$

**Keywords:** DTA, indium hydroxide, indium oxide, preparation and thermal decomposition, TG

### Introduction

The development of high technology in electronics is expected to cause an increase in demand for indium metal to industrial applications. As one important example we mention here the tin-doped-indium oxide (ITO, indium-tin-oxide) transparent conducting films, which are widely used as electrodes of all flat panel displays and touch panels, shielding infrared radiation and electromagnetic waves, etc. Hereupon the thermal analysis of the ITO films was executed by temperature programmed desorption or thermal desorption spectroscopy in high vacuum. Consequently the water vapor evolved from the ITC film was tentatively attributed to the thermal decomposition of the indium hydroxide, formed on the surface of the ITO particles [1]. Previously the present author examined the solvent extraction of indium(III) from aqueous acid solutions by acid organophosphorus compounds [2]. Because of the interest in indium metal, a number of research studies on the purification and recover of indium(III) by solvent extraction have been recently reported [3–6]. Thus the preparation and thermal decomposition of indium hydroxide, being necessary for the formation of indium oxide regarded as fundamental material to produce indium metal, has been investigated in the present study. Indium hydroxides appear in two varieties, classified as indium trihydroxide and indium oxyhydroxide [7]. In the present paper crystalline indium trihydroxide is treated.

### Experimental

The hydroxide of indium, which belongs to group IIIB, like aluminum and gallium, is in general prepared by the reaction between aqueous indium salt (nitrate, chloride or sulfate) solutions and alkaline solutions [8–13]. In this study, however, since the nitrate ion was relatively easy to take off from the precipitate by washing compared with chloride or sulfate ion, as a result of preliminary examinations, the nitrate salt solution was chosen as a starting reagent.

When the titration curves for the aqueous solution containing indium nitrate,  $\text{In}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ , of  $0.2 \text{ mol dm}^{-3}$  nitric acid by  $1 \text{ mol dm}^{-3}$  sodium or ammonium hydroxide solutions were examined at  $30^\circ\text{C}$ , precipitates were formed at pH 2.90 and 3.10, respectively. Accordingly, the following precipitation condition was taken on the basis of these results. Indium hydroxides were precipitated by pouring 20 mL of 0.6, 1.8, 3.0, 6.0 and  $12.0 \text{ mol dm}^{-3}$  of sodium or ammonium hydroxide solutions, at the rate of  $5 \text{ mL min}^{-1}$  into 20 mL of the aqueous solution containing indium nitrate of  $0.2 \text{ mol dm}^{-3}$  in  $0.5 \text{ mol dm}^{-3}$  nitric acid, at 30, 50 and  $70^\circ\text{C}$ . The precipitates were kept for 24 h in the mother liquor at the same temperature except for the study of the effect of aging time on the reaction. The resulting materials were separated by centrifugation, and washed with distilled water to get them as free as possible from cations and anions and then dried with acetone. The indium concentration in

\* 3–14–1, Daita, Setagaya-ku, Tokyo, 155 Japan

the aqueous solution was determined by EDTA titration using xylenol orange (XO) as indicator.

The thermally decomposed products were prepared by heating the samples at the stated temperatures for 1 h after being heated to this temperature at a rate of  $5^{\circ}\text{C min}^{-1}$  on the basis of the results of thermal analysis.

The acetone-dried samples were examined by TG and DTA, X-ray diffraction study and IR spectroscopy. TG and DTA were carried out on Shinku Riko model TGD-1500 differential thermo-balance using platinum-platinum/rhodium thermocouple at a heating rate of  $5^{\circ}\text{C min}^{-1}$  in air. For the measurement of differential thermal electromotive force,  $\alpha$ -alumina was used as a reference material. X-ray powder diffractograms were obtained on a Rigaku Denki diffractometer D-3F. IR spectra were determined by a Nujol or Fluorube mull method on JASCO model IR spectrometers IRA-1 and IR-F in the ranges of 4000–650 and 700–200  $\text{cm}^{-1}$ , respectively, using a capillary film between thallium halide plates or polyethylene.

## Results and discussion

For the indium hydroxides precipitated from aqueous indium nitrate solution by adding sodium hydroxide solution, the conditions of precipitation, the decomposition temperatures, i.e. the peaks in the DTA curves and the values of the molar ratio of constitution water,  $[\text{H}_2\text{O}]/[\text{In}_2\text{O}_3]$ , determined by the mass loss on ignition above  $100^{\circ}\text{C}$ , are shown in Table 1. Table 2 shows the same features of the precipitates

from aqueous indium nitrate solution obtained by the addition of ammonium hydroxide solution. Representative TG and DTA curves for some specimens are illustrated in Figs 1–4. The compositions of indium hydroxide products are deduced from the X-ray diffraction study and IR spectroscopy. Representative X-ray diffractograms and IR spectra are given in Figs 5–7.

From the results of the thermal analysis, it can be deduced that the thermal decomposition of indium hydroxide precipitates occurs in two steps. The DTA curve exhibits the first endothermic reaction centered at about  $80^{\circ}\text{C}$  and the second endothermic peak at nearly  $300^{\circ}\text{C}$ . In this case, however, when the endothermic reaction for a specimen appears at the lower temperature (below about  $270^{\circ}\text{C}$ ), the reaction band in the DTA curve becomes broad, indicating that the crystallization of its precipitate is poor. These reactions occur at points near the change in curvature of the TG curves. In Figs 1 and 3, the TG curves of the specimens prepared by the addition of sodium and ammonium hydroxide, respectively, the loss below  $100^{\circ}\text{C}$  is less than two molecules of water, regarded as the adhesive water, and the loss about  $300^{\circ}\text{C}$  corresponds to almost three water molecules, regarded as constitution water.

The broadness of the high temperature endothermic peak depends on the conditions of preparation (Tables 1 and 2). Most specimens obtained by adding ammonium hydroxide exhibit a broad endothermic peak below  $270^{\circ}\text{C}$  indicating a poor crystallization. This is in contrast to most specimens obtained by adding sodium hydroxide (compare Figs 2 and 4). Only

**Table 1** Thermal features of indium hydroxides precipitated under different conditions from aqueous indium nitrate solution by adding sodium hydroxide solutions (aging time 24 h)

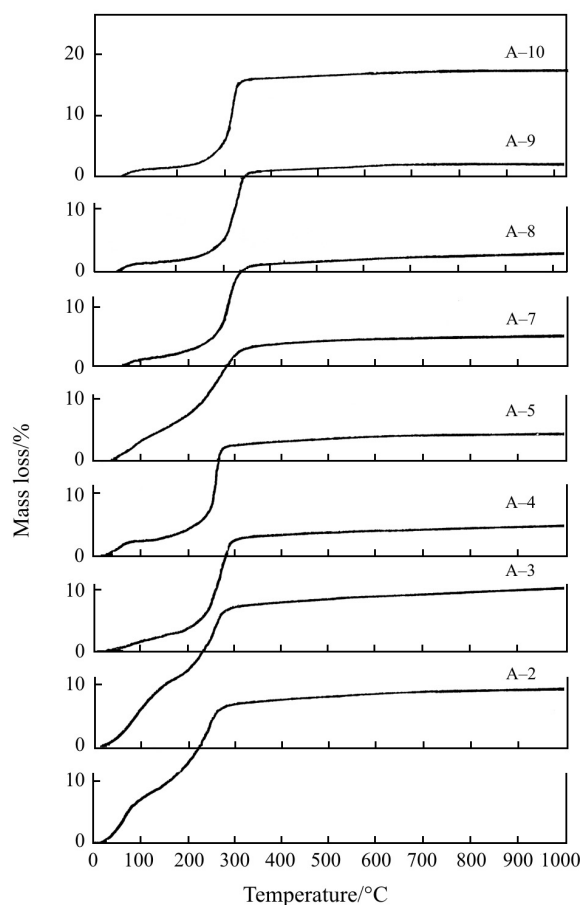
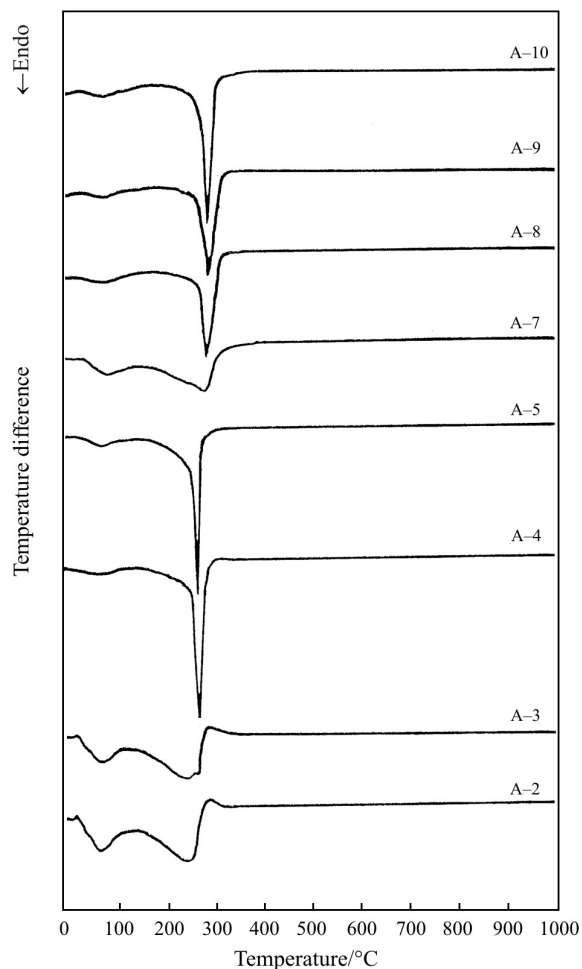
Specimen No.	Conditions of precipitation					DTA endothermic peaks		Molar ratio $[\text{H}_2\text{O}]/[\text{In}_2\text{O}_3]$	
	$\text{In}(\text{NO}_3)_3^{\text{a}}/\text{mol dm}^{-3}$	$\text{NaOH}/\text{mol dm}^{-3}$	Temp/ $^{\circ}\text{C}$	Aging time/h	$\text{pH}^{\text{b}}$	First <sup>c</sup> / $^{\circ}\text{C}$	Second <sup>c</sup> / $^{\circ}\text{C}$	Adhesive water	Constitution water
A-1	0.2	0.6	30	24	–	–	–	–	–
A-2	0.2	1.8	30	24	13.5	73	247(b) <sup>d</sup>	1.3	3.3
A-3	0.2	3.0	30	24	13.8	73	247(b) <sup>d</sup>	1.3	3.3
A-4	0.2	6.0	30	24	14.0	73	270	0.7	3.0
A-5	0.2	12.0	30	24	14.0	73	270	0.5	3.0
A-6	0.2	0.6	70	24	–	–	–	–	–
A-7	0.2	1.8	70	24	13.7	73	266(b) <sup>d</sup>	1.1	3.0
A-8	0.2	3.0	70	24	13.9	73	286	1.0	3.0
A-9	0.2	6.0	70	24	14.0	73	286	0.5	3.0
A-10	0.2	12.0	70	24	14.0	80	286	0.4	3.0
A-11	0.2	1.8	50	24	13.3	73	257(b) <sup>d</sup>	0.4	3.3
A-12	0.2	3.0	50	24	13.5	73	280	1.4	3.0

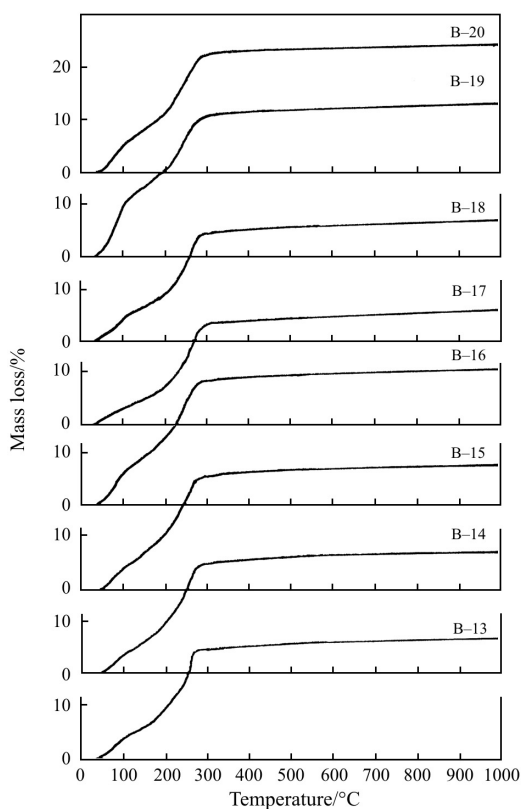
<sup>a</sup>) Aqueous solution containing  $0.5 \text{ mol dm}^{-3} \text{ HNO}_3$ , <sup>b</sup>) pH values after aging <sup>c</sup>) first and second endothermic reactions, <sup>d</sup>) (b) denotes a broad band

**Table 2** Thermal features of indium hydroxides precipitated under different conditions from aqueous indium nitrate solution by adding ammonium hydroxide solutions (aging time 24 h)

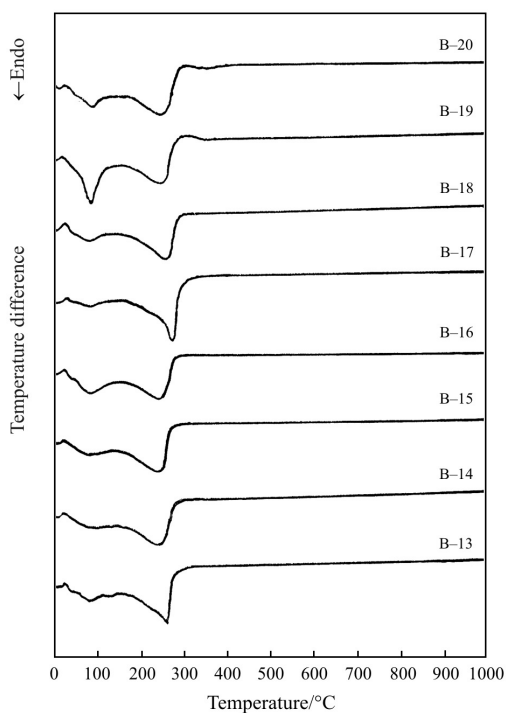
Specimen No.	Conditions of precipitation					DTA endothermic peaks		Molar ratio [H <sub>2</sub> O]/[In <sub>2</sub> O <sub>3</sub> ]	
	In(NO <sub>3</sub> ) <sub>3</sub> <sup>a</sup> /mol dm <sup>-3</sup>	NaOH/mol dm <sup>-3</sup>	Temp/°C	Aging time/h	pH <sup>b</sup>	First <sup>c</sup> /°C	Second <sup>c</sup> /°C	Adhesive water	Constitution water
B-13	0.2	1.8	30	24	9.6	80	263	1.0	3.3
B-14	0.2	3.0	30	24	10.0	80	246(b) <sup>d</sup>	1.0	3.4
B-15	0.2	6.0	30	24	10.5	80	246(b) <sup>d</sup>	1.1	3.5
B-16	0.2	12.0	30	24	10.9	80	246(b) <sup>d</sup>	1.7	3.6
B-17	0.2	1.8	70	24	9.4	80	273	0.8	3.2
B-18	0.2	3.0	70	24	10.1	80	260(b) <sup>d</sup>	1.0	3.4
B-19	0.2	6.0	70	24	10.5	80	246(b) <sup>d</sup>	2.0	3.4
B-20	0.2	12.0	70	24	10.8	80	246(b) <sup>d</sup>	1.5	3.4
A-21	0.2	1.8	50	24	9.4	80	266(b) <sup>d</sup>	0.9	3.3
A-22	0.2	3.0	50	24	9.8	80	266(b) <sup>d</sup>	0.9	3.4

<sup>a</sup>) Aqueous solution containing 0.5 mol dm<sup>-3</sup> HNO<sub>3</sub>, <sup>b</sup>) pH values after aging, <sup>c</sup>) first and second endothermic reactions, <sup>d</sup>) (b) denotes a broad band

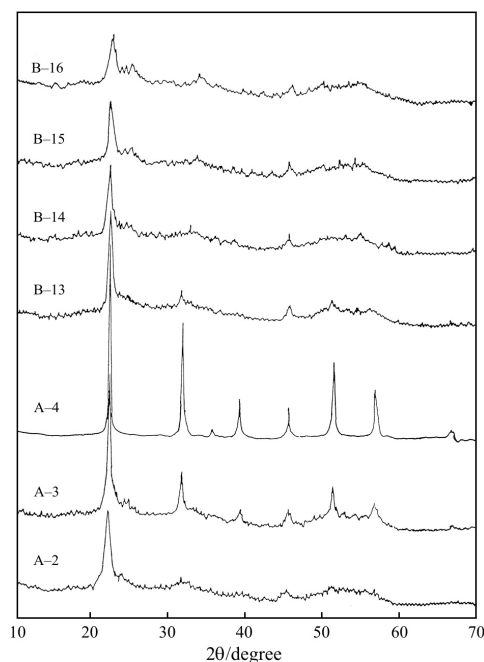

**Fig. 1** TG curves of indium hydroxides prepared by adding sodium hydroxide into indium nitrate aqueous solutions and aging time of 24 h (numerals on curves represent the specimen numbers in Table 1)

**Fig. 2** DTA curves of indium hydroxides prepared by adding sodium hydroxide into indium nitrate aqueous solutions and aging time of 24 h (numerals on curves represent the specimen numbers in Table 1)



**Fig. 3** TG curves of indium hydroxides prepared by adding ammonium hydroxide into indium nitrate aqueous solutions and aging time of 24 h (numerals on curves represent the specimen numbers in Table 2)



**Fig. 4** DTA curves of indium hydroxides prepared by adding ammonium hydroxide into indium nitrate aqueous solutions and aging time of 24 h (numerals on curves represent the specimen numbers in Table 2)

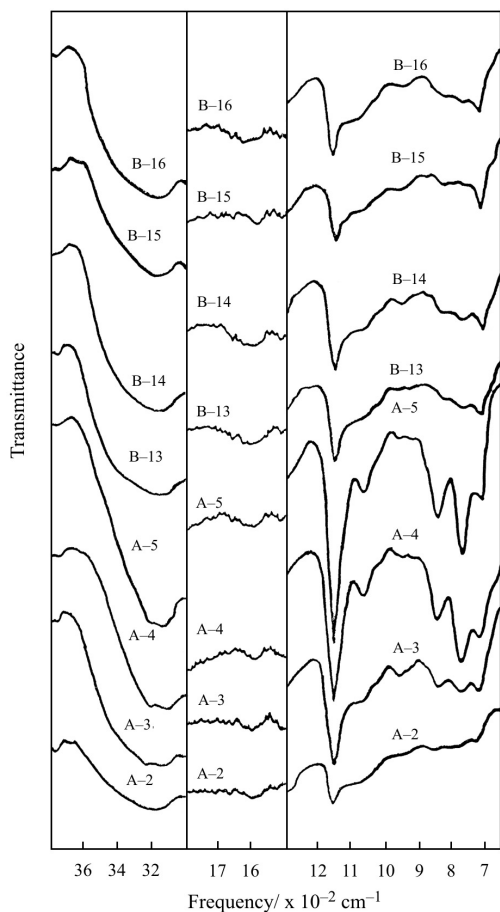


**Fig. 5** X-ray diffraction patterns of indium hydroxides prepared by adding sodium or ammonium hydroxide into indium nitrate aqueous solutions and aging time of 24 h (numerals on curves represent the specimen numbers in Tables 1 and 2)

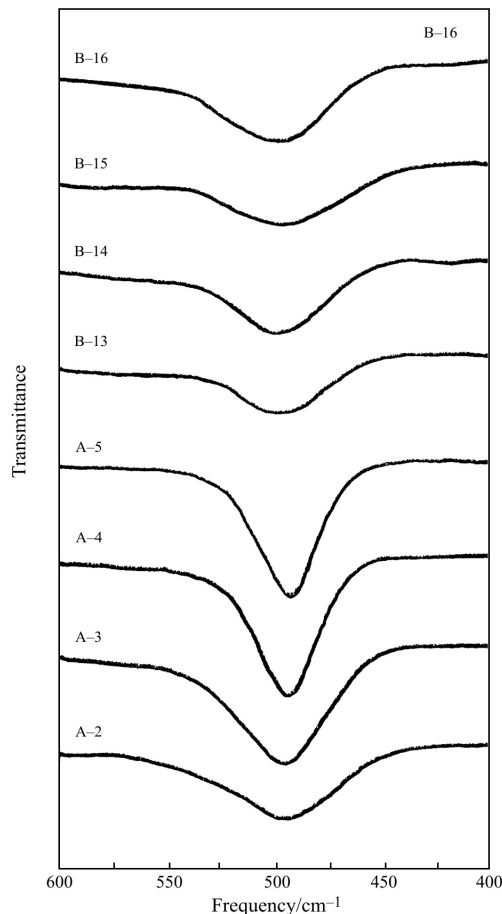
samples A-2 and A-3 prepared with small amounts of NaOH and aged at the low temperature (30°C) reveal a broad endothermic peak similar to the former, because of their poor crystallization. Furthermore, the crystallization of the precipitate becomes poorer with increasing amounts of ammonium hydroxide solution (Fig. 5). This might be due to the formation of a basic salt, such as  $\text{In}(\text{OH})_m(\text{NO}_3)_n$ , where  $m+n=3$ . Accordingly, it is obvious that for indium nitrate solution, the addition of sodium hydroxide solution is preferable to that of ammonium hydroxide solution to prepare well-crystallized indium hydroxide.

The samples precipitated from aqueous solution, described in Tables 1 and 2, were kept up to 24 h at a constant temperature in their mother liquor in order to obtain them well-crystallized. The effect of aging time at 30 and 70°C on the crystallization of the precipitates was deduced from their thermal features (Table 3). Some representative TG and DTA curves and X-ray diffractograms are shown in Figs 8–10. From these results it was concluded that the crystallization of the precipitates progresses with increasing aging time and temperature; well-crystallized precipitates are prepared by aging for 6 and 1 h at 30 and 70°C respectively.

In Figs 5 and 10, X-ray diffraction patterns of specimens described in Tables 1–3 are collected, showing the presence of cubic indium hydroxide [7, 14]. In the IR spectra (Figs 6 and 7), the precipitates exhibit the OH stretching bands (broad) with maxima at 3320 (shoulder), 3200 and 3100  $\text{cm}^{-1}$ , the OH



**Fig. 6** IR spectra (in the range 3800–650 cm<sup>-1</sup>) of indium hydroxides prepared by adding sodium or ammonium hydroxide into indium nitrate aqueous solutions and aging time of 24 h (numerals on curves represent the specimen numbers in Tables 1 and 2)

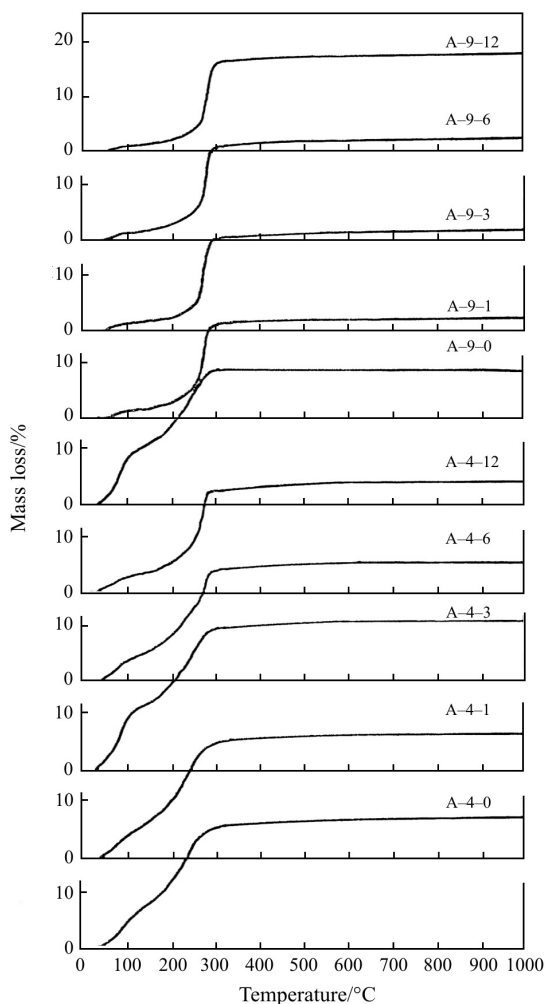


**Fig. 7** IR spectra (in the region of low frequency) of indium hydroxides prepared by adding sodium or ammonium hydroxide into indium nitrate aqueous solutions and aging time of 24 h (numerals on curves represent the specimen numbers in Tables 1 and 2)

**Table 3** Thermal features of indium hydroxides precipitated at 30 and 70°C from aqueous indium nitrate solution by adding sodium hydroxide solutions, obtained after different aging times

Specimen No.	Conditions of precipitation					DTA endothermic peaks		Molar ratio [H <sub>2</sub> O]/[In <sub>2</sub> O <sub>3</sub> ]	
	In(NO <sub>3</sub> ) <sub>3</sub> <sup>a</sup> /mol dm <sup>-3</sup>	NaOH/mol dm <sup>-3</sup>	Temp/°C	Aging time/h	pH <sup>b</sup>	First <sup>c</sup> /°C	Second <sup>c</sup> /°C	Adhesive water	Constitution water
A-4-0	0.2	6.0	30	0	13.9	83	240(b) <sup>d</sup>	1.3	3.5
A-4-1	0.2	6.0	30	1	14.0	83	240(b) <sup>d</sup>	1.0	3.5
A-4-3	0.2	6.0	30	3	14.0	83	240(b) <sup>d</sup>	1.8	3.4
A-4-6	0.2	6.0	30	6	14.0	80	280	0.9	3.3
A-4-12	0.2	6.0	30	12	14.0	73	276	0.6	3.3
A-9-0	0.2	6.0	70	0	13.9	87	240(b) <sup>d</sup>	2.0	3.3
A-9-1	0.2	6.0	70	1	14.0	73	276	0.4	3.0
A-9-3	0.2	6.0	70	3	14.0	73	283	0.4	3.0
A-9-6	0.2	6.0	70	6	14.0	73	283	0.4	3.0
A-9-12	0.2	6.0	70	12	14.0	73	286	0.4	3.0

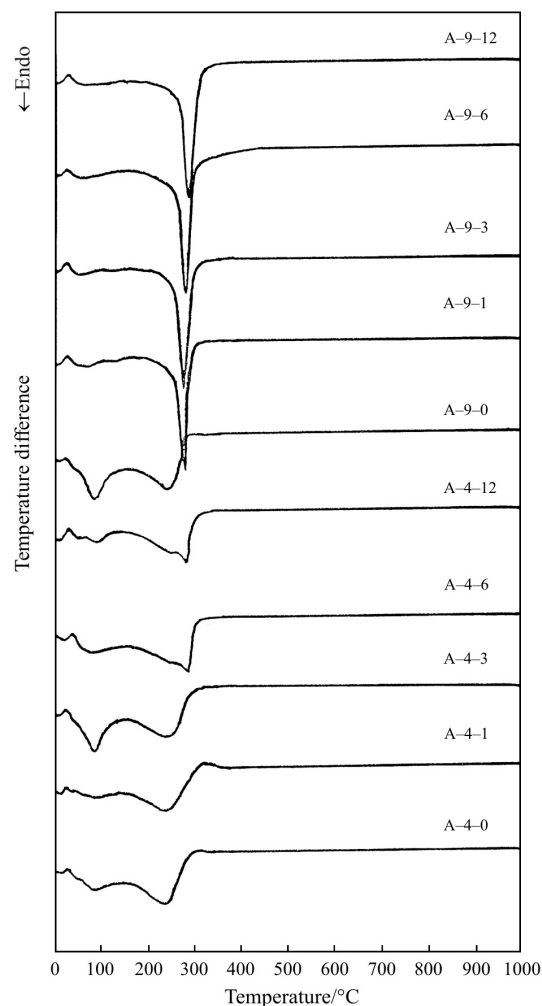
<sup>a</sup>Aqueous solution containing 0.5 mol dm<sup>-3</sup> HNO<sub>3</sub>, <sup>b</sup>pH values after aging, <sup>c</sup>first and second endothermic reactions, <sup>d</sup>(b) denotes a broad band



**Fig. 8** TG curves of indium hydroxides prepared by adding sodium hydroxide into indium nitrate aqueous solutions and different aging times (numerals on curves represent the specimen numbers in Table 3)

bending bands at 1585, 1150 and 1050  $\text{cm}^{-1}$ , the absorption due to the In–OH group at 890, 775 and 720  $\text{cm}^{-1}$ , and a broad band centered around 495  $\text{cm}^{-1}$  assigned to the In–O stretching frequency [8, 15–17]. In these spectra, the absorptions at 3320 and 1585  $\text{cm}^{-1}$  are ascribed to the OH stretching and bending vibrations, respectively, of adhesive water. Besides, the products of the heating at 300°C show the In–O stretching absorption bands at 720, 600, 560 and 535  $\text{cm}^{-1}$ , and O–In–O stretching vibrations at 485, 415, 365 and 330  $\text{cm}^{-1}$ . In these spectra the OH absorption bands almost disappear.

In Fig. 11 X-ray diffraction patterns of products obtained from specimens heated at above 300°C are collected, showing the diffraction lines of crystalline cubic indium oxide [7, 14]. A progressive increase in the intensities of the diffraction lines of this cubic phase exhibits with further heating up to 1000°C. Moreover, the IR spectra for the thermally decom-

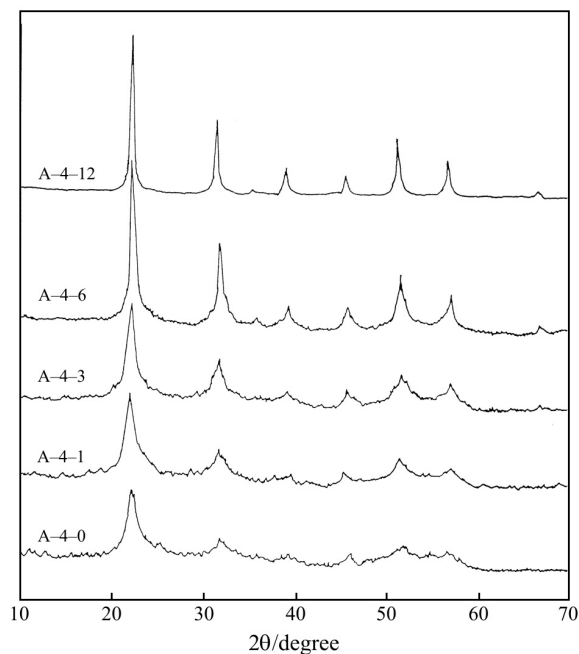


**Fig. 9** DTA curves of indium hydroxides prepared by adding sodium hydroxide into indium nitrate aqueous solutions and different aging times (numerals on curves represent the specimen numbers in Table 3)

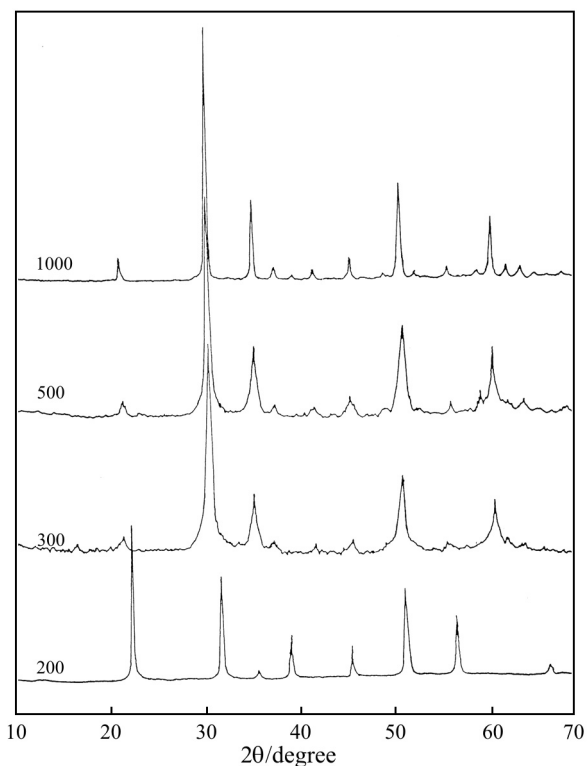
posed products derived from specimens heated at various temperatures reveal the characteristic absorption corresponding to the X-ray diffraction results (Figs 12 and 13). Therefore the following interpretation may be given to the DTA curve. The first endothermic peak at nearly 80°C is due to the release of adhesive water. The second endothermic peak at about 300°C arises from the dehydroxylation during the thermal decomposition of indium hydroxide to indium oxide. This explanation is also supported by the results of the molar ratio  $[\text{H}_2\text{O}]/[\text{In}_2\text{O}_3]$ , determined from mass losses in the TG curves, corresponding to the endothermic reactions at these thermal stages in the DTA curves, being <2 and 3, respectively. The hydrated hydroxide is  $\text{In}(\text{OH}) \cdot x\text{H}_2\text{O}$  where  $x \leq 2$ .

Furthermore, X-ray diffraction study of specimens A-4 and A-9 was carried out at different temperatures up to 1000°C. Below 200°C the patterns were

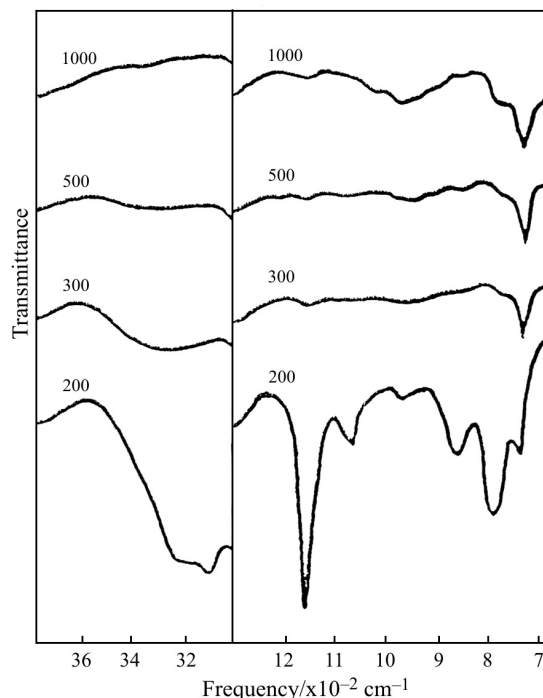




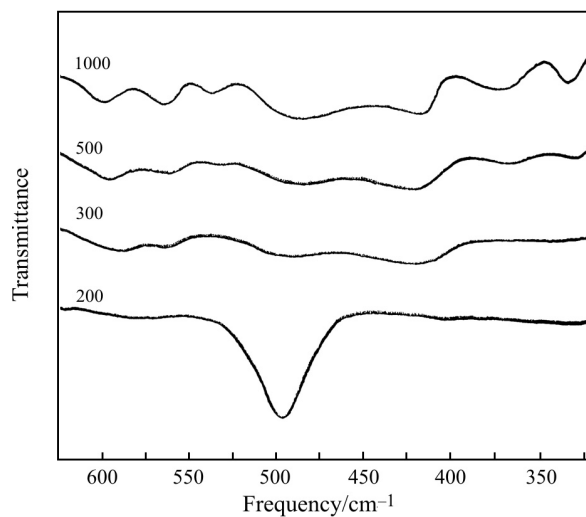
**Fig. 10** X-ray diffraction patterns of indium hydroxides prepared by adding sodium hydroxide into indium nitrate aqueous solutions and different aging times (numerals on curves represent the specimen numbers in Table 3)



**Fig. 11** X-ray diffraction patterns of the thermal products obtained from indium hydroxide (specimen A-4 described in Table 1) heated at various temperatures (numerals on curves represent the heating temperatures in °C)



**Fig. 12** IR spectra (in the range  $3800\text{--}650\text{ cm}^{-1}$ ) of the thermal products obtained from indium hydroxide (specimen A-4 described in Table 1) heated at various temperatures (numerals on curves represent the heating temperatures in °C)



**Fig. 13** IR spectra (in the region of low frequency) of the thermal products obtained from indium hydroxide (specimen A-4 described in Table 1) heated at various temperatures (numerals on curves represent the heating temperatures in °C)

those of cubic indium hydroxide. At  $300^{\circ}\text{C}$  they were of cubic indium oxide but the degree of crystallinity progressed with temperature up to  $1000^{\circ}\text{C}$ .

The thermal decomposition process of indium hydroxide is not so complicated as those of hydrous

salts of many other metals. For example, the thermal decomposition of  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in helium and in synthetic air gave the results that the dehydration occurred together with the decomposition of the nitrate group and then eight distinct stages of reaction were obtained, and that intermediate products of decomposition were hydroxy- and oxynitrates containing chromium in hexa- and trivalent states [18].

## Conclusions

Well-crystallized indium hydroxide is prepared by mixing aqueous indium nitrate solution with sodium hydroxide solution. By using TG, DTA, XRD and IR spectroscopy it is found that the thermal decomposition of crystalline indium hydroxide proceeds as follows:



where  $x \leq 2$ . It appears that the thermal decomposition of indium trihydroxide is much more simple than those of the hydroxides of aluminum and gallium [19].

## Acknowledgement

The author wishes to thank Mr. M. Honjo for assistance with the experimental work.

## References

- 1 Y. Sawada, S. Seki, M. Sano, N. Miyabayashi, K. Ninomiya, A. Iwassawa, T. Taugoshi, R. Ozao and Y. Nishimoto, *J. Therm. Anal. Cal.*, 77 (2004) 751.
- 2 T. Sato and K. Sato, *Hydrometallurgy*, 30 (1992) 369.
- 3 M. C. B. Fortes, A. H. Martins and J. S. Benedetto, *Braz. J. Chem. Eng.*, 20 (2003) 121.
- 4 X. Xu, Z. Xu and F. Zhou, *Rare Metals*, 22 (2003) 91.
- 5 X. Zhang, X. Lou, G. Yin and Y. Zhang, *Rare Metals*, 23 (2004) 6.
- 6 B. Gupta, A. Deep and P. Malik, *Anal. Chim. Acta*, 513 (2004) 463.
- 7 A. F. Wells, *Structural Inorganic Chemistry*, Clarendon Press, Oxford, 1975, pp. 450, 522.
- 8 R. Roy and M. Shafer, *J. Phys. Chem.*, 58 (1954) 372.
- 9 H. W. Weiser and W. O. Milligan, *J. Phys. Chem.*, 42 (1938) 673.
- 10 W. O. Milligan and H. W. Weiser, *J. Am. Chem. Soc.*, 59 (1937) 1670.
- 11 R. Fricke and A. Seitz, *Z. Anorg. Allg. Chem.*, 255 (1947) 13.
- 12 A. Palm, *J. Phys. Chem.*, 52 (1948) 595.
- 13 K. Schubert and A. Seitz, *Z. Anorg. Allg. Chem.*, 256 (1948) 226.
- 14 E. Staritzky, *Anal. Chem.*, 28 (1956) 553.
- 15 H. Hartert and O. Glemser, *Z. Electrochem.*, 60 (1956) 740.
- 16 T. Dupuis, *Mikrochim. Acta*, 2–4 (1964) 228.
- 17 T. Sato and K. Sato, *Hydrometallurgy*, 30 (1992) 372.
- 18 A. Malecki, B. Malecka, R. Gajerski and S. Lubus, *J. Therm. Anal. Cal.*, 72 (2003) 135.
- 19 T. Sato, *Preparation of Aluminium Hydroxides and Aluminas*, Litarvan, Nederland, Colorado, 1996, pp. 163, 181.

---

DOI: 10.1007/s10973-005-6905-3