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Synthesis and intracrystalline oxidation of nitrite-intercalated layered double hydroxides

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ABSTRACT

Nitrite-intercalated LDHs could be prepared by a two-stage process that involves coprecipitation in the presence of nitrite ions followed by stirring the product with excess of nitrite ions. The nitrite ion lies flat in these LDHs with its c_2-axis lying approximately perpendicular to the crystallographic c-axis. The interlayer nitrite ions in these LDHs could be quantitatively oxidized to nitrate ions using H_2O_2 solution. In the LDHs thus obtained the nitrate ion lies flat with its c_3-axis parallel to the crystallographic c-axis (D_{3h} symmetry) in the interlayer region resulting in lower basal spacing.

1. Introduction

Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds (HTLCs) or anionic clays are layered compounds that consist of positively charged metal hydroxide sheets with intercalated anions and water molecules in the interlayer region [1–6]. The general formula of LDHs is $[M^{II}_{(1-x)}M^{III}_{x}(OH)_2]A^{n-}_{x/n}\cdot mH_2O$, where M^{II} is a divalent metal such as Mg, Co, Ni, Cu, Zn or Ca; M^{III} is a trivalent metal such as Al, Cr, Fe or Ga; A^{n-} is anion with a valency n; and x defined as $[M^{III}]/([M^{III}]+[M^{II}])$ is usually between 0.25 and 0.33. These solids derive their structure from that of brucite, $Mg(OH)_2$. In brucite-like hydroxides, OH^- ions are hexagonally close packed and the M^{2+} ions occupy alternate layers of octahedral sites. Thus the structure can be described as a stacking of charge neutral $M(OH)_2$ layers. In LDHs a part x, of the M^{2+} ions are isomorphously substituted by M^{3+} ions leading to positively charged layers having the composition $[M^{2+}_{(1-x)}M^{3+}_{x}(OH)_2]^{x+}$. To compensate for the positive charge on the layers, anions, A^{n-} are intercalated in the interlayer region. LDHs show interesting properties such as anion mobility, anion exchange, surface basicity and reconstruction behavior. Due to these properties LDHs find many applications in varied fields such as sorption, catalysis, flame-retardation, polymer stabilization, electrochemistry, photochemistry and medicine to cite a few [7–17].

Intercalation reactions of layered solids are important as these can change the chemical, electronic and magnetic properties of the host lattice. In addition, most of the intercalation reactions take place at room temperature, making this method a simple route to new materials [18]. The intercalation chemistry of LDH hosts is extensive. A large variety of anions have been incorporated into the interlayer region of the LDHs. Intercalation can be achieved by direct synthesis via co-precipitation, anion exchange of a precursor, and rehydration of the calcined precursor [18]. Simple inorganic ions such as Cl^-, Br^-, SO_4^{2-}, and CO_3^{2-} and larger ions such as oxometalates, and anionic transition metal complexes have also been incorporated into LDHs [19]. Large biomolecules such as peptides, vitamins, polysaccharides and DNA have been successfully incorporated in the interlayer of LDHs [20,21].

Recently there have been reports on the interlayer reaction of intercalated anions in anionic clays. Our group has shown anionic clays could be used as an anchor for an organic substrate in a reaction [22]. Anionic clay-like nickel zinc hydroxy acetate was exchanged with maleate and fumarate ions. The intercalated anions were reacted with bromine water in such a way that the brominated product remained intercalated making the reaction a true intracrystalline reaction. Duan's group reported the intercalation of two kinds of amino acids, L-cysteine and L-cystine into MgAl LDH and the oxidation of the intercalated aminoacids by hydrogen peroxide and bromine [23]. The oxidation products under the confined region were found to be different from those obtained from the corresponding free aminoacids.

We wanted to investigate if such intracrystalline reactions are possible with intercalated inorganic anions. There are many inorganic anions that could be converted into another anion easily. We chose nitrite as the interlayer anion in this work for two reasons. Firstly no nitrite-LDHs have been reported so far though these have been observed as intermediates when nitrate ions

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were reduced using LDH-supported Pd/Cu catalysts [24,25]. Secondly the nitrite anion can be oxidized easily to nitrate under mild conditions.

One of the major features that govern the intercalation process is the orientation of the guest species in the interlayer region. The orientation of the intercalated anions depends on the hydroxide layer and the charge, shape, hydrophilic or hydrophobic nature and packing density of the anion in the interlayer region. Nitrate anion has received much attention because it can take up different orientations in the interlayer. Many models such as tilt-lying and stick-lying have been proposed in the literature for the orientation of nitrate ion [26].

In this work, we report the preparation of nitrite-intercalated LDHs and the interlayer oxidation of nitrite to nitrate using a mild oxidizing agent, H_2O_2. We observed that the interlayer nitrite was quantitatively oxidized to nitrate. We also found that the nitrate ion in the LDHs obtained by the intracrystalline oxidation has a different orientation compared to the nitrate ion in the LDHs obtained by conventional preparation methods.

2. Experimental

2.1. Preparation of $Mg_2Al(OH)_6NO_3 \cdot mH_2O$ and $Ni_2Al(OH)_6NO_3 \cdot mH_2O$

$M_2Al(OH)_6NO_3 \cdot mH_2O$ ($M = $ Mg, Ni) were prepared by the procedure due to Olanrewaju et al. [27]. 100 ml of an aqueous solution containing $M(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 6H_2O$ in the molar ratio 2:1 was added drop wise into 250 ml of a 1 M solution of NH_3 with constant vigorous stirring. After the addition was complete, the resultant slurries were aged at 65 °C overnight. The solid products obtained were washed free of ions with decarbonated water followed by acetone and dried at 65 °C in an air oven to constant weight. These samples are hereafter referred to as MgAl–NO_3 and NiAl–NO_3.

2.2. Preparation of $Mg_2Al(OH)_6NO_2 \cdot mH_2O$ and $Ni_2Al(OH)_6NO_2 \cdot mH_2O$

The nitrite-intercalated LDHs, $M_2Al(OH)_6NO_2 \cdot mH_2O$ were prepared by a two-stage process. An aqueous solution containing $MCl_2 \cdot 6H_2O$ and $AlCl_3 \cdot 6H_2O$ (133 ml) in the molar ratio 2:1 was added drop wise into a solution containing 1 M NH_3 solution (250 ml) containing ten times molar excess of the nitrite ion ($[NO_2^-]/[Al^{3+}] = 10$) with vigorous stirring. The resultant slurries were aged at 65 °C overnight in an air oven. To each of these slurries $NaNO_2$ (3 g per 50 ml) was added and the mixtures stirred in airtight containers for four days. The resultant solids were filtered, washed with decarbonated water followed by acetone and dried at 65 °C to constant weight. These samples are hereafter referred to as MgAl–NO_2 and NiAl–NO_2.

2.3. Oxidation of MgAl–NO_2 and NiAl–NO_2 LDHs by H_2O_2

To a suspension of MAl–NO_2 LDH ($M = $ Mg, Ni; 0.75 g in 15 ml decarbonated water) 15 ml of 30% H_2O_2 solution was added. The mixture was stirred under nitrogen atmosphere for seven hours. The products were isolated by centrifugation and dried at 65 °C overnight.

2.4. Characterization

Powder X-ray diffraction (pXRD) measurements were performed on a Bruker D8 Advance X-ray Diffractometer using Cu$K\alpha$ radiation ($\lambda = 0.154$ nm) at 40 kV, at a scanning rate of $2^\circ\,min^{-1}$. The infrared spectra of samples were collected using a Nicolet IR200 FT-IR spectrometer using KBr pellets, in the range 4000 to 400 cm^{-1} with 4 cm^{-1} resolution. The interlayer anion (nitrite/nitrate) contents were obtained by ion chromatography using a Metrohm 861 Advanced Compact ion chromatograph with Metrosep A Supp5 250 anion column and conductivity detector. The samples were dissolved in 1 N sulfuric acid and diluted suitably for this purpose. The metal contents of the samples were estimated by inductively coupled plasma (ICP) emission spectroscopy (Yobin Yvon 2000). The approximate formulae of the compounds were calculated by setting $[OH] = 2([M(II)+[Al])$; $[carbonate] = [Al]-[nitrate\ or\ nitrite]$ and the unaccounted mass to water. Thermogravimetric analysis of the samples was carried out using a Metter Toledo STAR^e SW 7.01 system under continuous flow of nitrogen with a heating rate of 5 °C/min.

3. Results and discussions

The composition analysis data of the as prepared LDHs and the products obtained on the oxidation of the nitrite LDHs are given in Table 1. The nominal chemical formulas obtained indicate that the LDHs were formed with the expected Mg/Al ratio of 2. While the as prepared nitrate LDHs are free of carbonate, slight carbonate contamination was observed in the nitrite LDHs and the carbonate content increased further in the oxidized products. Though care has been taken to run the reactions under N_2 atmosphere, atmospheric CO_2 contaminates the samples possibly during washing.

Ion chromatography was used to quantify the interlayer anions in the LDHs. Fig. 1 shows the chromatograms of the MgAl–NO_2 LDH and the H_2O_2-oxidized product of MgAl–NO_2. The nitrite ion elutes at 670 s and nitrate ion at 1190 s. In the oxidized product we observe a peak due to nitrate ion only and no peak due to nitrite ion is observed. These results confirm the quantitative oxidation of nitrite ion to nitrate ion in the interlayer region of the LDHs.

The pXRD patterns of MgAl–NO_2 LDH and the H_2O_2-oxidized product of MgAl–NO_2 and MgAl–NO_3 LDH are shown in Fig. 2. MgAl–NO_3 LDH in Fig. 2c shows a basal spacing of 8.9 Å (calculated from the 00ℓ reflections), suggesting that the nitrate ion is in a tilted orientation in the interlayer region, with its plane almost perpendicular to the hydroxide sheets [28]. This interlayer distance has been reported by a number of groups [29–31] and it is the most common interlayer spacing obtained for a nitrate intercalated 2:1 Mg–Al LDH. The broad peaks at $2\theta = 34.5$, 38.7 and 45.5° corresponding to (012), (015) and (018) reflections, respectively, indicate that this LDH is a $3R_1$ polytype with considerable stacking disorder [32]. The first reflection of the MgAl–NO_2 LDH (Fig. 1a) corresponds to a basal spacing of 7.9 Å suggesting that the nitrite ion is lying flat, in the interlayer region, with its plane parallel to the hydroxide sheets. The broad (012),

Table 1
Composition data of the LDHs used in this study.

Sample	Mass percentage			Approximate formula
	M^{II}	Al	A^- [a]	
MgAl–NO_3	17.6	9.56	20.9	$Mg_2Al_{0.98}(OH)_6(NO_3)_{0.93}(CO_3)_{0.02} \cdot 2.3H_2O$
MgAl–NO_2	18.8	10.2	13.3	$Mg_2Al_{0.98}(OH)_6(NO_2)_{0.75}(CO_3)_{0.12} \cdot 2.3H_2O$
Oxidized product	16.8	9.11	14.7	$Mg_2Al_{0.98}(OH)_6(NO_3)_{0.69}(CO_3)_{0.15} \cdot 3.5H_2O$
NiAl–NO_3	32.3	7.50	17.1	$Ni_2Al(OH)_6(NO_3) \cdot 3H_2O$
NiAl–NO_2	33.4	7.76	9.16	$Ni_2Al(OH)_6(NO_2)_{0.67}(CO_3)_{0.17} \cdot 3.5H_2O$
Oxidized product	31.7	7.36	11.1	$Ni_2Al(OH)_6(NO_3)_{0.66}(CO_3)_{0.17} \cdot 4H_2O$

[a] $A^- =$ nitrate or nitrite.

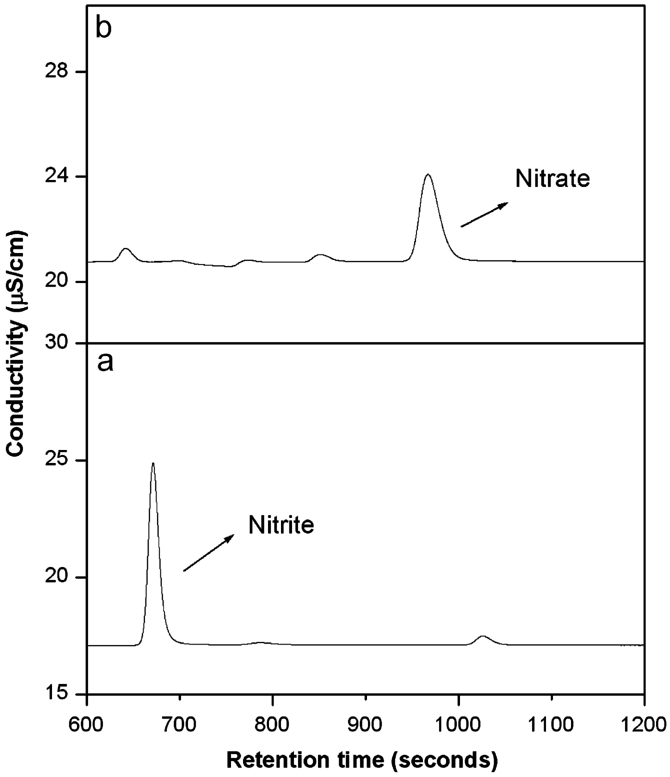

Fig. 1. Ion chromatograms of the solutions obtained from (a) MgAl–NO_2 LDH and (b) H_2O_2-oxidised product of Mg–Al–NO_2.

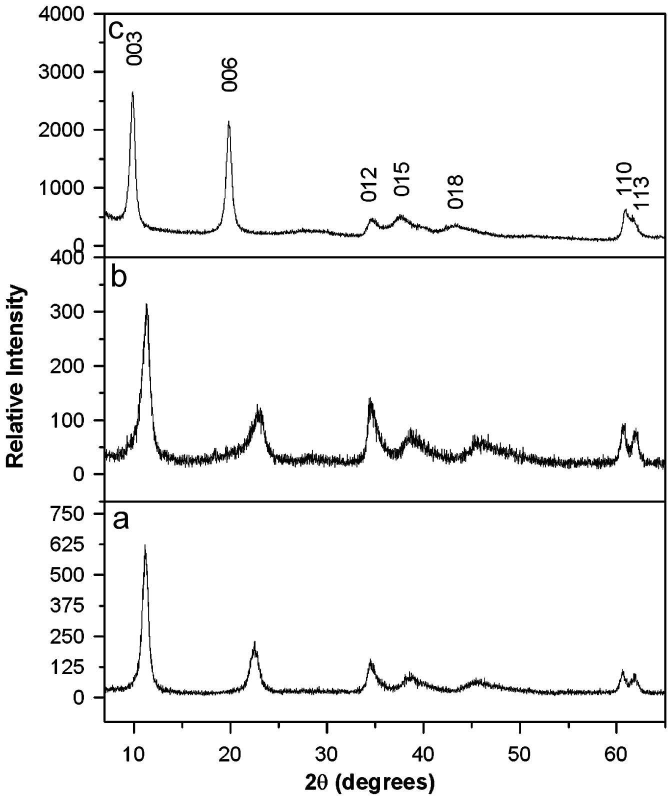

Fig. 2. The pXRD patterns of MgAl–NO_2 (a), H_2O_2-oxidised product of Mg–Al–NO_2 (b) and MgAl–NO_3 (c).

(015) and (018) reflections observed in the mid 2θ region suggest that this LDH also is a $3R_1$ polytype with stacking disorder. The LDH obtained by the oxidation of MgAl–NO_2 (Fig. 2b) does not match with the pattern obtained for MgAl–NO_3 LDH (Fig. 2c). The basal spacing here is 7.8 Å. This basal spacing is possible for a nitrate-intercalated LDH only if the nitrate ion in the interlayer region is lying flat with its plane parallel to the hydroxide sheets. The (110) and (113) reflections observed at $2\theta = 60.7^\circ$ and 62° match with that of the MgAl–NO_2 LDH (Fig. 2a) indicating that the a-parameter and hence the hydroxide slab structure has not been altered during the oxidation reaction. Possibly, as the precursor NO_2^- ion lies flat in the interlayer of the LDH its oxidation product, NO_3^- also takes up a similar orientation. It is also possible that the nitrate ions take up the flat orientation due to the reduced steric crowding brought about by the incorporation of divalent carbonate ions.

The pXRD results of NiAl LDH system are also similar to those of the MgAl LDHs. The pXRD pattern of NiAl–NO_3 LDH in Fig. 3c shows a basal spacing of 8.6 Å (calculated from the 00ℓ reflections), suggesting that the nitrate ion is in a tilted orientation in the interlayer region, similar to what is observed in the MgAl analog. The first reflection of the NiAl–NO_2 LDH (Fig. 3a) corresponds to a basal spacing of 7.8 Å suggesting that the nitrite ion is lying flat, in the interlayer region as in the case of the MgAl analog. The layer stacking in the nitrite LDH is $3R_1$ type unlike in the NiAl–NO_3 LDH as we observe the (012), (015) and (018) reflections. The nitrate LDH obtained by the oxidation of NiAl–NO_2 LDH (Fig. 3b) also shows a basal spacing of 7.8 Å indicating that the nitrate ion in the interlayer region is lying flat in the interlayer in this case too. This nitrate LDH is different from the NiAl–NO_3 LDH in the layer stacking too as we observe broad 01ℓ reflections indicating poorly ordered $3R_1$ polytype. As in the case of MgAl LDHs, the a-parameter of the nitrate LDH obtained by the oxidation of NiAl–NO_2 LDH is the same as that of the NiAl–NO_2 LDH confirming no change in the layer structure.

Fig. 4 shows the IR spectra of the MgAl LDHs. All the samples showed a broad absorption at 3500 cm^{-1} (not shown) due to O–H

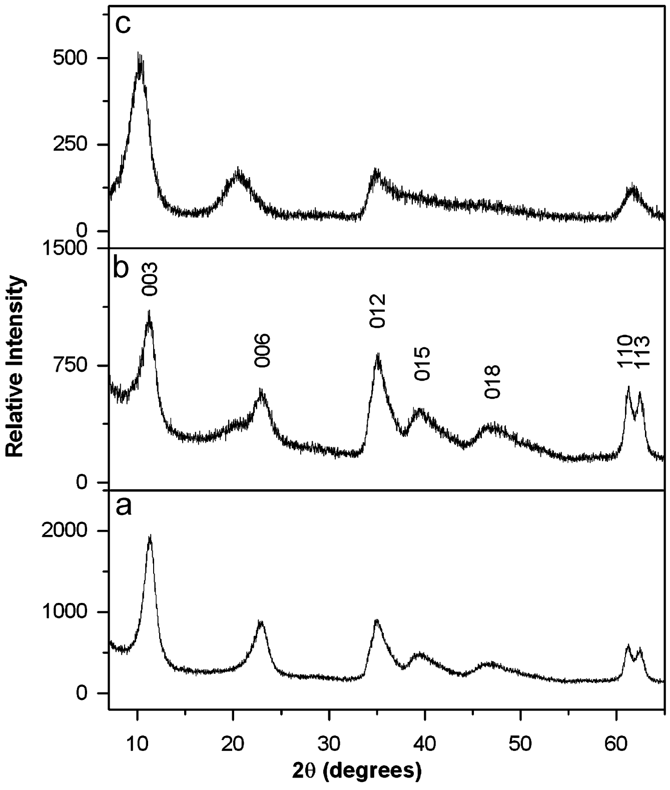

Fig. 3. The pXRD patterns NiAl–NO_2 (a), the H_2O_2-oxidised product of NiAl–NO_2 (b) and NiAl–NO_3 (c).

stretching vibration of the hydroxyl groups of the brucite-like-sheets and water in the interlayer space. The O–H bending vibration of the interlayer water is observed at 1630 cm^{-1}. MgAl–NO_3 LDH (Fig. 4c) shows a sharp absorption at 1384 cm^{-1}, which is due to the ν_3 mode of nitrate ion in D_{3h} symmetry. The absence of a peak at 1356 cm^{-1} confirms the complete absence of carbonate ions in this LDH. MgAl–NO_2 (Fig. 4a) shows a sharp absorption at 1267 cm^{-1} due to the nitrite ion. A weak peak at 1356 cm^{-1} suggests some carbonate contamination in the MgAl–NO_2 sample and it is in agreement with the composition analysis of this sample (Table 1). The appearance of a sharp peak at 1384 cm^{-1} and the absence of peak at 1267 cm^{-1} in the oxidized product of MgAl–NO_2 LDH (Fig. 4a) further confirm that the interlayer nitrite ions have been quantitatively oxidized to nitrate ions. A shoulder at 1356 cm^{-1} indicates the presence of carbonate ions in this sample too. Similar results were obtained in the case of NiAl LDH system too and these are shown in the Fig. 5.

The thermogravimetric (TG) data of MgAl–NO_3, MgAl–NO_2 and the H_2O_2-oxidised product of MgAl–NO_2 are shown in Fig. 6. All the three LDHs exhibit two mass loss steps. The first step, which is observed in the temperature range 35–200 °C in all the three cases, is due to the loss of surface adsorbed and intercalated water molecules. The second step due to a combination of dehydroxylation and deanation is different for the three LDHs. The thermogram of MgAl–NO_3 (Fig. 6c) shows the second mass loss centered around 400 °C, which matches with what has been observed by others for LDHs of similar composition [33]. In MgAl–NO_2 (Fig. 6a) the dehydroxylation–deanation step is centered at 340 °C as the nitrite ion decomposes more easily than the nitrate ion. In the thermogram of the MgAl–NO_3 LDH (Fig. 6b) this step is centered at 360 °C. Though LDHs in which nitrate ion lies flat in the interlayer have been reported earlier [26] their thermal decomposition behavior has not so far been studied. We cannot attribute without doubt the difference in thermal behavior to the interlayer

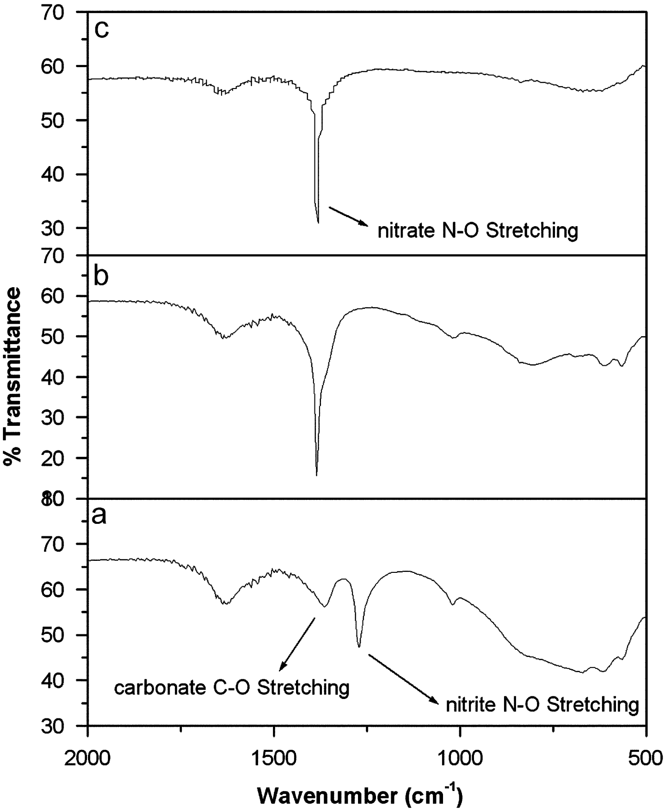

Fig. 5. IR spectra of NiAl–NO_2 (a), H_2O_2-oxidised product of NiAl–NO_2 (b) and NiAl–NO_3 (c).

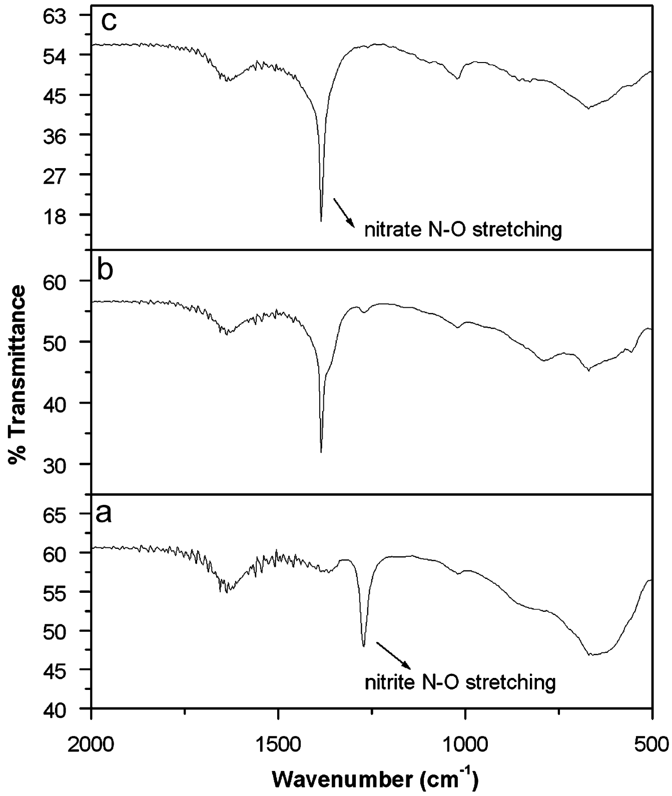

Fig. 4. IR spectra of MgAl–NO_2 (a), H_2O_2-oxidised product of MgAl–NO_2 (b) and MgAl–NO_3 (c).

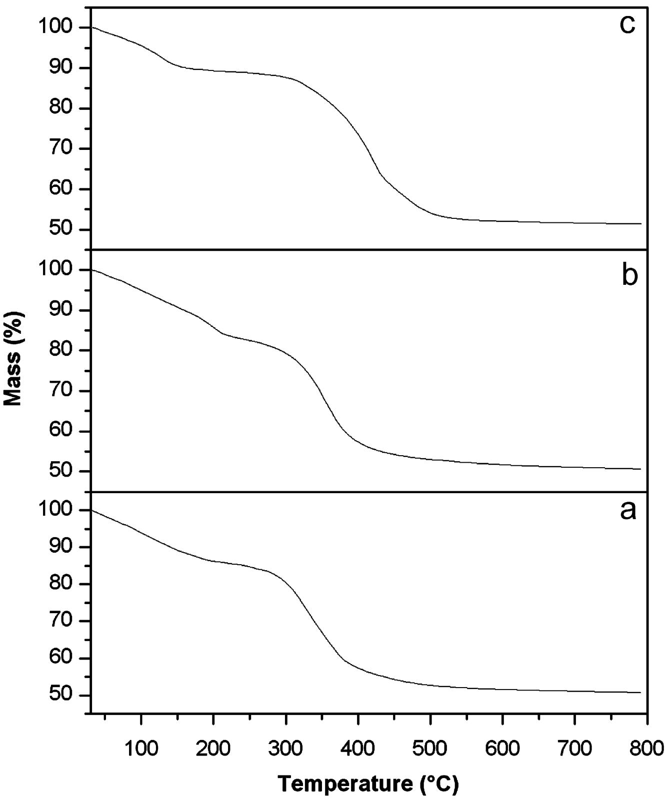

Fig. 6. TG curves of MgAl–NO_2 (a), H_2O_2-oxidised product of MgAl–NO_2 (b) and MgAl–NO_3 (c).

orientation of the nitrate ion as the sample has a reasonable amount of carbonate ions in the interlayer. This might have brought down the decomposition temperature as carbonate LDHs decompose at a much lower temperature (300 °C) [28]. The net mass losses observed in all three LDHs match with the compositions arrived at from wet chemical analysis (Table 1).

4. Conclusions

Nitrite-intercalated Mg–Al and Ni–Al LDHs could be prepared. These on oxidation with H_2O_2 give nitrate-intercalated LDHs in which the nitrate ions lie flat in the interlayer with its c_3-axis parallel to the crystallographic c-axis. Intracrystalline reactions of the kind described here could open up means to synthesize LDHs intercalated with unusual anions. As the orientation of the product anion could depend on the precursor anion we may obtain LDHs intercalated with anions in a desired orientation.

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