Precipitation synthesis of lanthanide hydroxynitrate anion exchange materials, $Ln_2(OH)_5NO_3 \cdot H_2O$ (Ln = Y, Eu–Er)

Sheena A. Hindocha, Laura J. McIntyre, Andrew M. Fogg *

Department of Chemistry, University of Liverpool, Liverpool, L69 7ZD, UK

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ABSTRACT

Layered lanthanide hydroxynitrate anion exchange host lattices have been prepared via a room temperature precipitation synthesis. These materials have the composition $Ln_2(OH)_5NO_3 \cdot H_2O$ and are formed for Y and the lanthanides from Eu to Er and as such include the first Eu containing nitrate anion exchange host lattice. The interlayer separation of these materials, approximately 8.5 Å, is lower than in the related phases $Ln_2(OH)_5NO_3 \cdot 1.5H_2O$ which have a corresponding value of 9.1 Å and is consistent with the reduction in the co-intercalated water content of these materials. These new intercalation hosts have been shown to undergo facile anion exchange reactions with a wide range of organic carboxylate and sulfonate anions. These reactions produce phases with up to three times the interlayer separation of the host lattice demonstrating the flexibility of these materials.

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1. Introduction

Anion exchange materials comprise positively charged layers with charge neutrality maintained by interlayer anions and have been the focus of numerous studies since the first reported synthesis of layered double hydroxides (LDHs) by Miyata and Kumura in 1973 [1]. Layered hydoxides have proved to be very flexible intercalation host lattices both in terms of their layer composition and the anion which can be incorporated in the interlayer gallery giving rise to a wide variety of applications in fields as diverse as catalysis [2,3] and molecular recognition [4–6]. The full range applications of LDHs were recently reviewed by Feng and Duan [7].

The field of anion exchange materials is dominated by the LDHs which typically combine a divalent cation e.g. $M^{2+} = Mg^{2+}$, Zn^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+} Ca^{2+} or Fe^{2+} and a trivalent cation e.g. $M^{3+} = Al^{3+}$, Cr^{3+}, Mn^{3+}, Fe^{3+}, Ga^{3+}, Co^{3+} or Ni^{3+} into the layers of a material with the general composition $[M^{2+}_{1-x} M^{3+}_x(OH)_2]^{\zeta+}(X^{n-}_{\zeta/n}) \cdot mH_2O$ [2,8–10]. The layer structure of these materials is related to brucite ($Mg(OH)_2$) and consists of edge sharing MO_6 octahedra [11,12]. Partial replacement of the divalent cations with trivalent ones creates positively charged layers and with charge-balancing inorganic or organic anions incorporated into the interlayer space.

Other families of layered hydroxide intercalation hosts include the hydroxy double salts (HDSs) and the hydroxynitrates. The general formulae for HDSs are, $[(M^{2+}_{1-x}N^{2+}_{1+x})(OH)_{3(1-y)}]$ $^+X^{n-}_{(1+3y)/n} \cdot zH_2O$ or $(M^{2+}Me^{2+})_5(OH)_8(X^{n-})_{2/n}$ where $M^{2+} =$ Zn^{2+}, Ni^{2+} or Cu^{2+} and $Me^{2+} = Co^{2+}$, Ni^{2+} or Cu^{2+} [13–16]. In these materials the radii of the two metal ions do not differ by more than 0.05 Å meaning that the layers are much less compositionally diverse than in the LDHs [15]. These materials comprise hexagonally packed hydroxyl ions where three-quarters of the octahedral sites are filled in alternate layers by the M^{2+} cations and Me^{2+} cations are coordinated tetrahedrally above and below vacant octahedral sites [16]. Exchangeable anions, typically nitrate, and water molecules are situated between the layers. The hydroxynitrate materials are analogous to HDSs except that they are single metal salts with the general formula $M(OH)_{2-x}$ $(NO_3)_x \cdot mH_2O$, where M = Co, Ni, Cu or Zn. These materials are not limited to inorganic interlayer anions and phases containing acetate have been prepared [17,18]. Analogously to the other layered hydroxide systems these materials, for example $Ni_{1-x}Zn_{2x}$ $(OH)_2(CH_3COO)_{2x} \cdot nH_2O$, have been shown to be capable of anion exchange reactions with inorganic species such as vanadate [19].

Hydroxynitrate salts are known for the larger lanthanide cations, $Ln(OH)_2NO_3 \cdot xH_2O$ (Ln = La, Pr, Nd, Sm and Gd; x = 1, 2) [20–23]. Despite the fact that in these materials the nitrate is coordinated directly to the lanthanide cation within the layers anion exchange has been observed for $La(OH)_2NO_3 \cdot H_2O$ by reaction with acetate, benzoate and terephthalate salts upon heating to 65 °C [24]. A second family of lanthanide hydroxynitrates, with the composition $Ln_2(OH)_5NO_3 \cdot xH_2O$ (x = 1.5, 2), has been prepared for Ln = Y and Yb [25–27]. Haschke reported an orthorhombic unit cell for $Ln_2(OH)_5NO_3 \cdot 2H_2O$ (Ln = Y, Yb) with $a \sim 6.0$ Å, $b \sim 3.8$ Å and $c \sim 8.5$ Å as well as the non-stoichiometric phases $Ln_2(OH)_{5.39}(NO_3)_{0.61}$ (Ln = Sm–Dy, Yb) and $Ln_2(OH)_{5.14}$ $(NO_3)_{0.86}$ (Ln = La, Pr, Nd) [25].

* Corresponding author. Fax: +44 151 794 3587.
E-mail address: afogg@liverpool.ac.uk (A.M. Fogg).

We have recently reported the hydrothermal synthesis of the first anion exchange intercalation hosts to combine the properties of the smaller lanthanide cations with the flexibility of intercalation compounds [28,29]. These materials, $Ln_2(OH)_5NO_3 \cdot 1.5H_2O$ ($Ln = $ Y, Gd–Lu), have an interlayer separtion of approximately 9.1 Å and were found to undergo facile anion exchange reactions at room temperature with a range of organic carboxylate and sulfonate salts. Subsequent to this initial report the synthesis, structures and anion exchange properties of the analogous chloride phases, $Ln_2(OH)_5NO_3 \cdot nH_2O$ ($Ln = $ Y, Nd–Yb) has been reported [30–32]. These materials show a range of hydration levels ($n \approx 1.20$–1.85) which as the water molecules are bound to the lanthanide cations leads to subtle differences in the layer structure which is comprised of 8 and 9 coordinate Ln sites. In the case of the $Yb_2(OH)_5NO_3 \cdot 1.5H_2O$ material polymorphism has been observed with both orthorhombic and monoclinic structures being determined [30]. In this paper we report the room temperature precipitation synthesis of a related family of anion exchange host lattices with the composition, $Ln_2(OH)_5NO_3 \cdot H_2O$ ($Ln = $ Y, Eu–Er).

2. Experimental section

2.1. Synthesis

The hydroxynitrate phases, $Ln_2(OH)_5NO_3 \cdot H_2O$ ($Ln = $ Y, La–Lu), were synthesised by a precipitation route. In a typical experiment, 25 mL of 1 M NaOH was added dropwise on to solid $Ln(NO_3)_3 \cdot xH_2O$ (0.016 mol for $Ln = $ Y, Dy, Er, Tm, Yb and 0.008 mol for $Ln = $ Eu, Tb, Ho) and stirred at room temperature for 30 minutes. The resulting solid was filtered under vacuum, washed with water and ethanol and left to dry, initially in air for 1 hour, and then dried in an oven at 120 °C for 1 hour.

For the anion exchange reactions 75 mg of the host lattices was suspended in 5 mL of an aqueous solution containing a three-fold molar excess of the required anion and stirred at room temperature overnight. The reactions were subsequently filtered under vacuum and the product washed with water and ethanol before being left to dry in air. The anions used in this study were the (di)sodium salts of phthalate, terephthalate, fumarate, maleate, malonate, succinate, suberate, decylsulfate, 1,5-naphthalenedisulfonate (1,5-NDS), 2,6- naphthalenedisulfonate (2,6-NDS) and anthraqunionedisulfonate (AQDS).

3. Characterisation

Powder X-ray diffraction (XRD) patterns of all the samples were recorded with $CuK\alpha_1$ radiation on a Stoe Stadi-P diffractometer in either Bragg Brentano or Debye Scherrer geometry. Thermogravimetric analysis (TGA) and elemental analysis were used to determine the compositions of the phases.

TGA was performed using a Seiko SII-TG/DTA 6300 thermal analyser. CHN analysis was performed on a FlashEA 1112 instrument and ICP analysis on a Ciros CCD optical emission spectrometer following complete dissolution of the samples in dilute HNO_3 was used to determine the metal content. Fourier transform infra red (FTIR) spectra were obtained using a Perkin Elmer Spectrum 100 spectrometer fitted with the Spectrum 100 Universal Diamond/ZnSe ATR.

4. Results and discussion

New anion exchange intercalation host lattices have been prepared via a room temperature precipitation route. The samples comprise microcrystalline powders and were found to have the composition $Ln_2(OH)_5NO_3 \cdot H_2O$ ($Ln = $ Y, Gd–Lu) by a combination of TGA and elemental analysis. The characterising data on these phases are summarised in Table 1. From the data it can be seen

Table 1
Characterising data for the layered lanthanide hydroxynitrate phases, $Ln_2(OH)_5NO_3 \cdot H_2O$.

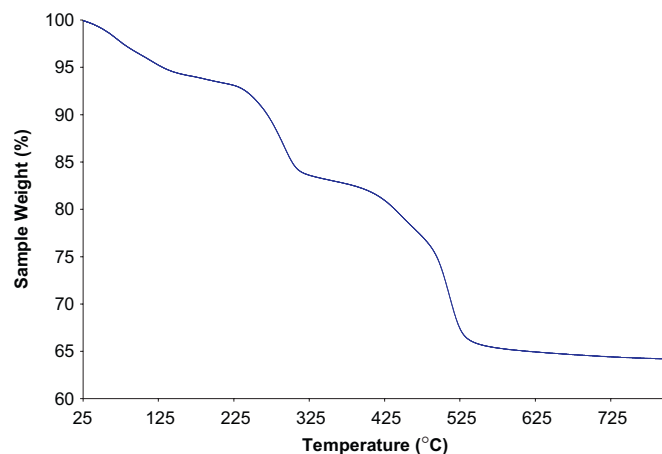| Ln	Composition	Interlayer separation (Å)	Elemental analysis	
			Obs. (%)	Calc. (%)
Y	$Y_2(OH)_5(NO_3)_{0.90}(CO_3)_{0.05} \cdot H_2O$	8.60	N (4.45) H (1.90) C (0.38)	N (3.71) H (2.08) C (0.18)
Eu	$Eu_2(OH)_5(NO_3)_{0.70}(CO_3)_{0.15} \cdot H_2O$	8.40	N (2.64) H (1.39) C (0.68)	N (2.22) H (1.14) C (0.41)
Tb	$Tb_2(OH)_5(NO_3)_{0.78}(CO_3)_{0.11} \cdot H_2O$	8.40	N (2.47) H (1.27) C (0.30)	N (2.29) H (1.48) C (0.27)
Ho	$Ho_2(OH)_5(NO_3)_{0.74}(CO_3)_{0.13} \cdot H_2O$	8.48	N (2.46) H (1.24) C (0.37)	N (2.13) H (1.45) C (0.32)

Fig. 1. TGA trace for $Y_2(OH)_5NO_3 \cdot H_2O$ showing mass losses of 5.9% below 170 °C, an additional 10.8% by 350 °C and a further 18.6% by 700 °C.
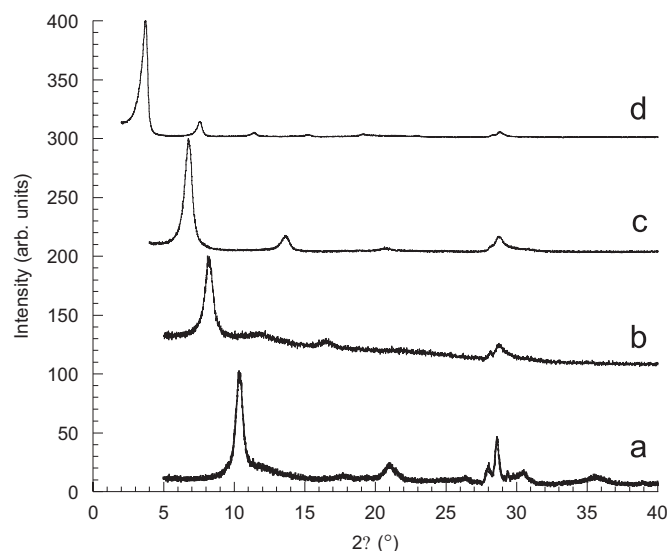

Fig. 2. Powder XRD patterns of: (a) $Y_2(OH)_5NO_3 \cdot H_2O$, (b) $Y_2(OH)_5(trans-C_4H_2O_4)_{0.5} \cdot H_2O$, (c) $Y_2(OH)_5(p-C_8H_4O_4)_{0.5} \cdot H_2O$ and (d) $Y_2(OH)_5(C_{10}H_{21}-SO_3)_{0.5} \cdot H_2O$.

that a small amount of carbonate contamination occurs for all of the compounds which is a commonly encountered problem in the synthesis of layered hydroxides via a precipitation route and has been seen previously in the lanthanide phases as well as with the LDHs [32,33]. The new materials will be exemplified here by the Y phase with data on the remaining compounds included in the ESI. Fig. 1 shows the TGA data for $Y_2(OH)_5NO_3 \cdot H_2O$ from which three distinct mass losses are apparent which is consistent with observations on other layered hydroxide systems. The initial mass loss, below 170 °C, corresponds to the removal of one co-intercalated water molecule from the interlayer gallery (observed mass loss = 5.9%; calculated mass loss for $Y_2(OH)_5NO_3 \cdot H_2O$ = 5.3%). This is followed by partial dehydroxylation of the layers (obs. −10.8%; calc. −10.6%) between 150 and 350 °C leaving a material of composition $Y_2O_2(OH)(NO_3)_{0.90}(CO_3)_{0.05}$ [27,29].

Decomposition is complete by 700 °C forming Y_2O_3 with a further mass loss of 18.6% (calc. −17.6%) and no further mass loss is observed above this temperature.

Powder XRD patterns, Fig. 2, reveal that these phases are poorly crystalline in comparison with the $Ln_2(OH)_5NO_3 \cdot 1.5H_2O$ ($Ln = Y$, Gd–Lu) materials which were prepared via a hydrothermal route [28,29]. From the data $0\,0\,l$ reflections characteristic of a layered material are apparent along with a couple of non-$0\,0\,l$ reflections. The basal spacing of these materials, approximately 8.5 Å, is less than that observed for the $Ln_2(OH)_5NO_3 \cdot 1.5H_2O$ ($Ln = Y$, Gd–Lu) phases (approximately 9.1 Å). The lower interlayer separation in these materials is consistent with the reduced level of hydration. Haschke has previously reported the hydrothermal synthesis of materials with the composition $Ln_2(OH)_5NO_3 \cdot 2H_2O$ ($Ln = Y$, Yb) which were formed as impurities in the preparation
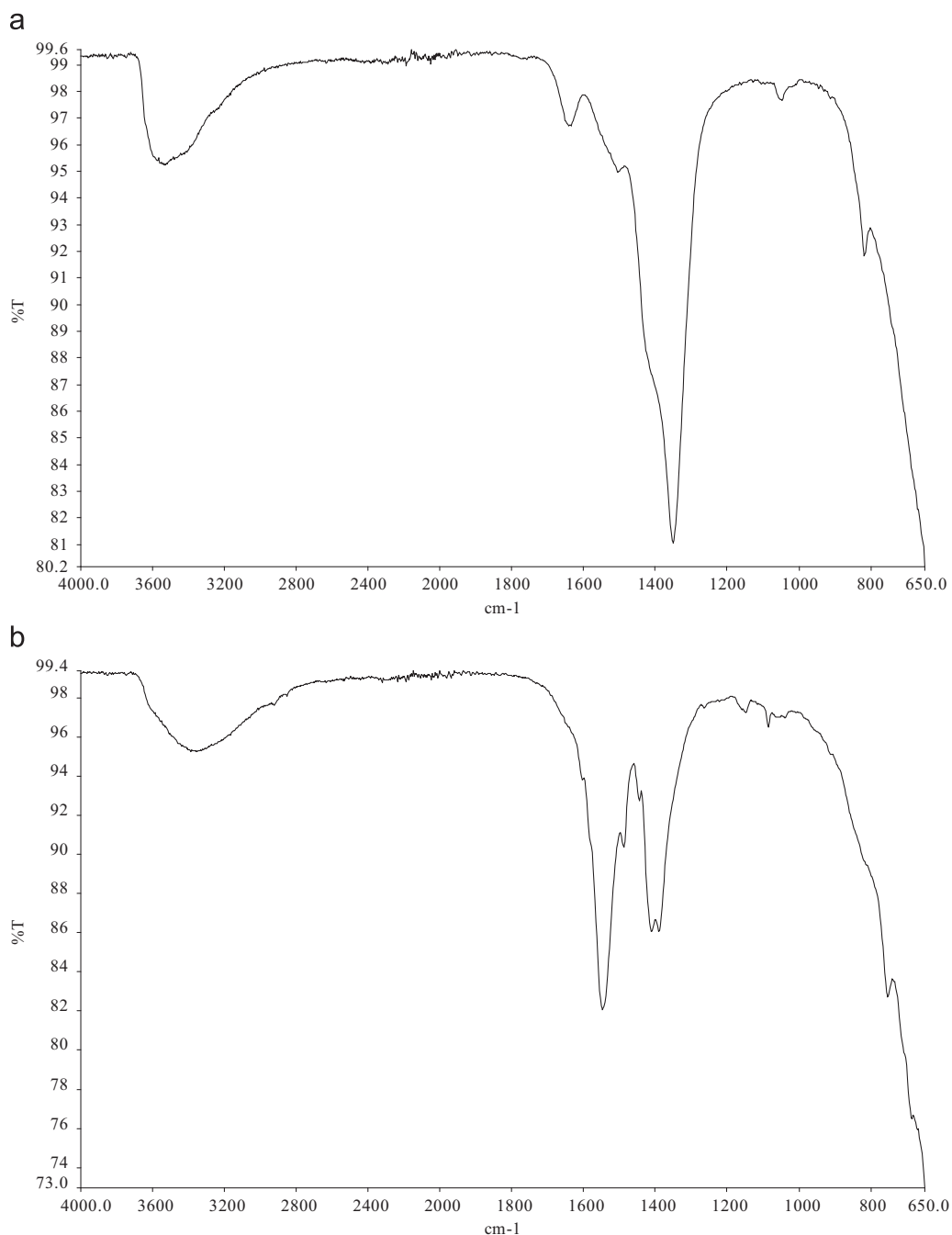

Fig. 3. FTIR spectra for: (a) $Y_2(OH)_5NO_3 \cdot H_2O$ and (b) $Y_2(OH)_5(p\text{-}C_8H_4O_4)_{0.5} \cdot H_2O$.

of $Ln_2(OH)_5NO_3$ and have an interlayer separation comparable to those seen in these materials. However, the orthorhombic unit cells given do not index the reflections observed from these materials and owing to the relatively poor crystallinity and small number of observed non-$0\,0\,l$ reflections of these materials the diffraction data has not been indexed [25]. In contrast to the chloride materials none of the structures of the nitrate intercalates have been determined. Close inspection of the powder XRD data did not reveal the presence of any other known phases. In this study it was not possible to prepare the Yb phase with the powder XRD pattern suggesting the formation of multiple, poorly crystalline phases. This contrasts with the hydrothermal synthesis of $Yb_2(OH)_5NO_3 \cdot 1.5H_2O$ with the higher level of hydration observed in that case seemingly leading to the formation of crystalline phases [29]. These observations are also consistent with those made on the chloride system where a hydrothermal synthesis was successful with Yb but precipitation under reflux was not [30,32]. Similar observations were made with Tm and Lu indicating a limiting cation size for this phase and as a result the Tm, Yb and Lu materials were not studied further. It was also found that this phase did not form with Dy which as for Yb formed several different poorly crystalline phases and whilst Gd and Er yielded this phase the samples were impure. Amongst the larger lanthanides La forms $La(OH)_2NO_3$ whilst the others yield only amorphous material under these conditions.

Fig. 3(a) shows the FTIR spectrum of $Y_2(OH)_5NO_3 \cdot H_2O$ and spectra for the other host lattices are included in the ESI. The spectrum shows a broad band, centred at approximately $3500\,cm^{-1}$, which corresponds to the combination of the O–H stretches of the layer hydroxyl groups and co-intercalated water molecules. The bending vibration of the water molecules is at $1640\,cm^{-1}$. The presence of the nitrate anions in the interlayer gallery is indicated by the broad band at approximately $1350\,cm^{-1}$ which is characteristic of an uncoordinated nitrate anion and is in agreement with previous observations on other layered hydroxides intercalated with nitrate [24,29,34]. However, due to the carbonate contamination in these materials it is necessary to use the presence of additional bands at approximately 1050 and $1760\,cm^{-1}$ to confirm the presence of the nitrate anion in these phases. The latter is a combination mode typical of nitrate and the former the v_1 mode which is observed as a result of the reduction in symmetry in the intercalate.

Much of the interest in layered hydroxides is centred on their ability to undergo anion exchange reactions and the opportunity to introduce anions with a specific property e.g. catalytic, pharmaceutical or optical which cannot be incorporated directly. In order to demonstrate the anion exchange capacity of the $Ln_2(OH)_5NO_3 \cdot H_2O$ ($Ln = Y$, Eu, Tb, Ho) phases, reactions were performed with a range of organic carboxylate and sulfonate anions. It was found that the $Ln_2(OH)_5NO_3 \cdot H_2O$ ($Ln = Y$, Eu, Tb, Ho) materials undergo complete anion exchange at room temperature. This was confirmed by the absence of characteristic host reflections in the powder XRD patterns and of nitrogen in the elemental analysis. Complete anion exchange, forming $Y_2(OH)_5A_{0.5} \cdot xH_2O$, was observed from reactions between $Y_2(OH)_5NO_3 \cdot H_2O$ and terephthalate, fumarate, malonate, succinate, decylsulfate, 2,6-NDS. The reaction with maleate was incomplete as indicated by the presence of N in the elemental analysis. Representative powder XRD patterns of some of the anion exchange products of $Y_2(OH)_5NO_3 \cdot H_2O$ are shown in Fig. 2 and the characterising data is summarised in Table 2 for the Y phases and in the ESI for the remaining materials. The powder XRD data reveal that these are flexible intercalation hosts with interlayer separations of up to 24.5 Å, almost three times that of the nitrate intercalates, being observed in the anion exchange derivatives. A comparison of these materials with the anion exchange derivatives of the $Ln_2(OH)_5NO_3 \cdot 1.5H_2O$ phases indicates that the aromatic anions give interlayer separation comparable to those seen previously whilst those for the aliphatic ones are generally slightly larger suggesting a more perpendicular orientation for the anions in this case [29].

The FTIR spectrum of $Y_2(OH)_5(p\text{-}C_8H_4O_4) \cdot H_2O$, which provides further confirmation that complete replacement of the nitrate has occurred, is shown in Fig. 3(b). The dominant features of the spectrum are the symmetric and anti-symmetric COO^- stretches at 1550 and $1390\,cm^{-1}$ and the broad O–H band at approximately $3350\,cm^{-1}$. The position of the carboxylate stretches in these materials is consistent with those typically observed for other layered hydroxide systems [29,35].

TGA of the anion exchange products (see ESI) indicates that the layer stoichiometry does not change during the exchange process and the traces are comparable to those seen for other carboxylate intercalates. Typically, the data consist of three mass losses corresponding to the removal of co-intercalated water molecules followed by the decomposition of the hydroxide layers and ultimately the guest anion. In the case of $Y_2(OH)_5(p\text{-}C_8H_4O_4)_{0.5} \cdot H_2O$ the observed total mass loss during the decomposition to Y_2O_3 is 43.8% compared to a theoretical value of 41.0%.

5. Conclusions

This paper describes the synthesis and anion exchange chemistry of layered lanthanide hydroxide intercalation host lattices with the general composition, $Ln_2(OH)_5NO_3 \cdot H_2O$ ($Ln = Y$, Eu–Er) and an interlayer separation of approximately 8.5 Å. These

Table 2
Characterising data for the anion exchange derivatives of $Y_2(OH)_5NO_3 \cdot H_2O$.

Anion	Composition	Interlayer separation (Å)	Elemental analysis	
			Obs. (%)	Calc. (%)
Terephthalate	$Y_2(OH)_5(p\text{-}C_8H_4O_4)_{0.5} \cdot H_2O$	13.11	C (13.66)	C (13.24)
			H (2.67)	H (2.50)
Fumarate	$Y_2(OH)_5(C_4H_2O_4)_{0.5} \cdot H_2O$	10.78	C (7.58)	C (7.11)
			H (2.65)	H (2.39)
Malonate	$Y_2(OH)_5(C_3H_2O_4)_{0.5} \cdot H_2O$	10.83	C (5.93)	C (5.42)
			H (2.51)	H (2.43)
Succinate	$Y_2(OH)_5(C_4H_4O_4)_{0.5} \cdot H_2O$	11.30	C (7.59)	C (7.09)
			H (2.75)	H (2.68)
Decyl sulfate	$Y_2(OH)_5(C_{10}H_{21}SO_3) \cdot 3H_2O$	24.57	C (21.96)	C (22.31)
			H (5.54)	H (5.99)
2,6-NDS	$Y_2(OH)_5(C_{10}H_6(SO_3)_2)_{0.5} \cdot 3H_2O$	15.45	C (12.72)	C (13.05)
			H (2.64)	H (3.06)

phases are prepared via a room temperature precipitation synthesis and include the first Eu anion exchange host lattice. They were found to be very flexible host lattices undergoing facile anion exchange reactions at room temperature with a wide variety of organic carboxylate and sulfonate anions forming materials with interlayer separations of up to 25 Å.

Supplementary information

Electronic Supplementary Information (ESI) available: Additional characterising data (powder XRD, TGA, FTIR and elemental analysis) is available.

Acknowledgements

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2009.01.039.

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