Reversible thermal behaviour of layered double hydroxides: a thermogravimetric study

N. S. Puttaswamy and P. Vishnu Kamath*

Department of Chemistry, Central College, Bangalore University, Bangalore 560 001, India

Layered double hydroxides (LDHs) of Mg with trivalent cations such as Al, Cr and Fe show two mass loss steps on heating; the low-temperature (25–250 °C) loss is due to dehydration and the high-temperature (250–450 °C) loss is due to decomposition. Both steps are reversible and the oxide residues obtained after calcination at 700 °C reconstruct back to the hydroxide phase. On the other hand the LDHs of Ca and Ni dehydrate reversibly but their decomposition reaction is irreversible. The LDHs of Zn and Co lose mass continuously up to 700 °C without any well resolved steps and the loss is irreversible. These results have implications on the synthesis of selective catalysts by calcination of LDHs.

Layered double hydroxides (LDHs) constitute a class of compounds of the general formula $[M^{II}_{1-x}M'^{III}_{x}(OH)_2]A^{n-}_{x/n}] \cdot mH_2O$, ($M^{II}$ = Ca, Mg, Co, Ni, Cu or Zn, M^{III} = Al, Cr or Fe, $x = 0.16$–1.0, $A^{n-} = NO_3^-$, Cl^-, SO_4^{2-}, CO_3^{2-}, polyoxometallate or any organic anion and $m = 0.1$–1.0).[1] The LDHs are isostructural with the mineral hydrotalcite having formula $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$. This composition corresponds to $x = 0.25$ and $m = 0.5$. The LDHs adopt a hexagonal layered structure which can be derived from that of brucite, $Mg(OH)_2$, by substituting a fraction of the Mg^{2+} ions by Al^{3+} ions. This imparts a positive charge to the hydroxide layers, leading to incorporation of anions in suitable proportions in the interlayer region.[2] The chemistry of the interlayer region endows these materials with many interesting properties and they are used as sensors,[3] anion exchange resins[4] and as electrodes in alkaline secondary cells.[5]

LDHs have also been extensively used as precursors to oxide catalysts[6–8] of high specificity for certain reactions. Oxide catalysts are generally obtained from LDHs by thermal decomposition. In view of the importance of oxide catalysts obtained from LDHs, it is of interest to understand in detail the thermal behaviour of the LDHs. Here we report the results of our thermogravimetric investigations on a large number of LDHs. In view of the wide range of compositions over which LDHs can be synthesized, we have chosen for the purpose of the present study only those having the composition of mineral hydrotalcite ($x = 0.25$), $A^{n-} = CO_3^{2-}$.

Experimental

All LDHs were prepared by the method of Reichle[9] by coprecipitating the divalent and trivalent metals, by the drop-wise addition of a mixed-metal nitrate solution (containing stoichiometric proportions of the metal ions) to a solution of NaOH and Na_2CO_3. The final pH after coprecipitation was in the range 11–12. Most of the LDHs prepared by this route were poorly crystalline. The precipitates were aged at 65 °C for 12 h, filtered and washed with large quantities of distilled water and dried to constant mass at 100 °C. These were used as such for thermogravimetric studies. The filtrates were negative to qualitative spot tests indicating complete precipitation of the metals. The Mg–Cr and Ni–Cr LDHs were found to be entirely amorphous. They were ordered upon hydrothermal treatment at 120 °C for 24 h, which resulted in a poorly ordered phase. The LDHs of Ca and Zn were prepared for a composition of $x = 0.33$[10] in keeping with the composition of the mineral hydrocalumite.[11] The Zn–Cr LDH was prepared by the method of Boehme et al.[12] The Ca–Al LDHs were prepared

electrochemically by cathodic reduction of a mixed-metal salt solution containing Ca and Al in the required ratio.[13]

A few representative LDHs were analysed by wet chemical analysis (gravimetric procedures for two metallic constituents[14]). The expected ($x = 0.25$; based on the proportion of salts used for coprecipitation) and observed metal contents agreed reasonably well (observed x values are Mg–Al LDH, 0.248; Mg–Fe LDH, 0.258; Ni–Al LDH, 0.252; Ni–Fe LDH, 0.255). Quantitative precipitation has also been observed by others.[15]

Thermogravimetric data were recorded on a home-made system by heating ca. 100 mg of the sample suspended in a platinum crucible at a heating rate of 2.5 °C min⁻¹ in air. For each sample, a complete thermogram was first recorded in the range 25–800 °C, to identify the different mass losses. The reversibility of each step was investigated by recording the gain in mass, if any, of the sample on cooling. Mass gain curves were recorded by terminating the heating programme at the end of each step seen in the complete thermogram and holding the sample at that temperature to constant mass. The furnace was then switched off and the mass of the sample monitored as a function of temperature until the ambient temperature was reached and subsequently as a function of time. A mass gain in excess of 95% of the initial mass was considered to be reversible.

As-prepared as well as heat-treated samples on cooling were subjected to physical characterization. Powder X-ray diffraction patterns were recorded on a JEOL JDX8P or Rigaku-Dmax 1C powder diffractometer using Cu-Kα ($\lambda = 1.541$ Å) radiation. As the LDHs are poorly ordered phases, the diffraction patterns were not of a quality that could be used for refinement of peak positions. The patterns were assigned by a trial and error procedure starting with the lattice parameters of model compounds taken from the literature.[16] IR spectra were recorded using a Nicolet Impact 400D FTIR spectrometer driven by OMNIC Software.

Results

Table 1 lists the prominent d-spacings of the prepared LDHs. All the patterns could be indexed on hexagonal cells ($a = 3.07$–3.15 Å, $c = 23.3$–23.7 Å), in keeping with the literature data.[16] The LDHs of Zn with Cr and Ca with Al contain intercalated nitrates and have a c-parameter in the range 25.5–26.6 Å.
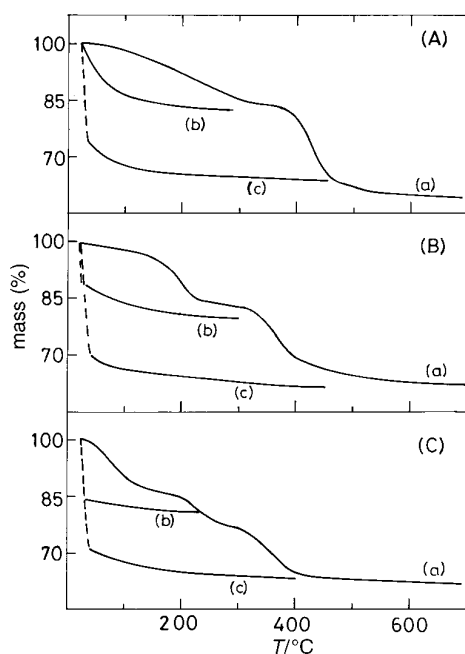
LDHs of Mg

Fig. 1 shows the thermograms of the Mg–Al, Mg–Fe and Mg–Cr LDHs. All three systems show two mass losses. A low-

Table 1 Summary of the powder X-ray diffraction data of layered double hydroxides

| hkl^a	Mg–Al	Mg–Fe	Mg–Cr	Ni–Al	Ni–Fe	Ni–Cr	Zn–Al	Zn–Cr	Ca–Al
				$d/\text{Å}$					
003	7.69	7.81	7.94	7.86	7.80	7.66	7.69	8.84	8.51
006	3.91	3.897	3.96	3.88	3.87	3.92	3.80	4.44	4.27
009	2.612	2.629	–	2.589	2.598	2.578	–	2.957	2.858
100							–	–	2.715
011							2.657	2.673	–
014							–	–	2.482
015	2.354	2.372	–	2.313	2.317	2.346	2.307	–	2.386
018	1.996	–	–	–	–	2.000	1.947	–	–
01$\underline{1}$3	1.531								
$a/\text{Å}$	3.15	3.15	–	3.07	3.08	3.15	3.08	3.10	3.11
$c/\text{Å}$	23.46	23.66	23.76	23.30	23.40	23.52	22.79	26.64	25.51

^{a}The patterns were assigned according to these indices on a hexagonal cell.

Fig. 1 TG curves of Mg–Al (A), Mg–Fe (B) and Mg–Cr (C) LDHs. Curves (a) are the complete thermograms, (b) and (c) are the cooling curves. Dashed lines indicate mass gain during 18–48 h of standing in the ambient atmosphere.

temperature loss is seen at 25–250 °C and the high-temperature loss is seen at 250–450 °C. The observed mass losses are compared with those expected on the basis of the formula mass in Table 2. All the LDHs of Mg dissociate completely around 450 °C and the net mass loss computed according to

eqn. (1)

$$[Mg_6M_2(OH)_{16}CO_3]\cdot 4H_2O \rightarrow 5MgO + MgM_2O_4 \quad (1)$$
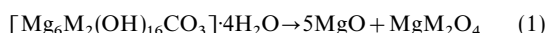
matches well with the total observed mass loss. However the mass loss associated with the first step (up to 250 °C) is more than what would be expected from a simple dehydration step indicating that there is an overlap of the dehydration and decomposition reactions. Samples heat-treated at all temperatures up to 700 °C were found to regain up to 99% of their initial mass on cooling. This reversible nature of both dehydration and decomposition reactions was indeed surprising. The reversibility was checked by powder X-ray diffraction as well as by IR spectroscopy. Fig. 2 and 3 show the powder X-ray diffraction patterns of as-prepared and heat-treated samples of the Mg–Al and Mg–Fe LDHs. The results for the Mg–Cr system are similar except that the samples after complete mass gain do not regain crystallinity. Table 3 lists prominent d-spacings of the heat-treated samples. It is evident that the
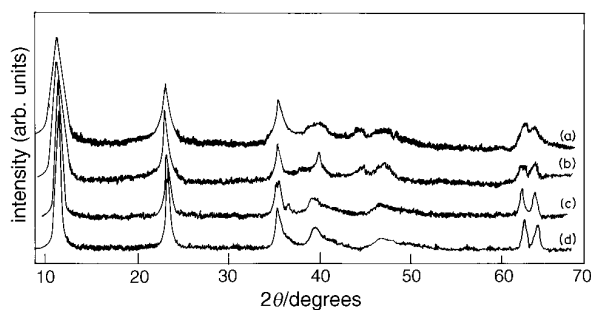
Fig. 2 Powder X-ray diffraction patterns of Mg–Al LDHs heat-treated at 700 °C (a), 450 °C (b) and 250 °C (c) compared with that of the as-prepared sample (d)

Table 2 Summary of thermogravimetric data of LDHs

hydrotalcite	molecular formula	mass loss steps	expected mass loss (%)		observed mass loss (%)		behaviour
			dehydration	total	dehydration	total	
Mg–Al	$[Mg_6Al_2(OH)_{16}CO_3]\cdot 4H_2O$	2	12	43.0	13.7	43.1	reversible
Mg–Fe	$[Mg_6Fe_2(OH)_{16}CO_3]\cdot 4H_2O$	2	11	39.3	16.6	39.5	reversible
Mg–Cr	$[Mg_6Cr_2(OH)_{16}CO_3]\cdot 4H_2O$	2	11	39.7	15.0	38.7	reversible
Ni–Al	$[Ni_6Al_2(OH)_{16}CO_3]\cdot 4H_2O$	2	8.8	32.1	11.7	32.1	reversible (dehydration only)
Ni–Fe	$[Ni_6Fe_2(OH)_{16}CO_3]\cdot 4H_2O$	2	8.3	29.9	9.5	29.8	reversible (dehydration only)
Ni–Cr	$[Ni_6Cr_2(OH)_{16}CO_3]\cdot 4H_2O$	1	–	30.3	–	30.9	irreversible
Ca–Al	$[Ca_2Al(OH)_6\frac{1}{2}CO_3]\cdot 2\frac{1}{2}H_2O$	2	15.8	42.6	15.8	41.3	partial rehydration only
Zn–Al	$[Zn_2Al(OH)_6\frac{1}{2}CO_3]\cdot 2\frac{1}{2}H_2O$	1	–	36.1	–	36.0	irreversible
Zn–Cr	$[Zn_2Cr(OH)_6\frac{1}{2}CO_3]\cdot 2\frac{1}{2}H_2O$	1	–	33.6	–	32.2	irreversible
Co–Al	$[Co_6Al_2(OH)_{16}CO_3]\cdot 4H_2O$	1	–	39.9	–	40.4	irreversible
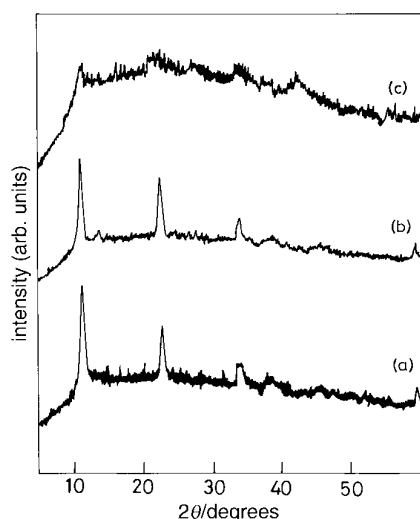
Fig. 3 Powder X-ray diffraction patterns of Mg–Fe LDHs heat-treated at 450 °C (c) and 250 °C (b) compared with that of the as-prepared sample (a)

Table 3 Summary of PXRD data of heat-treated layered double hydroxides

hkl^a	$d/\text{Å}$					
	Mg–Al 250 °C	Mg–Al 700 °C	Mg–Fe 300 °C	Mg–Fe 450 °C	Ni–Al 300 °C	Ni–Fe 250 °C
003	7.89	7.82	7.89	8.00	7.79	7.79
006	3.95	3.93	3.95	4.02	3.91	3.84
009	2.605	2.605	2.632	–	2.586	–
012	–	–	–	2.627	–	2.626
015	2.330	2.307	2.331	–	2.308	–
018	1.992	1.971	2.001	–	–	1.971
$a/\text{Å}$	3.10	3.15	3.13	3.10	3.05	3.12
$c/\text{Å}$	23.46	23.58	23.7	24.12	23.27	23.04

^{a}The patterns were assigned according to three indices on a hexagonal cell.

Mg–Al and Mg–Fe LDHs reconstruct to the original structure after both dehydration and decomposition.

Fig. 4 shows illustrative IR spectra of the as-prepared and heat-treated samples of the Mg–Al LDH. The as-prepared sample shows a strong absorption in the range 3600–3400 cm^{-1} arising from the OH stretching vibrations and
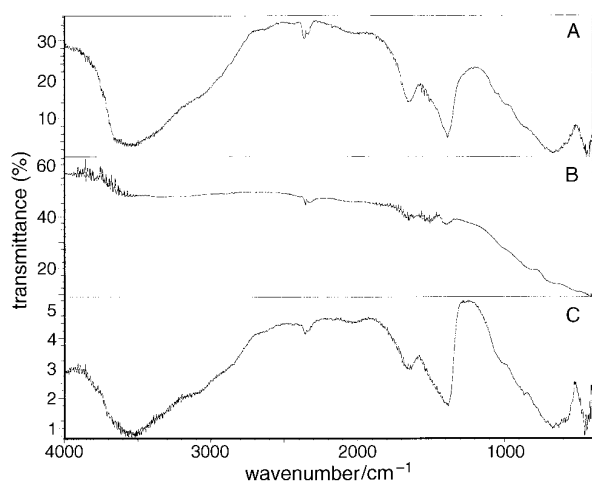
Fig. 4 IR spectrum of the as-prepared Mg–Al sample (A) compared with that of the freshly heat-treated (700 °C) (B) and cooled (C) samples

characteristic peaks due to intercalated carbonate ions in the region 1400–1000 cm^{-1}. Immediately after heat treatment at 700 °C the sample shows vastly different features and a clear absence of peaks due to hydroxy and carbonate groups indicating the complete dehydroxylation and decarboxylation of the sample. However, on cooling the residue, it once again exhibits the typical IR spectrum of the LDHs. Similar observation are made with the Mg–Fe and Mg–Cr LDHs.

LDHs of Ca

The LDH of Ca with Al was investigated and the thermogram is shown in Fig. 5. The LDHs of Ca show a three step mass loss on heating: the temperatures at which the losses occur are higher than observed for the LDHs of Mg. Dehydration is complete at 300 °C, while decomposition is complete only after prolonged standing at 850 °C. As is evident, dehydration is reversible, while after decomposition only partial mass gain is observed on cooling. Both XRD and IR spectroscopy confirm these observations.
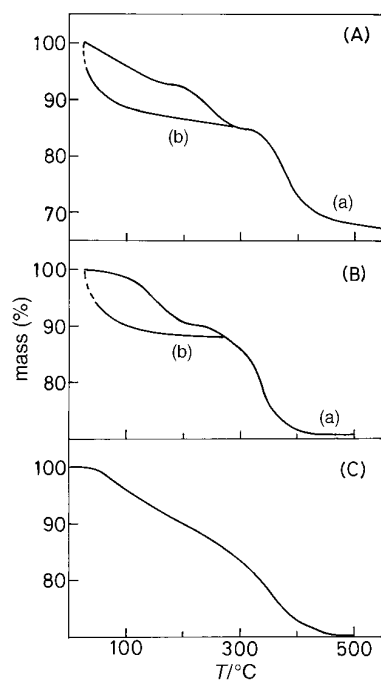
LDHs of Ni

The LDHs of Ni with Al, Cr and Fe were investigated by thermogravimetry. All the LDHs of nickel decompose irreversibly below 500 °C with the expected mass loss. The Ni–Al and Ni–Fe LDHs show a clear two step mass loss, of which the low-temperature loss (below 300 °C) can be attributed to a reversible dehydration reaction (Fig. 6). On the other hand, the Ni–Cr LDH loses mass continuously (40–700 °C) without any well resolved steps. In all cases the oxide residues obtained after decomposition do not gain any mass on cooling. XRD clearly shows the reversible nature of the dehydration step (Fig. 7). The residues after decomposition show broad lines at positions corresponding to the structure of NiO.

LDHs of Zn and Co

The LDHs of Zn with Al and Cr lose mass in a single step extending from 50 to 600 °C. The observed net mass losses of 36% and 39.2% (Fig. 8), respectively, are consistent with what is expected from dehydration and decomposition. On cooling the oxide residues do not regain any mass ruling out the possibility of any reconstruction of the hydroxide. The LDHs
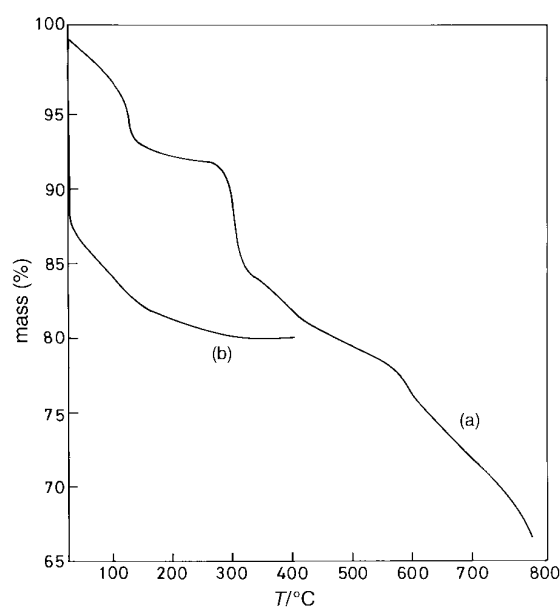
Fig. 5 TG curve (a) of the Ca–Al LDH. Curve (b) is the mass gain curve on cooling.

Fig. 6 TG curves for the Ni–Al (A), Ni–Fe (B) and Ni–Cr (C) LDHs. Curves (a) are the thermograms, (b) are the cooling curves.
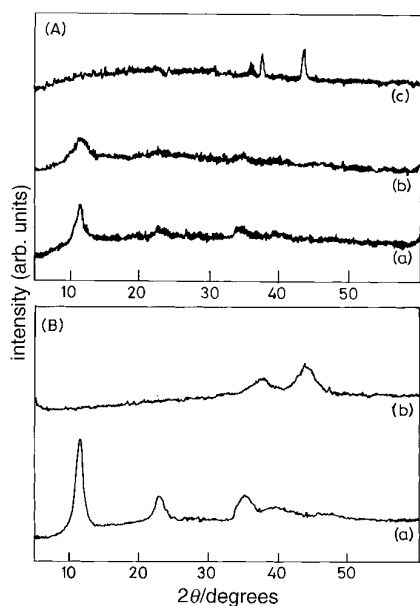

Fig. 7 (A) Powder X-ray diffraction patterns of Ni–Fe LDH heat-treated to 750 °C (c) and 300 °C (b) compared with that of the as-prepared sample (a). (B) Powder X-ray diffraction pattern of the Ni–Al LDH heat-treated to 700 °C (b) compared with that heated to 300 °C (a). The as-prepared sample is identical to curve (a).

of Co decompose irreversibly in a single step below 400 °C to Co_3O_4.

Discussion

Most of the LDHs studied appear to undergo a two step mass loss and decompose completely below 500 °C. The net mass loss observed is consistent with the formation of mixed-oxide residues. The LDHs, despite their complexity, appear to be stochiometric compounds with a well defined structural water and intercalated anion content, in complete contrast to the
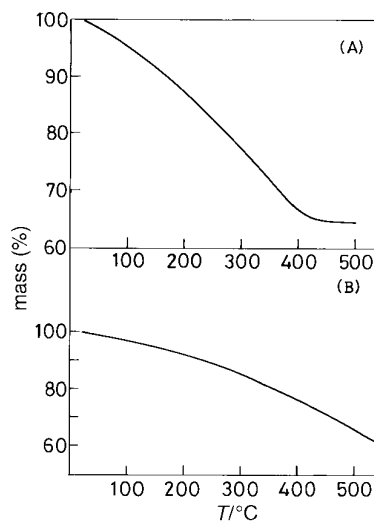
Fig. 8 TG curves of Zn–Al (A) and Zn–Cr (B) LDHs. Mass loss for Zn–Cr is complete at 700 °C.

unary hydroxides such as those of Ni and Co.[17] The loss of structural water can be reversed on cooling and the samples regain their original mass. Powder XRD data also exemplify these observations and the c-parameters (which are very sensitive to the intercalated water content) of the reconstructed samples are identical to the c-parameters of the as-prepared hydroxides.

The LDHs of Mg present a special case in that they reconstruct even after calcination at 700 °C. The reversible thermal behaviour of the Mg–Al system in the low-temperature (below 350 °C) regime has been observed by others.[8,18] Our results show that this behaviour is seen over a wider temperature range as well as in other systems such as the Mg–Fe and Mg–Cr LDHs. It therefore appears that although calcined oxides are used as catalysts,[6] the active material is indeed the parent hydroxide itself. The work of Constantino and Pinnavaia[8] has shown that the parent LDH material is by itself a highly selective catalyst.

The reversible decomposition observed in the Mg–Al system has been attributed[19] to the formation of an Al-containing defect rocksalt phase of the type $Mg_{1-x}Al_{2x/3} \square_{x/3}O$, which is unstable and reconstructs back to the LDH phase on prolonged exposure to air and carbon dioxide. There is a consensus[1b,19] that spinel formation does not take place till well over 1000 °C and only after spinel formation is the reversible behaviour lost.

Whether the reversible behaviour arises due to the carbonate ions or the M^{III}/M^{II} ratio is a point of interest.

Although carbonates decompose at a higher temperature compared to the hydroxide precursors, in the LDHs, dehydration and decarboxylation coincide and occur together at a temperature closer to the decomposition temperature of the pure hydroxides.

IR spectra show that the carbonate ions are intercalated in D_{3h} symmetry and there is no direct bonding of the carbonate groups to the metal.

In conclusion, we have shown that the thermal behaviour of LDHs is either partially or completely reversible.

References

1 (*a*) K. A. Carrado, A. Kostapapas and S. L. Suib, *Solid State Ionics*, 1988, **26**, 77; (*b*) F. Cavani, F. Trifiro and A. Vaccari, *Catal. Today*, 1991, **11**, 173.
2 S. Miyata, *Clays Clay Miner.*, 1975, **23**, 369.
3 J. E. Moneyron, A. DeRoy and J. P. Besse, *Sens. Actuators B*, 1991, **4**, 189.
4 A. Ookubo, K. Ooi and H. Hayashi, *Langmuir*, 1993, **9**, 1418.
5 P. V. Kamath, M. Dixit, L. Indira, A. K. Shukla, V. G. Kumar and N. Munichandriah, *J. Electrochem. Soc.*, 1994, **141**, 2956.
6 T. Sato, K. Kato, T. Endo and M. Shimada, *React. Solids*, 1986, **2**, 253.
7 W. T. Reichle, *J. Catal.*, 1985, **94**, 547.
8 R. L. Constantino and T. J. Pinnavaia, *Inorg. Chem.*, 1995, **34**, 883.
9 W. T. Reichle, *Solid State Ionics*, 1986, **22**, 135.
10 K. E. Malki, A. De Roy and J. P. Besse, *Mater. Res. Bull.*, 1993, **28**, 667.
11 H. F. W. Taylor, *Min. Mag.*, 1973, **39**, 304.
12 H-P. Boehm, J. Steinle and C. Vieweger, *Angew. Chem.*, *Int. Ed. Engl.*, 1977, **16**, 265.
13 G. H. A. Therese and P. V. Kamath, *J. Appl. Electrochem.*, submitted.
14 G. Raj, *Advanced Practical Inorganic Chemistry*, Goel Publishing House, Meerut, India, 1994.
15 F. Kooli, K. Kosuge, T. Hibino and A. Tsunashima, *J. Mater. Sci.*, 1993, **28**, 2769.
16 Powder Diffraction Files, Joint Committee on Powder Diffraction Standards, PN, 1967.
17 P. Oliva, J. Leonardi, J. F. Laurent, C. Delmas, J. J. Braconnier, M. Figlarz, F. Fievet and A. deGuibert, *J. Power Sources*, 1982, **8**, 229.
18 F. Rey, V. Fornes and M. Rojo, *J. Chem. Soc.*, *Faraday Trans.*, 1992, **88**, 2233.
19 T. Sato, K. Kato, T. Endo and M. Shimada, *React. Solids*, 1986, **2**, 253.