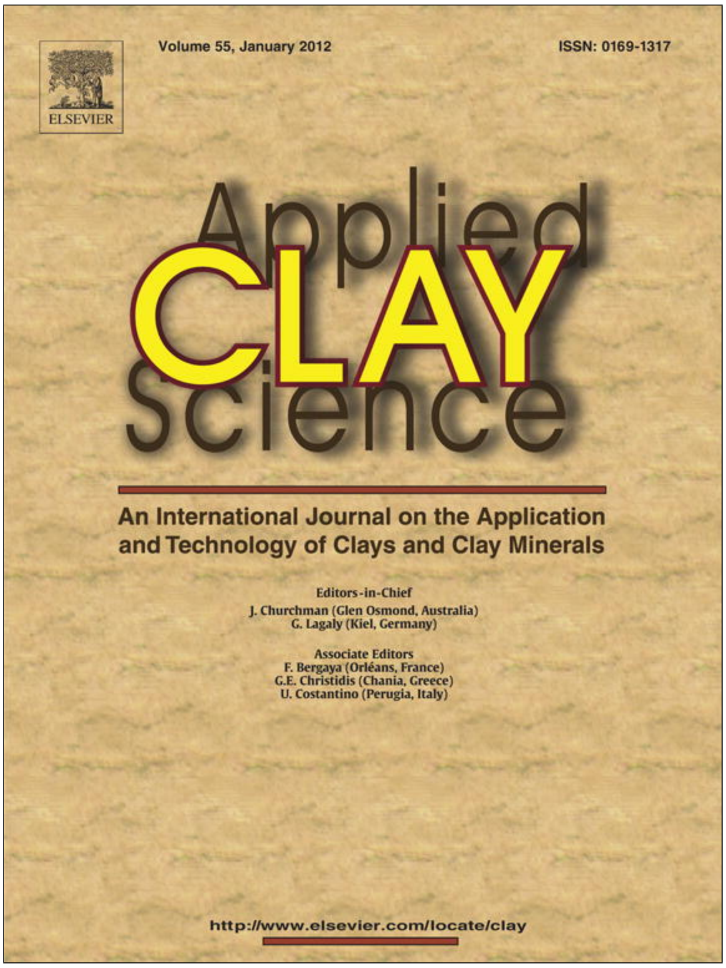

Volume 55, January 2012 ISSN: 0169-1317

Applied CLAY Science

An International Journal on the Application and Technology of Clays and Clay Minerals

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Applied Clay Science 71 (2013) 27–31

Contents lists available at SciVerse ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Layered double hydroxides with low Al content and new intercalate structures

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ARTICLE INFO

Article history:
Received 28 March 2012
Received in revised form 25 July 2012
Accepted 31 October 2012
Available online xxxx

Keywords:
Hydrolysis of metal-alcoholates
Intercalates with alkoxy anions
X-ray diffraction
Bragg distances

ABSTRACT

Layered double hydroxides (LDHs) containing Mg^{2+} and Al^{3+} as divalent and trivalent cations, respectively, have been synthesized by a procedure based on hydrolysis of a mixture of metal alcoholates, and have been characterized mainly by Wide Angle X-ray diffraction (WAXD) and Fourier Transform Infrared (FTIR) measurements. The used procedure is suitable to prepare LDHs with Al molar fractions, $x_{Al} = Al/(Al+Mg)$, as low as 0.1. The same LDH preparation procedure, for $x_{Al} < 0.1$, produces thermally stable intercalates with alkoxy anions, exhibiting layers similar to those of brucite, which maintain a high degree of order only in the hexagonal packing of the hydroxide groups. In particular, the basal periodicity increases from nearly 0.8 nm up to nearly 1.3 nm, due to the parallel staking of hexanolate groups in the clay galleries.

1. Introduction

Layered double hydroxides (LDHs) are a family of layered materials consisting of positively charged brucite-like host layers and charge-balancing interlayer anions (Allmann, 1968; Clearfield, 1988; Miyata, 1983; Newman and Jones, 1998). LDH compounds have found several applications mainly in molecular separations (Bish, 1980) and catalysis (Mas et al., 2008; Mckenzie et al., 1992; Sels et al., 1999). Recently the interest in such materials has been further increased by industrial applications of polymer nanocomposites including cationic (Carretero-Gonzales et al., 2008; Galimberti et al., 2007, 2009; Joly et al., 2002; Lepoittevin et al., 2003; Manias et al., 2001; Vaia et al., 1995) and anionic (Chen et al., 2004; Costantino et al., 2009; Gardner et al., 2001; Hibino, 2004; Hibino and Jones, 2001; Leroux et al., 2001; Liang et al., 2010; Ma et al., 2006, 2008; O'Leary et al., 2002; Sorrentino et al., 2007; Wu et al., 2005) clays.

The LDH structure is based on $M^{2+}(OH)_6$ octahedral units sharing edges in order to build $M(OH)_2$ brucite-like layers. The isomorphic substitution of some M^{2+} with M^{3+} cations with similar ionic radius renders the layer positively charged (Fig. 1). The whole structure is constituted by the stacking of such layers intercalating charge-balancing anionic species and water molecules. LDHs are represented by the general formula: $[M^{2+}_{(1-x)}M_x{}^{3+}(OH)_2]^{x+}\ A^{n-}_{x/n}\cdot mH_2O$, where the divalent and trivalent cations may be Mg^{2+}, Zn^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Al^{3+}, Fe^{3+}, Ga^{3+}, Cr^{3+}, etc., A^{n-} may be nearly any organic or inorganic anion, and x is the trivalent cation substitution degree (Cavani et al., 1991; Evans and Slade, 2006; Meyn et al., 1990; Rives, 2001).

Notwithstanding the claims that LDH compounds can be formed for x values in the general formula in the range 0.1–0.66 (Noweck et al., 2003), there are many indications that pure phases may form only for a narrower range $0.17 \le x \le 0.37$ (Bellotto et al., 1996; Brindley and Kikkawa, 1979; Costantino et al., 1998; Di Cosimo et al., 1998; Miyata, 1980; Vaccari, 1999).

This paper deals with LDHs containing Mg^{2+} and Al^{3+} as divalent and trivalent cations respectively. The synthetic procedure used is based on hydrolysis of a mixture of metal alcoholates in desired concentrations. It is shown that this procedure is suitable to prepare LDHs with low Al molar fractions (x_{Al}) and that, for $x_{Al} < 0.1$, can produce highly stable intercalates with alkoxy anions.

2. Experimental

2.1. Materials

Aluminium flakes (thickness 1.0 mm, 99.9%), magnesium granules (20–230 mesh, 98%), hexanol (98%) and methanol (anhydrous, 99.8%) were purchased by Sigma-Aldrich. Ammonia solution (30 wt.%) was obtained from Carlo Erba Reagenti. All materials were used as received.

2.1.1. Preparation of the hydrotalcites

Two sets of Mg-Al LDHs, with different Al molar fractions (x_{Al}), were obtained.

Samples of the first set, with $0.27 < x_{Al} < 0.42$, were prepared by hydrolysis of aluminium and magnesium hexanolates, starting from the metals in hexanol, according to the method described by Noweck et al. (example 8, Noweck et al., 2003).

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http://dx.doi.org/10.1016/j.clay.2012.10.016

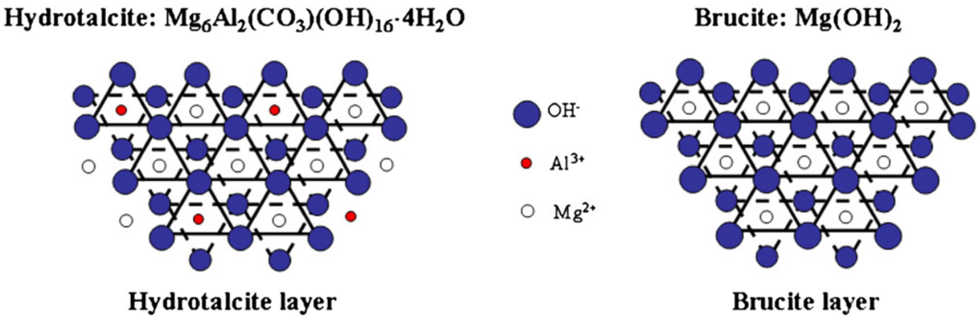

Fig. 1. Projections of an octahedral layer on the *ab* plane for: (a) hydrotalcite, Mg:Al = 3:1 ($x=0.25$); (b) brucite. Mg^{2+} and Al^{3+} ions are indicated by open and solid small circles, respectively.

Samples of the second set, with $0.09<x_{Al}<0.25$, were prepared by modifying Noweck's procedure and performing hydrolysis of a mixture of Aluminum hexanolate and Magnesium methanolate. A compound preparation is reported as an example of the applied experimental procedures.

2.1.2. Preparation of LDH with $x_{Al}=0.09$

0.23 g (0.008 mol) of aluminium flakes and 10 mL (0.08 mol) of hexanol were placed into a 1000-mL three neck flask. The mixture was heated to 423 K. The evolution of hydrogen indicated the start of the reaction between the metal and the alcohol. After about 1 h, the mixture was cooled to 343 K. 2 g (0.08 mol) of magnesium granules and 70 mL (1.72 mol) of methanol were added into the flask. The mixture of alcoholates was hydrolyzed in a receiver holding 70 mL (3.9 mol) of de-ionized and de-gassed water containing 0.52 mL (0.01 mol) of ammonia 30 wt.% A white precipitate formed immediately. The resultant slurry was aged for 48 h. Then it was vacuum dried at 343 K.

Commercial samples of hydrotalcites with $x_{Al}=0.32$ and 0.36 were obtained from Sasol Germany GmbH (trade name Pural Mg63 HT) and from Akzo Nobel (trade name Perkalite LD), respectively.

2.2. Characterization techniques

The evaluation of the trivalent cation substitution degree (x_{Al}) was effected by a Perkin-Elmer Mod.A Analyst 100 atomic absorption spectrometer, equipped with a deuterium background corrector, a premix, 10 cm titanium single slot burner head for flame experiments, using acetylene and nitrous oxide as fuel and oxidant respectively, and a 5 cm nitrous oxide burner head. Single-element Perkin Elmer Lumina Lamp hollow-cathode lamps were used. All measurements were carried out after the relative ashing and atomization curves had been studied for each element considered.

Wide-angle X-ray diffraction (WAXD) patterns with nickel filtered Cu-Kα radiation were obtained, in reflection, with an automatic Bruker D8 Advance diffractometer. For an easier comparison with most literature data, contrary to the case of our previous paper (Galimberti et al., 2007), the intensities of the WAXD pattern have not been corrected for polarization and Lorentz factors.

Infrared spectra were obtained at a resolution of 2.0 cm^{-1} with a Vector 22 Bruker spectrometer equipped with deuterated triglycine sulphate (DTGS) detector and a KBr beam splitter. The frequency scale was internally calibrated to 0.01 cm^{-1} using a He–Ne laser. 32 or 16 scans were signal averaged to reduce the noise.

TGA-FTIR analysis was carried out on a TG 209F1 manufactured by Netzsch Geraetebau connected to the Vector 22 Bruker spectrometer via a gas line and a 10 cm gas cell (TGA-FTIR interface), from 20 to 800 °C, at a heating rate of 10 °C, under N_2 flow. Infrared spectra of the evolved gases were collected every 60 s.

3. Results and discussion

3.1. Structural characterization of LDH samples

X-ray diffraction patterns (CuKα) in the 2θ range 2°–80° of LDH samples, as prepared by the procedure described by Noweck et al. (2003) and by the procedure described in the present paper are shown in Fig. 2A and B, respectively. The Miller indexes and Bragg

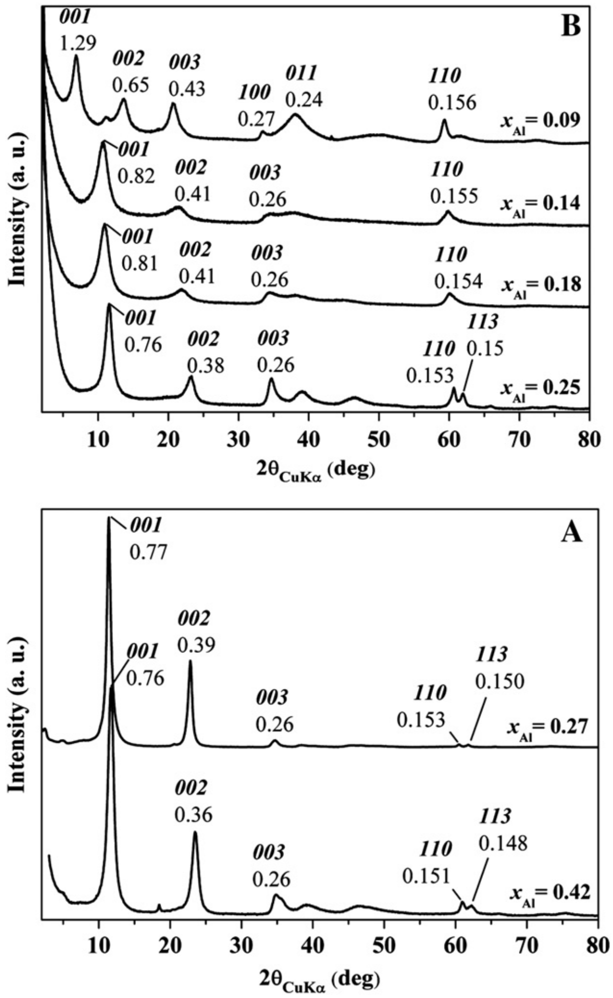

Fig. 2. X-ray diffraction patterns (CuKα) in the 2θ range 2°–80° of LDH samples, as prepared by the procedures: (A) described by Noweck et al. (2003); (B) of the present paper. The trivalent cation substitution degree (x_{Al}) and Miller indexes and Bragg distances of the main reflections of the LDH crystalline structures are indicated.

distances of the main reflections of the LDH crystalline structures are also indicated. The derived x_{Al}, both in the precursor solution and in the solid, Bragg distances and correlation lengths for 001 reflection are reported in Table 1.

It is clearly apparent that, for x_{Al} in the range 0.1–0.3, the new procedure produces LDH samples, although the 00ℓ reflections are definitely broader (Fig. 2B) than for the traditional procedure (Fig. 2A). In fact, the correlation length of the crystals along a direction perpendicular to the structural layers, as evaluated on the basis of the half-height width of the 001 reflections, is larger than 12 nm for the sample with $x_{Al}=0.27$ of Fig. 2A while is in the range 5–8 nm for the samples of Fig. 2B.

Particularly interesting are the results obtained for x_{Al} lower than 0.1. In fact a completely different pattern is observed, with three well defined 00ℓ reflections, which indicate an increase of structural order and an increase of the distance between adjacent structural layers from nearly 0.8 nm typical of the LDHs up to 1.29 nm. This suggests the formation of an intercalate structure analogous to those observed by Gardner et al. (2001) for alkoxide-intercalated derivatives. The observed spacing for hexanolate intercalate (1.29 nm) results much higher than those observed for lower alcohols (max value 0.92 nm). A shoulder is visible at $2\theta=11.1°$ ($d=0.8$ nm) and can be attributed to a LDH phase segregation.

For the LDH samples of Fig. 2, as well as for other similar samples prepared by us or described in the literature (Brindley and Kikkawa, 1979; Van Oosterwyck-Gastuche et al., 1967), the Bragg spacing relative to the 001, 002 and 110 reflections have been reported versus x_{Al} in Fig. 3A and B. In Fig. 3C, the d_{110} data have been re-plotted by using an enlarged scale, thus showing a significant decrease of this spacing with x_{Al}, although with a slope being smaller (of roughly of one order of magnitude) than for the 00ℓ reflections.

The large increase of $d_{00\ell}$ as a consequence of x_{Al} reduction has been attributed to the decrease of the layer charge density. Of course, the basal spacings (d_{001}, d_{002}) also depend on the chemical nature of the interlayer anions as well as on water content. The smaller increase of d_{110} has been attributed to the reduced size of Al ions with respect to Mg ions (Brindley and Kikkawa, 1979; Miyata, 1980; Van Oosterwyck-Gastuche et al., 1967).

The FTIR transmission spectra in the wave number range 4000–500 cm^{-1} of the samples whose X-ray diffraction patterns are reported in Fig. 2A and B are reported in Fig. 4A and B, respectively. The spectra of the samples obtained by the traditional procedure include the typical peak (1650–1640 cm^{-1}) of the bending mode of interlayer water and the typical peak (1368 cm^{-1}) of the stretching mode of interlayer carbonate (Frost and Kloprogge, 1999). On the other hand, all the spectra of the LDH samples obtained by the new procedure clearly present, (beside water and carbonate peaks) the absorbance peaks in the range 2960–2800 cm^{-1} typical of the alkyl groups (mainly hexyl but also methyl) as well as a peak in the range 1090–1080 cm^{-1} characteristic of alkoxy groups (Gardner et al., 2001; Valente et al., 2007), far from the C-O stretching of hexanol (1060 cm^{-1}). In summary, the FTIR information clearly indicates the presence in the galleries of the LDH, as prepared by the new procedure, of hexanolate and carbonate anions beside water.

It is worth adding that the spectra of the samples with lower Al content present a sharp peak at 3705 cm^{-1}, which is typical of hydroxyl stretching vibration of brucite crystals (Frost and Kloprogge, 1999).

Table 1
Characterization data of LDH samples, whose XRD patterns are reported in Fig. 2.

Solution $x_{Al}=Al/(Al+Mg)$	Solid $x_{Al}=Al/(Al+Mg)$	d_{001} (nm)	D_{001} (nm)
0.33	0.42	0.76	8.2
0.25	0.27	0.77	12.1
0.25	0.25	0.76	7.5
0.17	0.18	0.81	5.7
0.11	0.14	0.82	5.3
0.09	0.09	1.29	7.3

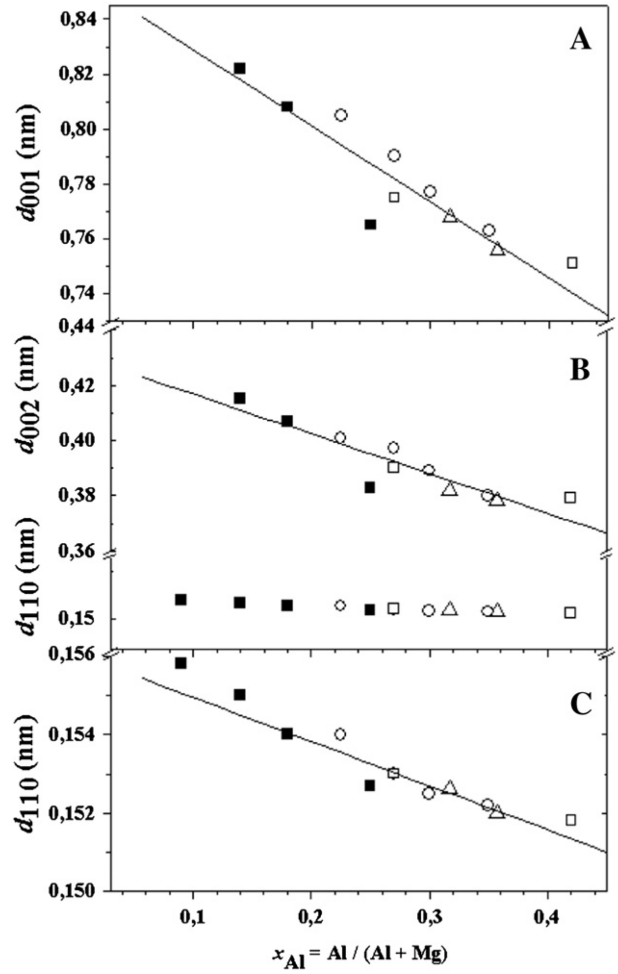

Fig. 3. Bragg spacing of 001 (A), 002 and 110 (B) reflections versus x_{Al} for LDH samples: (filled squares) samples of Fig. 2; (empty triangles) commercial samples; literature data from Brindley and Kikkawa (1979) have also been added as empty circles. The d_{110} data are also plotted by using an enlarged scale (C).

Particularly relevant in Fig. 4B is the close similarity of the FTIR spectrum of the sample presenting x_{Al} equal to 0.09 with that of the LDH sample with x_{Al} equal to 0.14, although this sample present completely different X-ray diffraction pattern (upper curve in Fig. 2B).

A possible interpretation of these data is that the hexanolate ions that are present in the clay galleries of all the samples of Fig. 4B, are organized in a parallel arrangement for the sample with $x_{Al}=0.09$, giving rise to the intercalate structure with periodicity of 1.29 nm.

3.2. Thermal stability of LDH with $x_{Al}=0.09$

The thermal stability of the sample with $x_{Al}=0.09$, whose X-ray diffraction pattern of Fig. 2B suggests the occurrence of an intercalate structure with a periodicity of 1.29 nm, has also been investigated. The X-ray diffraction pattern remains nearly unaltered as a consequence of thermal treatments up to nearly 523 K (Fig. 5A), as also reported by Massersmith and Stupp (1995), for a Ca-based LDH intercalated with poly(vinyl alcohol). The X-ray diffraction pattern of the same sample after treatment at 573 K, which involves the loss of a low molecular mass compounds (roughly 15 wt.% carbon dioxide and hexanol, as determined by TGA-FTIR analysis), is shown in Fig. 5B. The pattern remains essentially unaltered in the region with $2\theta>25°$, while in the low 2θ region the three basal 00ℓ reflections

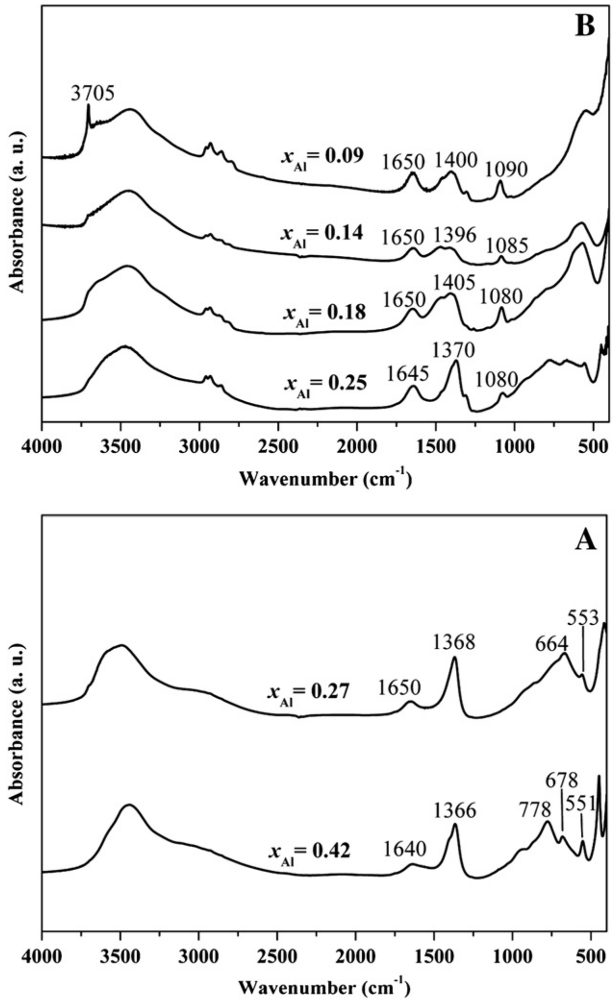

Fig. 4. FTIR transmission spectra in the wavenumber range 4000–500 cm^{-1} of the LDH samples, as prepared by the procedures: (A) described by Noweck et al. (2003); (B) of the present paper. The corresponding X-ray diffraction patterns are reported in Fig. 2A and B, respectively. The trivalent cation substitution degree (x_{Al}) and wavenumbers of the main absorbances are indicated.

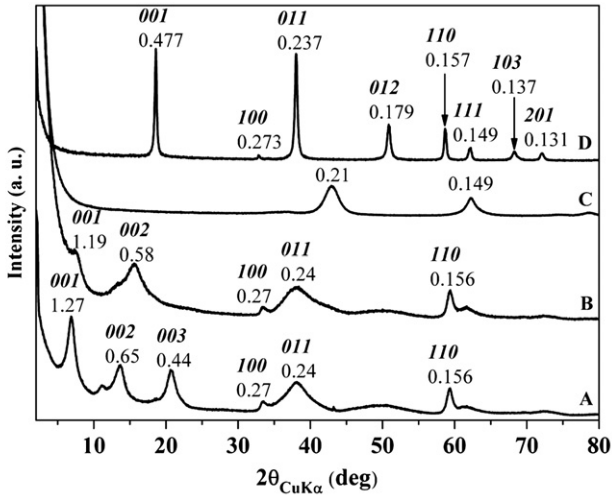

Fig. 5. X-ray diffraction patterns (CuKα) in the 2θ range 2°–80° of the LDH samples with $x_{Al} = 0.09$, whose X-ray diffraction pattern is shown in Fig. 2B, after thermal treatments at: (A) 523 K; (B) 573 K; (C) 600 K. For the sake of comparison the pattern of a well formed brucite ($Mg(OH)_2$) structure is reported in (D). The Miller indexes and Bragg distances of the main reflections are indicated.

are replaced by two broader reflections located at $d = 1.19$ and 0.58 nm. These results clearly confirm that the prepared LDH with $x_{Al} = 0.09$ exhibits an intercalate structure. It is also apparent that the thermal treatment reduces the correlation length of the crystals perpendicular to the structural layers and also produces a significant reduction of the basal periodicity, decreasing from 1.29 nm to 1.19 nm.

The X-ray diffraction pattern of the same sample after treatment at 600 K (Fig. 5C) clearly indicates the formation of magnesium oxide. Hence, the thermal treatments of the intercalate structure do not give rise to LDH, by removal of the organic modifier, but lead to a direct transformation of the intercalate structure into the oxide.

It is worth adding that both X-ray diffraction patterns of the intercalates of Fig. 5A and B present only two sharp reflections (different from the 00ℓ), i.e. those located at $d = 0.27$ nm and $d = 0.156$ nm. As clearly shown by a comparison with the X-ray diffraction of a well-formed brucite sample (Fig. 5D), these narrow reflections are in the same positions of the only hk0 reflections of brucite (100 and 110, respectively). In this respect, it is worth adding that also the broader reflection at $2\theta = 38.2°$ could be due to the short-range order of the brucite-like 011 planes.

This suggests that the thermally stable intercalate structure with low Al content (Fig. 5A) is constituted by disordered layers similar to those of brucite, where a high degree of order is maintained only in the hexagonal packing of the hydroxide layers. The large increase of periodicity perpendicular to these layers with respect to hydrotalcites (from nearly 0.8 nm up to nearly 1.3 nm) is possibly determined by a different organization of the charge-balancing anionic species, whose chemical nature (according to the FTIR spectra of Fig. 4B) is essentially independent on the trivalent cation substitution degree (x_{Al}). In particular, an intercalate structure, with a parallel staking of the hexanolate groups, could be suggested for the sample with $x_{Al} = 0.09$ and basal spacing of 1.29 nm.

4. Conclusions

The paper presents a synthetic procedure, based on hydrolysis of a mixture of metal alcoholates, which is suitable to prepare LDHs with low Al molar fractions ($x_{Al} = Al/(Al + Mg)$ as low as 0.1), which are characterized by large basal spacings (d_{001} up to 0.84 nm) as well as by increased d_{110} values (up to 0.156 nm). FTIR spectra indicate that the LDHs, as prepared according to this procedure, in their galleries present hexanolate anions beside carbonate anions and water.

The same LDH preparation procedures, for $x_{Al} < 0.1$, produce intercalates with alkoxy anions. In particular, the basal periodicity increases from nearly 0.8 nm up to nearly 1.3 nm, due to the parallel staking of hexanolate groups. These structures remain nearly unaltered as a consequence of thermal treatments up to nearly 523 K.

These intercalate structures present, beside three 00ℓ reflections, two sharp X-ray reflections corresponding to the 100 and 110 reflections of brucite. This indicates that the intercalate structures exhibit layers similar to those of brucite, which maintain a high degree of order only in the hexagonal packing of the hydroxide groups.

Analogous intercalates with different guests can be expected both by direct synthesis as well as by guest exchange procedures. Analogous intercalates with active guests, such as carboxylate anions (Itoh et al., 2003; Zhang et al., 2004) antimicrobial benzoates (Costantino et al., 2009; Sorrentino et al., 2007) and anti-inflammatory drugs (Mohanambe and Vasudevan, 2005) could be particularly suitable as fillers of polymer nanocomposites.

Acknowledgements

We thank Prof. Maurizio Galimberti for useful discussions. Financial support “Ministero dell'Istruzione, dell'Università e della Ricerca” is gratefully acknowledged.

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