Structural characterization of chlorine intercalated Mg-Al layered double hydroxides: A comparative study between mechanochemistry and hydrothermal methods

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Abstract

The chlorine intercalated Mg-Al layered double hydroxides (Mg-Al-Cl-LDH) with chemical formula of $\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2\text{Cl}_x$ were successfully prepared by the one step mechanochemical activation and hydrothermal methods. For a comparative study of the mechanically activated samples versus hydrothermally treated specimens, the structural features such as crystallite size, lattice strain, crystallinity, the interlayer spacing, and the unit cell volume of samples were examined. Results revealed that the phase purity of products was strongly influenced by different ion substitution degrees ($X=0.12, 0.18, 0.3$, and 0.42). From X-ray diffraction (XRD) analysis, Brucite and Hydrotalcite were dominant phases at low ions substitution (X), while Gibbsite and Hydrotalcite were main peaks at high ions substitution (X) for both methods. Pure Hydrotalcite was obtained in the midrange. The unit cell volume and interlayer spacing of LDH obtained from both processes was also strongly influenced by degrees of substitutions so that it shows a downward trend as ion content increased. FESEM and TEM observations revealed that the LDH powders possess a typical platelet-like microstructure, so that the average crystallite size of hydrothermal samples was greater than milled samples. Detailed analysis of the phase behavior and structural trends revealed that Mg-Al-Cl-LDH can be synthesized much more easily and rapidly in high energy ball mill as compared with an analogous LDH prepared by hydrothermal method. However, the product obtained from hydrothermal method showed the greater crystallinity.

Keywords: Hydrotalcite; Mg-Al-Cl-LDH; Mechanochemistry; Hydrothermal; Structural characteristics.

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1. Introduction

Hydrotalcite has been demonstrated to have great utility owing to their wide range of possible applications in catalysts carriers, drug delivery, gene delivery vectors, ion exchange, water treatment, and polymer processing aid [1].

Hydrotalcites (HTs) are ionic lamellar solids with positively charged layers (Brucite-like layers), in which some of the Mg^{2+} ions in octahedral positions are replaced by Al^{3+} ions [2]. The chemical formula of HTs is $\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2 \text{A}^{n-}_x$, where A^{n-} represents the charge balancing anions. Basically, the interlayers of HTs are separated by water molecules and anions such as CO_3^{2-} , Cl^- , SO_4^{2-} , OH^- or NO_3^- [3]. Among those compensating anions, chlorine intercalated layered double hydroxide (Mg-Al-Cl-LDH) is preferred as the ease of anion exchange is improved [4]. In general, chloride form possesses versatile properties in biomedical application due to rich functionality, extensive availability, good biocompatibility, controlled release of carried gene, and potential capability of target delivery [5,6]. Mg-Al-Cl-LDH can then be completely decomposed by acidic body fluid and releases the adsorbed drug or gene after they reach the delivery point [7].

Many different methods have been applied for synthesis of HTs including co-precipitation [8], hydrolysis [9], sol-gel [10], microwave-assisted structure reconstruction [11], hydrothermal [12], sonication [13] and mechanical alloying (MA) [14]. The most conventional method is the co-precipitation of the metal salts from a mixed solution at room temperature and constant pH. It has been demonstrated that not only this method is time consuming and produces large amounts of wastes, but also the final precipitate comprises substantial amounts of amorphous Brucite ($\text{Mg}(\text{OH})_2$) and Gibbsite ($\text{Al}(\text{OH})_3$) of questionable composition [15]. Therefore, HTs requires extend aging at elevated temperature or under hydrothermal conditions in order to reach well defined crystallinity [7].

The search for new procedures that allows the rapid production of LDH compounds, which can easily be scaled to commercial size, with appropriate structural characteristics has directed the attention to solid state reactions owing to its simplicity and versatility [16]. In mechanochemistry process, melting is not necessarily occurring and products with nanostructural features and good homogeneity are produced [17]. By employing this process, large amounts of solutions, the emission of noxious gases and the release of wastewater can be avoided [18]. Hence, this solvent-free, simple, and cost effective method is potentially a viable route for the mass preparation of HTs.

The synthesis of different anion intercalated LDH via mechanochemical activation method have been studied by numerous researchers. The preparation of Mg-Al-LDHs through mixing magnesium hydroxide with aluminum nitrate, sulfate, and chloride in high energy ball mill was reported by Isupov et al. [19]. Khusnutdinov et al. [20] utilized the same procedure to produce hydroxycarbonate form of HT-like. The synthesis of Zn-Al-LDHs via grinding and autoclaving the solid precursors at 150 °C for 1day was also investigated by Chitrakar et al. [21].

Considering all characteristics of chlorine intercalated LDH prompted the work reported here where a series of HTs have been synthesized under mechanochemistry and hydrothermal conditions with different amount of ion substitutions. The as-obtained products were characterized by XRD, FESEM, TEM, and EDS techniques to compare structural trends and phase behavior of products. The crystallite size, lattice strain, crystallinity degree, interlayer spacing, and unit cell volume of powders were also determined.

2. Experimental procedures

2.1. Synthesis of Mg-Al-Cl-LDH by mechanochemistry method

Magnesium chloride (99%), Aluminum chloride (99 %), and Sodium hydroxide pellets (97%) were purchased from ACROS and used as received. The mechanochemical activation was done in a high energy ball mill (8000M Mixer/Mill) using hardened chromium steel vials (vol. 65 ml) under air atmosphere. The weight ratio of ball-to-powder (BPR) was 10:1. To synthesize $\text{Mg}_{0.82}\text{Al}_{0.18}(\text{OH})_2\text{Cl}_{0.18}$, the desired amounts of MgCl_2 , AlCl_3 , and NaOH were milled at three different milling times (15, 60, and 300 min). The mole ratio of magnesium to aluminum was equal 4. The substitution degree of Cl^- was chosen equal 0.18; hence the mechanochemical reaction (R1) was as follows:

The designed degree of substitution of chlorine was demonstrated by the x value in the general formula of $\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2\text{Cl}_x$, where x values were chosen equal to 0.12, 0.18, 0.3, and 0.42, so the synthesized nanopowders were designated as M1, M2, M3, and M4, respectively. Thus, the target composition was adjusted according to the following general reaction (R2):

The powders were washed three times with deionized water (20 ml) on a paper filter, and then were dried under oven at 80°C for 1h.

2.1. Synthesis of Mg-Al-Cl-LDH by hydrothermal method

Mg-Al-Cl-LDH with different amount of ions substitutions (0.12, 0.18, 0.3, and 0.42) was prepared via hydrothermal technique according to the following recipe. The products were labeled as H1, H2, H3 and H4, respectively. The target composition was adjusted according to Table 1.

Take $\text{Mg}_{0.82}\text{Al}_{0.18}(\text{OH})_2\text{Cl}_{0.18}$, for instance, 1.8006 g of Aluminum chloride and 9.0256 g of Magnesium chloride were dissolved into 20 mL of deionized water and stirred at ambient temperature. 8 g of NaOH was dissolved into 20 mL of deionized water until clear solution was obtained. The solution was put into a burette and allowed to drop into the Mg/Al solution until the pH reaches 10. Then the whole mixture was transferred to a Teflon lined stainless steel autoclave. The

autoclave introduced into an electric oven at 120°C for 2h. The supernatant was filtered and washed three times with deionized water (20 ml).

2.3. Characterization techniques

The x-ray analysis was performed on a Bruker D8 Advance ECO using $Cu-K\alpha$ radiation ($\lambda \approx 1.54\text{\AA}$). The patterns were scanned from 5 to 80 degrees 2θ at a step size of 0.03 degrees. The XRD profiles were compared to standards compiled by the Joint Committee on Powder Diffraction and Standards (JCPDS), which involved card #14-0191 for Hydrotalcite, #44-1482 for Brucite, and #01-0264 for Gibbsite. The crystallite size and lattice strain of the powders were measured by the Williamson-Hall equation (I) [22]:

$$B\cos\theta = 0.9\lambda/D + \eta\sin\theta \quad (I)$$

where λ is the wavelength of $Cu-K\alpha$ (0.154056 nm), D is the crystallite size, η is the internal micro-strain, θ is the Bragg angle (degree), and B is the full width half max (in radians). The values of η and D were obtained by plotting $B\cos\theta$ versus $\sin\theta$, where η and $0.9\lambda/D$ represent the slope and the intercept of the line, respectively. Based on equation (II), the crystallinity degree (X_c) was obtained from the XRD profiles using the following [23]:

$$X_c = 1 - \left(\frac{V_{015/009}}{I_{009}} \right) \quad (II)$$

where X_c is the crystallinity degree, I_{009} is the intensity of (009) plane, and $V_{015/009}$ is the hollow between (015) plane at $2\theta = 39.13$ and (009) plane at $2\theta = 34.73$. The interlayer spacing (d) can be determined by averaging the basal peaks according to the equation (III) [24]:

$$d = \frac{1}{n} (d_{(003)} + 2d_{(006)} + \dots + nd_{(00n)}) \quad (III)$$

The lattice parameters (a , and c) can be determined for (003) and (110) Miller's planes at $2\theta = 11.49$ and $2\theta = 60.46$ from the following relation (IV):

$$\frac{1}{d^2} = \frac{4}{3} \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \quad (IV)$$

where h , k , and l are the Miller indices. The unit cell volume (V) of samples was also calculated using the following equation [25]:

$$V = (a^2c)\sin 60^\circ \quad (V)$$

The size and morphological features of the specimens were characterized using FE-SEM (FEI Helios Nanolab 400 SEM) and TEM (JEOL JEM 1200 EXII) that operated at the acceleration voltage of 18 kV and 120 kV, respectively. EDS analysis attached to the FESEM was used to determine the chemical constituents in selected areas.

3. Results and discussions

3.1. Phase determination

Fig 1 shows XRD patterns of all samples ($\text{Mg}_{0.82}\text{Al}_{0.18}(\text{OH})_2\text{Cl}_{0.18}$) milled at three different milling times (15, 60, and 300 min). It should be mentioned clearly that Hydrotalcite is present as indicated by the lettered peaks (HT) that arise from the Hydrotalcite. Based on Fig. 1a, the main products of 15 min milling run were Brucite and HT. The mechanochemical reaction was not completed in this time frame as evidenced by the presence of Brucite, while it completely vanishes with increasing of milling time to 60 min, and a pure phase composition of chlorine intercalated HT was formed. This trend continued with further increase in the milling time up to 300 min while a partial trace of Periclase (MgO) appeared. This confirms that HT decomposed slightly as the milling time increased. Fig. 1b and 1c display the magnified XRD region between $2\theta = 9^\circ$ to 14° , and $2\theta = 21^\circ$ to 25° , respectively. According to this figure, the reflection intensities of HT peaks increased from 15 to 60 minutes of milling. In contrast, it decreased and became broader with extra milling time (300 min). This result suggests that proper crystalline structure was formed at 60 min milling time. In addition, the peaks corresponding to Mg-Al-Cl-LDH were shifted gradually toward higher d spacing owing to presence of chlorine ions in hydrotalcite structure, and changes in lattice parameters. These outcomes demonstrated that mechanosynthesized Mg-Al-Cl-LDH were affected strongly by milling time (15-300 min).

The XRD patterns of Mg-Al-Cl-LDH with different amount of ions substitutions ($X = 0.12, 0.18, 0.3$, and 0.42) prepared by hydrothermal (H) and mechanochemistry (M) are exhibited in Fig. 2. As can be seen, it is clear that there is close structural similarity between the two compounds from the nearly identical diffraction data. Fig. 2a shows the XRD profiles of hydrothermally treated samples. From these profiles, all the main peaks belonged to the characteristic peaks of HT (JCPDS#14-0191). At low Al substitution (0.12) Brucite and HT co-exist, and at very high Al substitutions (0.42) Gibbsite appears as additional phase with HT. Pure HT was obtained in the midrange (0.18), while HT is dominant phase at x equal 0.3, and a weak peak corresponding to Gibbsite still remains. Fig. 2b illustrates mechanosynthesized samples at four different ion replacements. Based on these patterns, all the characteristic peaks of HT can be easily recognized. It is worthy to note that the phase identification of the milled samples is almost the same as the hydrothermal powders; however the peak broadening increased as the ion contents increased.

The intensity differentiation and the line broadening of XRD patterns in the range of $2\theta = 7^\circ$ to 25° are shown in Fig. 3. According to this figure for hydrothermally treated samples (Fig. 3a), with increasing ion substitution of 0.18 and 0.42 (H2, and H4), the intensities of HT peaks increased and the peaks became narrower, while it decreased drastically for H1 and H3 samples and the peaks became broaden. In addition, the peaks corresponding to HT for H2 sample were shifted gradually toward higher d spacing which may due to changes in lattice parameters. Based on Fig. 3b, similar trend can be also observed for the milled samples; however the peak intensity of HT became more intense for M2 among other samples. The results suggest that the product (Mg-Al-Cl-LDH) with ion replacement of 0.18 (H2, and M2) and greater phase purity was formed successfully through both hydrothermal and mechanochemistry methods.

3.2. Crystallite size and lattice strain

The crystallite size (D), and lattice strain (η) of products synthesized by hydrothermal and mechanochemistry methods as a function of ion substitutions degree ($X = 0.12, 0.18, 0.3$, and 0.42) are shown in Fig. 4. According to the calculated data, the average crystallite sizes and lattice strains of HT out of both processes were considerably affected by different ion substitutions (Fig. 4a). The average crystallite size of specimens prepared hydrothermally was obtained in the range of 17.9 ± 0.3 to 20 ± 0.2 nm (H1-H4) indicating nonlinear trends. The evaluation of lattice strain revealed that the trend of lattice strain magnitude was upward as ion replacements increased from 0.12 to 0.3 (0.0006 ± 0.00001 to 0.0209 ± 0.0002), while it became downward with further substitution to 0.42, which was 0.0089 ± 0.0001 . For the milled samples (Fig. 4b), the crystallite size was gained in the range of 12 ± 0.2 to 18 ± 0.4 , while it reached a maximum value of 17.9 ± 0.2 in M2 sample ($X = 0.18$). In contrast, the reverse trend occurred for the lattice strain value, and it dropped considerably from 0.147 ± 0.003 to 0.0125 ± 0.0004 when ion replacement rose from 0.12 (M1) to 0.18 (M2). These values increased gradually by further ion substitutions (0.3 and 0.42). The determined amounts of lattice strain indicated that, the average lattice strain influenced considerably by increasing ion replacements. It should be noted that the average rate of crystallite size in hydrothermally treated samples is higher than that in milled samples. This indicates that the product with higher crystallinity degree obtained from hydrothermal process as compared with milled samples. The crystallinity degree of products will be discussed in more detail later.

3.3. Crystallinity degree (X_c)

Fig 5 shows the FWHM values at different Bragg angles for hydrothermal and milled samples. In general, the FWHM values demonstrated the occurrence of anisotropic line broadening, which may be caused by three factors: the presence of stacking faults, the existence of dislocations and none equivalence of the grain sizes along different crystallographic directions [17]. This phenomenon here was presumably owing to the grain size anisotropy. The FWHM values of three different ion substitutions ($X = 0.18, 0.3$, and 0.42) are exhibited in Fig 5a, b and c, respectively. From the obtained data, the average values of FWHM in milled specimens for all different ion replacement are greater than the hydrothermally treated ones. This outcome is good agreement with the calculated results of crystallite size of both processes which is indicating the greater crystallite size belongs to lower FWHM values.

For further evaluation of the structural features, the degree of crystallinity of the powders was determined, as shown in Fig 6. In general, control of the crystallinity of HT is necessary for its biological applications. As can be seen, the fraction of crystalline phase of hydrothermally prepared samples is almost twice as milled samples. Based on Fig 6, with increasing of the ion content (X) from 0.18 to 0.42 in hydrothermal samples (H2-H4), the crystallinity degree decreased moderately from 83 ± 4 to $74 \pm 3\%$, respectively. Similarly, this downward trend was obtained in milled samples,

which was $38\pm 2\%$ in $X = 0.18$ (M2), and reached a minimum, $16\pm 1\%$, at $X = 0.42$ (M4). Results demonstrated that the product with higher crystalline phase can be produced through hydrothermal method.

3.4. Lattice parameters and interlayer space

To confirm the formation of HT, the lattice parameters of specimens were calculated and compared with standard values. Fig 7 exhibits the a -axis, c -axis values, and unit cell volume of HT as a function of three different ion contents (0.18, 0.3, and 0.42). Based on the standard data (STD) of HT (JCPDF#14-0191), a -axis and c -axis values were $3.07\text{\AA}$, and $23.23\text{\AA}$, respectively. As compared with the data calculated from equation IV, the a -axis and c -axis values for hydrothermal (Fig 7a) and milled samples (Fig 7b) were different; however it shows an overall descending trend as ion content (X) increased from 0.18 to 0.42. It can also be seen that chlorine intercalated LDH led to small changes in the a -axis and c -axis as compared with conventional type of HT. According to Fig. 7c, with increasing of X content from 0.18 to 0.42, unit cell volumes of the hydrothermal and milled samples decreased considerably from 196.89 ± 0.01 to $184.94\pm 0.02\text{ \AA}^3$ and 192.7 ± 0.02 to $185.6\pm 0.0\text{ \AA}^3$, respectively. From the data, it is clear that the disparities in values of unit cell volume resulted mainly from growths in the c constant, rather than from the a parameter. This shrinkage of unit cell volume can also be attributed to the more substitution of chlorine in HT structure. These findings prove that the structural features of the mechanosynthesized and hydrothermally treated Mg-Al-Cl-LDH were affected strongly by ion replacements.

Fig. 8 contains a plot of basal plane d-spacing as a function of ion substitution ($X = 0.18, 0.3$, and 0.42) and a comparison study of mechanochemical activation and hydrothermal methods. The data demonstrated that the interlayer spacing of Brucite like structure is strongly influenced by ion contents (X), so that it declined from $7.949\pm 0.001\text{ \AA}$ to $7.745\pm 0.002\text{ \AA}$ for milled samples (M2-M4). These values also decreased from $7.895\pm 0.001\text{ \AA}$ to $7.752\pm 0.002\text{ \AA}$ for hydrothermal specimens (H2, H3), and then increased to $7.797\pm 0.002\text{ \AA}$ as ion content enhanced to 0.42 (H4). It is worthy to note that the reduction of interlayer spacing in higher ion contents is, likely, due to the shrinkage of the basal space by the removal of water. This basal spacing is also very sensitive to the type of anion in the gallery.

3.5. Microscopic observations

The FESEM and TEM images of the synthesized powders with ion replacement of 0.18 (H2, and M2) are shown in Fig. 9. Fig. 9a illustrates that the LDH powders possesses a typical platelet-like microstructure which are assembled by numerous interlaced curved nanoplates. The enlarged FESEM image in Fig. 9b displays the detailed morphologies of the LDH nanopowders that has a compact, homogeneous and well-crystallized nanostructure. As shown in Fig. 9c, the hydrothermal nanopowders (H2) is composed of layered structure with mean particle size of about 40 nm. As can be seen in Fig. 9d, the milled nanoparticles (M2) exhibit a high tendency to agglomerate due to their large surface to volume

ratio. Precise examination at higher magnification demonstrates that each agglomerate comprises of many fine round particles with platelet morphology (Fig. 9e). Generally, solid state diffusion dominates the coalescence of solid-like particles particularly in milled specimens [26]. TEM image of milled sample presents laminar structure which is essentially characteristic for hydrotalcite mineral and the stacking of the layers. The ill-defined crystallite structures of the milled sample demonstrates agglomerations of the crystallites. The average particle size of 30 nm that is observed for M2 by TEM is smaller than the 40 nm that is seen for H2. This shows that the average particle sizes from TEM are significantly bigger than the crystallite sizes extracted from the XRD profiles, given that XRD only probes the size of the crystalline domains of the agglomerated particles. The results are in good accordance with literature [27].

The chemical composition of hydrothermal treated and milled samples (H2, and M2) was also examined through EDS analysis from which typical profiles have been selected and presented in Fig. S1 (supplementary data 1). To provide more accurate results, the EDS analysis recorded over three different points on the hydrothermal (Fig. S1a) and milled samples (Fig. S1b). From the EDS profiles, the main components of both samples were oxygen, magnesium, aluminum, and chlorine. Note that contamination owing to the excessive wearing of vials and balls was absent. From the obtained data, the average amount of magnesium and aluminum present on hydrothermal sample (H2) was calculated to be 32.41 and 9.92 mass %, respectively, while this value for milled sample (M2) was 32.77 and 8.94 mass %, respectively. The mole ratio of magnesium to aluminum was also achieved 3.62, and 4.07 for H2 and M2, respectively, which was a little lower than the actual mole ratio (4.55). It should be mentioned that the similarity of the recorded data over three different points on the both samples indicates a homogenous microstructure.

4. Conclusions

In this study, Mg-Al-Cl-LDH was successfully synthesized through hydrothermal and mechanochemical activation processes. Two methods yielded a product with very similar structural characteristics. Results demonstrated that the formation and structural features of Mg-Al-Cl-LDH were influenced significantly by different ion substitutions (0.12, 0.18, 0.3, and 0.42). Based on phase analysis, Brucite and HT were main phases at low ion substitution ($X = 0.12$), while Brucite was replaced by Gibbsite at high ion substitution ($X = 0.42$) in both methods. Hydrotalcite with appropriate purity was formed in the midrange. The average values of FWHM in milled specimens for all different ion replacement were higher than the hydrothermally treated ones. The outcomes indicated that the interlayer spacing of HT obtained from both procedures decreased as ion content increased. Microscopic evaluations showed the platelet like structures of Mg-Al-Cl-LDH samples with greater mean particle size of hydrothermal samples as compared with milled ones. Results demonstrated that the product with high crystallinity degree was obtained from hydrothermal method which can be used

as a promising LDH for biomedical application especially for gene delivery. However, mechanochemistry as a facile and simple method can be utilized for the mass production of Mg-Al-Cl-LDH with acceptable crystalline phase.

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List of Figures Caption

Fig. 1 XRD profiles of milled samples ($\text{Mg}_{0.82}\text{Al}_{0.18}(\text{OH})_2\text{Cl}_{0.18}$) as a function of milling time (a), the magnified region between $2\theta = 9^\circ$ to 25° (b), and $2\theta = 21^\circ$ to 25° (c).

Fig. 2 XRD profiles of samples as a function of ion contents degree (X) prepared by Hydrothermal (a) and Mechanochemistry methods (b).

Fig. 3 XRD profiles along with the magnified regions between $2\theta = 7^\circ$ – 25° for samples prepared by Hydrothermal (a) and Mechanochemistry methods (b).

Fig. 4 Crystallite size, and lattice strain of samples prepared by Hydrothermal (a) and Mechanochemistry methods (b) as a variation of different ion contents (X).

Fig. 5 FWHM of milled (M) and hydrothermally (H) treated samples at three different ion contents (X): (a) $X=0.18$, (b) $X=0.3$, and (c) $X=0.42$.

Fig. 6 Crystallinity degree of samples prepared by Hydrothermal (H), and Mechanochemistry (M) methods as a variation of ion contents (X).

Fig. 7 lattice constants of hydrothermal specimens (a), mechanochemical samples (b), and Unit cell volume of specimens (c) prepared by Hydrothermal (H), and Mechanochemistry (M) methods as a variation of ion contents (X).

Fig. 8 Interlayer spacing of specimens prepared by Hydrothermal (H), and Mechanochemistry (M) methods as a function of ion contents degree(X).

Fig. 9 (a,b) FESEM and (c) TEM images of hydrothermal sample (H2). (d,e) FESEM and (f) TEM images of milled sample (M2).

List of Table Caption

Table 1 Details of solution components.

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Series	Degree of substitution $\text{Mg}_{(1-x)}\text{Al}_x(\text{OH})_2\text{Cl}_x$	MgCl ₂ (g)	AlCl ₃ (g)	Phase composition	Mg/Al
H1	0.12	9.0256	1.8006	Mg _{0.88} Al _{0.12} (OH) ₂ Cl _{0.12}	7.33
H2	0.18	8.4102	2.7009	Mg _{0.82} Al _{0.18} (OH) ₂ Cl _{0.18}	4.55
H3	0.3	7.1794	4.5015	Mg _{0.7} Al _{0.3} (OH) ₂ Cl _{0.3}	2.33
H4	0.42	5.9487	6.3021	Mg _{0.58} Al _{0.42} (OH) ₂ Cl _{0.42}	1.38

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Structural characterization of chlorine intercalated layered double hydroxide: A comparative study between mechanochemistry and hydrothermal methods

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