

# Delamination and Re-assembly of Surfactant-Containing Li/Al Layered Double Hydroxides

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Exchange of the chloride anion intercalated in  $[\text{LiAl}_2(\text{OH})_6]\text{Cl}$  with a range of surfactants is reported. Attempts to delaminate (or exfoliate) the surfactant-exchanged intercalates, where the surfactant was an alkyl sulfate, were unsuccessful. In contrast, delamination of the layered double hydroxides  $[\text{LiAl}_2(\text{OH})_6][\text{C}_{12}\text{H}_{25}\text{C}_6\text{H}_4\text{SO}_3 \cdot n\text{H}_2\text{O}]$  and  $[\text{LiAl}_2(\text{OH})_6][\text{C}_8\text{H}_{17}\text{C}_6\text{H}_4\text{SO}_3 \cdot n\text{H}_2\text{O}]$  was successful. The necessity of the alkyl chain of the surfactants was demonstrated by the failure of  $[\text{LiAl}_2(\text{OH})_6][\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3 \cdot n\text{H}_2\text{O}]$  to delaminate. The delamination of the unique Li/Al LDH is thus found to be dependent on the guest surfactant structure in terms of both chain length and head group moiety.

## Introduction

The preparation of highly dispersed phases from layered materials has attracted considerable interest, particularly as a means of preparing new nanocomposites.<sup>1-4</sup> To fully exploit this versatile approach, it is desirable that a wide range of compounds can be made to delaminate / exfoliate. The bulk of previous studies have focused on dispersions of clay minerals, as these have a relatively low layer charge density and can be readily modified by exchange of the interlayer cations to give systems that delaminate under very mild conditions.<sup>5</sup> Layered double hydroxides (LDHs), on the other hand, have positively charged layers, with exchangeable anionic guests.<sup>1</sup> Examples of delamination of LDHs are relatively limited, the first example being the delamination of  $\text{Zn}_2\text{Al}(\text{OH})_6(\text{C}_{12}\text{H}_{25}\text{SO}_4)$  in refluxing butanol.<sup>6,7</sup> More recently  $\text{Mg}_2\text{Al}(\text{OH})_6(\text{C}_{12}\text{H}_{25}\text{SO}_4)$  has been delaminated by heating to reflux in acrylate monomers.<sup>8</sup> Another reported method involved a glycine containing Mg/Al LDH heated to reflux in formamide,<sup>9</sup>

While the vast majority of LDHs contain  $\text{M}^{2+}$  and  $\text{M}^{3+}$  cations, the Li/Al LDHs are a unique exception. Hexagonal  $[\text{LiAl}_2(\text{OH})_6]\text{Cl}$  is readily synthesised by stirring a suspension of gibbsite in aqueous lithium chloride,<sup>10</sup> while the rhombohedral product is obtained by using the  $\text{Al}(\text{OH})_3$  polymorphs, bayerite or nordstrandite.<sup>11</sup> We were interested in delamination of Li/Al LDHs as a potential route to nanoparticulate  $\text{Al}(\text{OH})_3$  where the particle size may be controlled by the nature of the material used

in the initial synthesis of the intercalate. Here we report the delamination of Li/Al LDHs, where the success of the delamination is highly dependent on the nature of the surfactant guest.

## Experimental

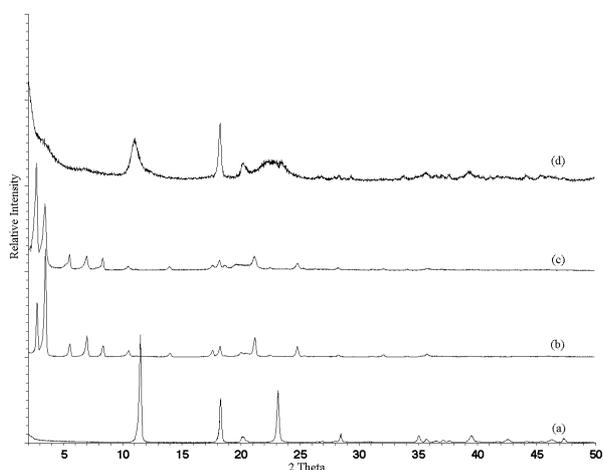
$[\text{LiAl}_2(\text{OH})_6]\text{Cl}$ ,  $[\text{LiAl}_2\text{-Cl}]$ , was synthesised following the published procedure.<sup>10</sup> Powder X-ray diffraction data were recorded using a Bragg Brentano type Siemens D500 diffractometer with  $\text{CuK}_\alpha$  radiation (40 kV and 30 mA) at a scanning rate of  $1.2^\circ/\text{min}$ , a step of  $0.2^\circ$  over a  $2\theta$  range of  $2-80^\circ$ . Samples were viewed under a scanning electron microscope (Phillips XL30) at 10-20kV, and a working distance of 5-10 mm, after coating with gold. Transmission electron micrographs were acquired with a JEOL JEM 2011, using an accelerating voltage of 200 kV. Small angle X-ray scattering experiments were performed using a NanoSTAR SAXS instrument equipped with a 2-D detector using a  $\text{Cu K}_\alpha$  beam ( $\lambda = 0.154184 \text{ nm}^{-1}$ ), 130  $\mu\text{m}$  in diameter at the sample position. Scattered beams were detected by a position sensitive area detector placed at a distance of 0.65 m from the sample resulting in a  $q$  range of  $0.1 - 3 \text{ nm}^{-1}$ . Here  $q = 4\pi\sin\theta/\lambda$ ,  $2\theta$  is the scattering angle and  $\lambda$  is the wavelength of the X-rays. The real space dimension,  $d$ , is often related to  $q$  by  $2\pi/d$ . The 2-D data were radially averaged and the 1-D intensities were corrected for background scattering from butanol and electronic noise.

## Surfactant-LDH preparation

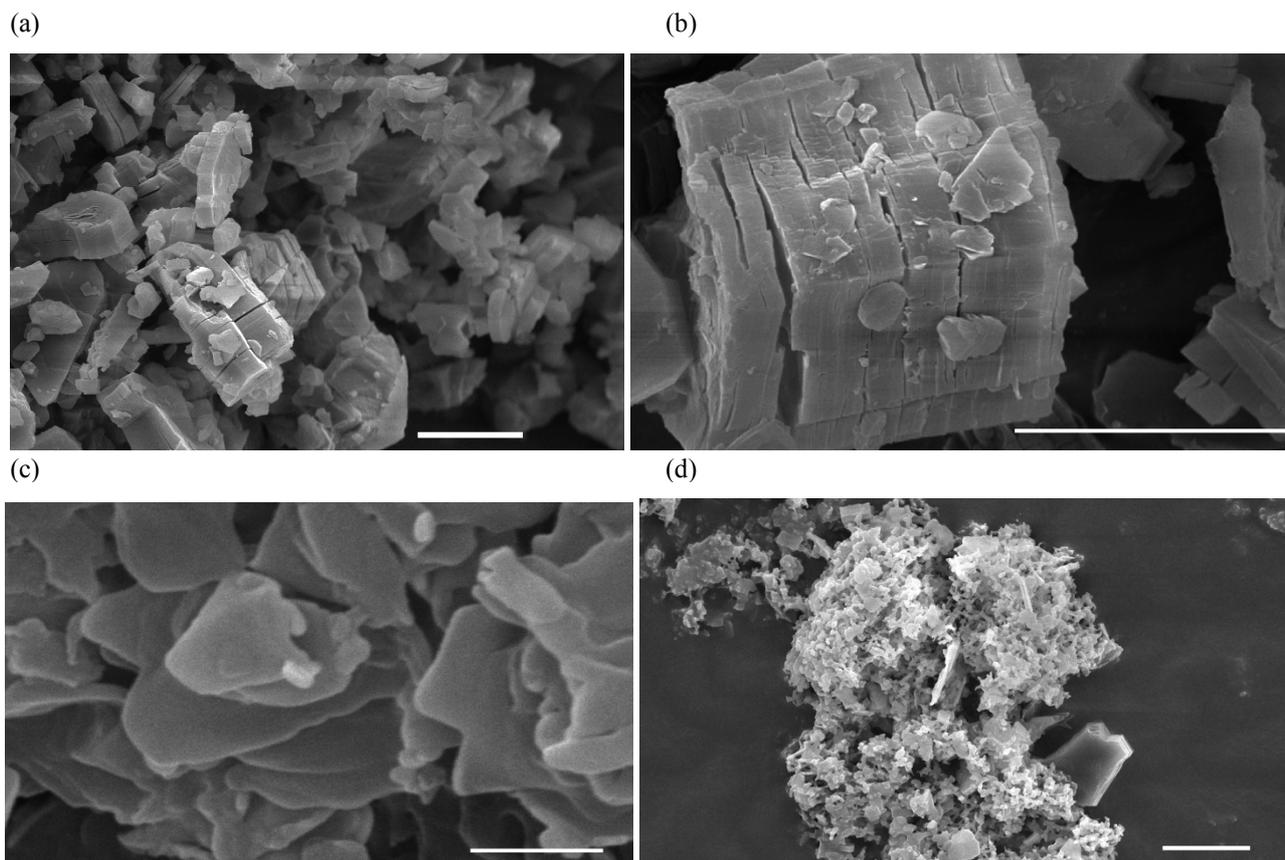
The preparation of surfactant modified  $[\text{LiAl}_2(\text{OH})_6]\text{Cl} \cdot \text{H}_2\text{O}$  LDH was realised by an anion exchange reaction in deionised water with a 1.54 molar excess of each of the surfactants: sodium octyl sulfate (SOS), sodium dodecyl sulfate (SDS), sodium 4-octylbenzenesulfonate (OBS), and sodium dodecylbenzenesulfonate<sup>12</sup> (DBS) by stirring at room temperature for 1 hour, followed by filtration and washings with distilled water. The residues were dried in an oven at  $50^\circ\text{C}$ , and stored in a desiccator. Intercalation of surfactants was monitored by X-ray diffraction. Combustion analysis indicated greater than 80% exchange was achieved in all cases.

## Exfoliation and reassembly of surfactant-LDH

Following the literature procedure,<sup>7</sup> exfoliation of the surfactant-exchanged LDHs was achieved by refluxing 1.5 g surfactant intercalated  $[\text{LiAl}_2(\text{OH})_6]\text{X} \cdot \text{H}_2\text{O}$  in 1 L butanol at  $120^\circ\text{C}$  for 16 hours. The resulting suspension (formed where  $\text{X} = \text{OBS}$  and



**Fig. 1** Diffraction patterns of (a)  $[\text{LiAl}_2\text{-Cl}]$  (b)  $[\text{LiAl}_2\text{-OBS}]$  (c)  $[\text{LiAl}_2\text{-OBS}]$ (recovered), and (d)  $[\text{LiAl}_2\text{-Cl}]$ (recovered).



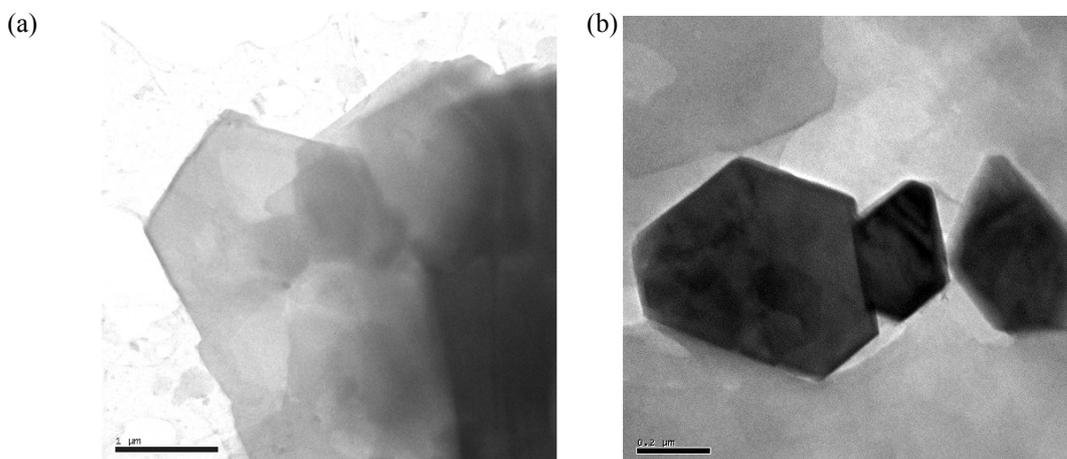
**Fig. 2** Scanning electron micrographs of (a)  $[\text{LiAl}_2\text{-Cl}]$  synthesised from gibbsite with average crystallite size of  $\sim 5 \mu\text{m}$  (b) after reaction with OBS, (c) after exfoliation and evaporation of suspension, and (d) after reassembly of LDH by addition of chloride ions to suspension. (bar,  $10 \mu\text{m}$ , except (c),  $1 \mu\text{m}$ )

DBS) was decanted from any unsuspended material, which was isolated washed and weighed to determine the extent of exfoliation. When tetraethylammonium chloride was added to the exfoliated suspension there was immediate precipitation of the exfoliated particles as a bulky white solid which was isolated and characterised by powder XRD and SEM.

## Results and Discussion

$[\text{LiAl}_2(\text{OH})_6]\text{Cl}$ ,  $[\text{LiAl}_2\text{-Cl}]$ , was synthesised following the published procedure,<sup>10</sup> and the chloride was readily exchanged with dodecyl sulfate (DS), as indicated by combustion analysis and powder XRD (interlayer spacing increased from  $0.77 \text{ nm}$  to  $2.59 \text{ nm}$ , Figure S1). This surfactant was selected as all other reports of LDH delamination involve DS exchanged intercalates.<sup>6-9</sup> Attempts to delaminate this material by heating to

reflux in butanol were unsuccessful. It has been reported that the delamination process is sensitive to the nature of the starting material, particularly the extent of hydration.<sup>7</sup> Drying the product for different times, and at varying temperatures did not, however, change the result. A number of other surfactants were then tested, including octyl sulfate (OS), octylbenzenesulfonate (OBS) and dodecylbenzenesulfonate (DBS). The surfactant-containing LDHs were characterised by combustion analysis and powder XRD; anion exchange of greater than 80% was achieved in all cases. Scanning electron micrographs of the surfactant-exchanged LDHs showed some fracturing of the crystals along the basal plane (Figure 2b). The interlayer spacings observed for  $[\text{LiAl}_2\text{-OS}]$  was  $2.04 \text{ nm}$ , Figure S2, and for  $[\text{LiAl}_2\text{-DBS}]$   $3.08 \text{ nm}$ , Figure S3 (interlayer spacing for the DBS exchanged material has been reported previously as  $3.07 \text{ nm}$ <sup>12</sup>). In most, but not all cases, exchange with OBS produced a biphasic material



**Fig. 3** Transmission electron micrographs produced by evaporation of butanol suspensions of  $[\text{LiAl}_2\text{-OBS}]$ . Products were synthesised from gibbsite with average crystallite size of (a)  $\sim 5 \mu\text{m}$ , and (b)  $\sim 1 \mu\text{m}$ .

with interlayer spacings 3.18 and 2.55 nm (2 peaks in Figure 1b at  $2\theta = 2.77$  and  $3.46^\circ$ ) presumably due to varying hydration and/or guest orientation (similar behaviour has been observed with other Li/Al LDH materials<sup>13</sup>).

Delamination of the surfactant-containing LDHs was found to proceed with [LiAl<sub>2</sub>-OBS] and [LiAl<sub>2</sub>-DBS], but not with the octyl sulfate derivative. Successful delamination was indicated by the formation of a translucent butanol solution, after heating the suspension to reflux for 16 hours. The extent of delamination and stability of the suspension was found to depend on the particle size of the starting material. Using intercalate synthesised from gibbsite with an average crystallite size of  $\sim 5$   $\mu\text{m}$ , dispersions of 1.1 g of intercalate in 1 L of butanol were obtained. These suspensions were stable for only 12 hours. When the particle size of the gibbsite starting material was  $\sim 1$   $\mu\text{m}$ , 1.6 g/L of intercalate was suspended, and the suspensions were stable for more than 7 days. The extent of delamination is comparable to that achieved with Zn<sub>2</sub>Al(OH)<sub>6</sub>(C<sub>12</sub>H<sub>25</sub>SO<sub>4</sub>) in butanol, but less than that achieved with Mg<sub>2</sub>Al(OH)<sub>6</sub>(C<sub>12</sub>H<sub>25</sub>SO<sub>4</sub>) in acrylate.<sup>8</sup> It is also notable that the Li/Al LDH has a high charge density compared to other LDH materials,<sup>2</sup> which may also contribute to the limited extent of delamination.

Evaporation of the suspension results in the deposition of platelets oriented predominantly parallel to the surface of the substrate (Figure 2c). This is consistent with the presence of the exfoliated intercalate in the suspension. TEM micrographs were obtained by transferring a drop of the suspensions onto a grid. The images show collections of platelets largely oriented parallel to the grid surface (Figure 3). The particle dimensions observed were consistent with the particle size of the starting material used. The unique synthesis of the Li/Al LDH, achieved by reaction of solid gibbsite, enables the particle size of the intercalate product to be easily controlled. This control can now be extended to the nanoparticles produced here.

Powder XRD of the solid resulting from evaporation of the suspension was as expected for starting material, and exhibited only slight line broadening (Figure 1(c)). This is consistent with the behaviour of other delaminated LDHs, although in one case the phase produced on evaporation was reported to incorporate butanol as well as the surfactant.<sup>6</sup> Upon addition of chloride (as NEt<sub>4</sub>Cl) to the butanol suspension, rapid flocculation of the particles occurred, and powder XRD indicated that the LDH isolated is most probably the chloride containing material (Figure 1(d)). In this case the peak broadening is quite severe; scanning electron micrographs of the original [LiAl<sub>2</sub>-Cl] and the reassembled product show a significant change in particle size (Figure 2(a,d)) This is additional evidence supporting the presence of the delaminated LDH in the butanol suspension.

Some direct evidence for the presence of LDH particles in the suspension was also obtained. Figure 4 shows the small angle X-ray scattering (SAXS) from [LiAl<sub>2</sub>-DBS] in the butanol suspension. The SAXS data was modelled with a cylindrical model to determine platelet thickness. The intensity of the SAXS pattern,  $I$ , is related to the scattering vector,  $q$ , and the radius,  $r$ , and thickness,  $T$ , of the plates by:

$$I = A P(q,r,T) + b \quad (1)$$

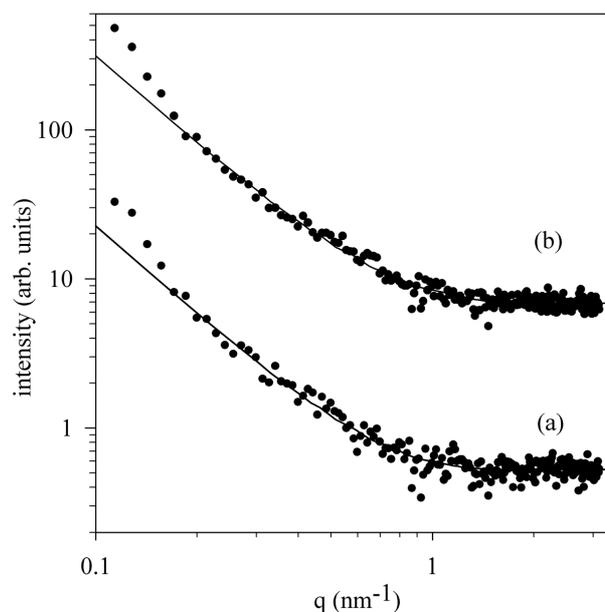
Here,  $b$  is the background scattering,  $A$  is a scale factor dependent on the number of particles and electron density differences between the platelets and the solvent and  $P(q,r,T)$  is the form factor for scattering from a cylinder<sup>14</sup>:

$$P(q,r,T) = \int_0^{p/2} \left[ \frac{2J_1(qr \sin \alpha)}{qr \sin \alpha} \frac{\sin(qT/2 \cos \alpha)}{qT/2 \cos \alpha} \right]^2 \sin \alpha d\alpha$$

$J_1(x)$  is the first order Bessel function and  $\alpha$  is the angle between the platelet axis and  $q$ . The platelet radius was held constant during the modelling procedure as this dimension is above that

which will contribute to X-ray scattering in this regime. The modelling was performed with the Igor Pro software package with model macros provided by NIST. The cylinder form was found to fit well to data points for  $q > 0.17 \text{ nm}^{-1}$ . The platelet thicknesses were modelled to be  $2.8 \pm 0.2$  and  $3.5 \pm 0.3$  nm for the  $\sim 1$   $\mu\text{m}$  starting material and  $\sim 5$   $\mu\text{m}$  starting material respectively. The poor fit at lower  $q$  values is most likely due to differences in scattering from the large scale structures in the walls of the capillaries containing the platelet suspension and butanol used as background.

The peak at  $2\theta = 2.86^\circ$  ( $q = 2.03 \text{ nm}^{-1}$ ) in the XRD



**Fig. 4** SAXS from [LiAl<sub>2</sub>-DBS] suspension in butanol synthesised from (a) 5  $\mu\text{m}$  crystallite size (b) 1  $\mu\text{m}$  crystallite size gibbsite starting material. The data points in (b) have been scaled by 10 times for clarity. The dots are experimental data points and the line is the fit of Eqn. 1 to the data. The error margins on the data points are not shown, but are approximately 10%.

pattern of [LiAl<sub>2</sub>-DBS] should also be observed in the SAXS data if the ordering evident in the solid is present when the material is in suspension. The absence of the peak implies the platelets are randomly oriented in suspension and further confirms that the SAXS is from a colloidal suspension of predominantly delaminated  $\sim 3$  nm platelets.

The results described above suggest that delamination of the Li/Al LDH is dependent on the structure of the surfactant guests, with the benzene sulfonate 'head group' stabilising the delaminated materials whereas the sulfate functionalised surfactants do not. To confirm that the alkyl chain is also required, the *p*-toluenesulfonate intercalate was prepared.<sup>12</sup> Attempts to delaminate this LDH were unsuccessful. Further work is required to determine the minimum alkyl chain length required to delaminate the LDH, and to determine if there is any correlation between chain length and stability of the suspension formed.

In conclusion, the LiAl<sub>2</sub> layered double hydroxide has been delaminated to produce colloidal suspensions. This is the first study to suggest that the delamination of an LDH is sensitive to the specific chemical structure of the surfactant guest. A simple path to nanoparticulate plate-like gibbsite is available through this process. Further work is underway to explore the properties of such materials, as well as to further investigate the formation and stability of the colloidal suspensions.

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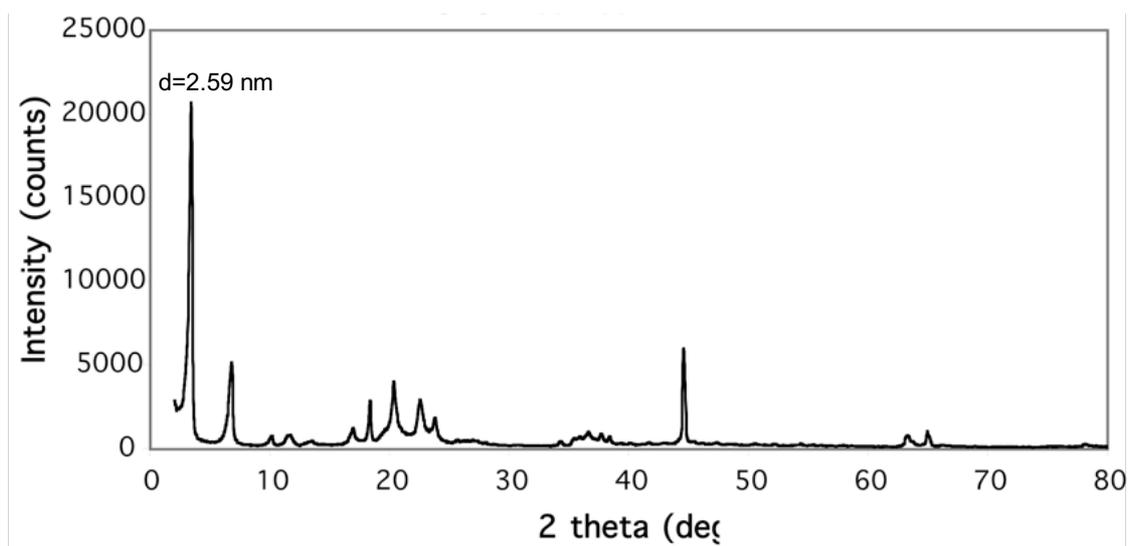


Fig. S1. Diffraction pattern of [LiAl<sub>2</sub>-SDS]

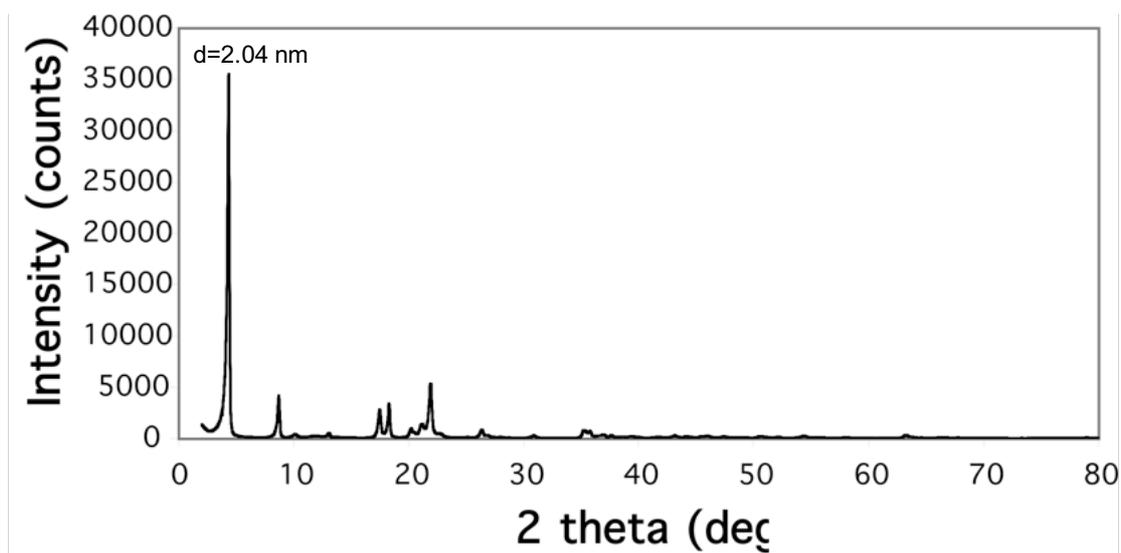


Fig. S2. Diffraction pattern of [LiAl<sub>2</sub>-OS]

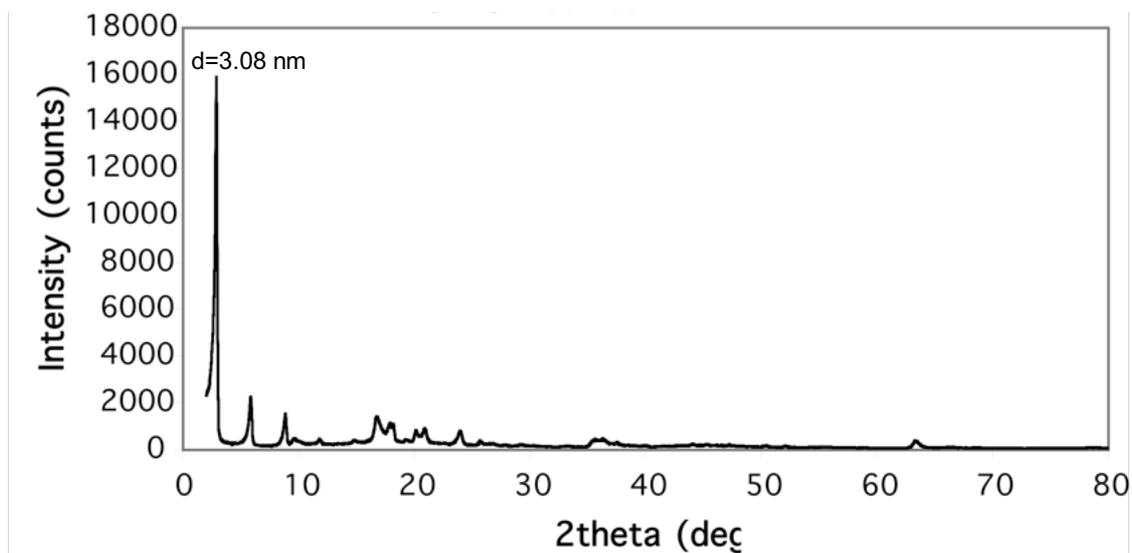


Fig. S3. Diffraction pattern of [LiAl<sub>2</sub>-DBS]