Local environment and composition of magnesium gallium layered double hydroxides determined from solid-state ^1H and ^{71}Ga NMR spectroscopy

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Abstract:

Ordering of gallium(III) in a series of magnesium gallium (MgGa) layered double hydroxides (LDH's), $[\text{Mg}_{1-x}\text{Ga}_x(\text{OH})_2(\text{NO}_3)_x \cdot y\text{H}_2\text{O}]$ was investigated using solid-state ^1H and ^{71}Ga NMR spectroscopy as well as powder X-ray diffraction. Three different proton environments from $\text{Mg}_3\text{-OH}$, $\text{Mg}_2\text{Ga-OH}$ and intergallery water molecules were assigned and quantified using $\{^1\text{H}, ^{71}\text{Ga}\}$ HETCOR and ^1H MAS NMR. A single ^{71}Ga site originating from the unique Ga site in the MgGa LDH's was observed in ^{71}Ga MAS and 3QMAS NMR spectra. Both ^1H MAS NMR spectra recorded at 21.1 T (900MHz) and elemental analysis show that the synthesized MgGa LDH's had a lower

Mg:Ga ratio than that of the starting reactant solution. The origin of this is the formation of soluble $[\text{Ga}(\text{OH})_4]^-$ complexes formed during synthesis, and not due to formation of insoluble gallium (oxy)hydroxides. No sign of Ga-O-Ga connectivities or defects were detected for the MgGa LDH's.

1. Introduction

Layered double hydroxides (LDH's) find wide spread application for drug delivery, catalysis, ion-exchange and environmental remediation [1-4]. Tailoring the chemical composition of the LDH's is a key factor in controlling their function. LDH's are derived from the brucite structure ($\text{Mg}(\text{OH})_2$), where the substitution of a divalent cation, M(II), with a trivalent cation, M(III), is accompanied by the insertion of an appropriate number of anions and water molecules in the interlayer (Figure 1). The formula for these LDH's is $[\text{M}(\text{II})_{1-x}\text{M}(\text{III})_x(\text{OH})_2\text{A}^{n-}_{x/n} y\text{H}_2\text{O}]$ where $1/6 < x < 1/3$, A is an anion necessary for charge balance and y water molecules, the actual water content depends on A and the method of preparation. Many different anions ranging from simple anions such as chloride and oxyanions to complex organic anions may be intercalated in the LDH's. Generally, up to one third M(III) ions can be incorporated in the layer. For higher concentrations the structure will contain neighboring M(III), which is unfavorable due to electrostatic repulsion[5]. The M(III) ions can be either ordered or randomly distributed in the cation layer giving rise to a different number and relative concentration of the $\text{M}(\text{II})_{3-x}\text{M}(\text{III})_x\text{-OH}$ groups ($x = 0, 1, 2, 3$)[6], as illustrated in Figure 1. Thus, the ordering of M(III) and M(II)/M(III) ratios can be determined if the -OH groups can be quantified. It has been demonstrated that solid-state NMR (SSNMR) provides this information and gave a detailed insight into local environment of the cation in magnesium aluminum (MgAl) LDH's[6-11], including the distribution of Al in the cation layer, the presence of structural defects - information which is very difficult determined with X-ray diffraction techniques, which rely on long range order. The dynamics and orientation of both inorganic and organic anions in the interlayer has been extensively studied by Kirkpatrick et al.[12-18]. Thus, SSNMR has proven important in obtaining structural information, complementing the information achieved from X-ray diffraction.

SSNMR studies have found MgAl LDH's to be ordered, but they may contain structural defects on the atomic level [7-11]. There are contradicting observations as to whether the structure contains Al-O-Al connectivities or not, which has been ascribed to different methods of preparation. Sideris et al. observed no Al-O-Al connectivities in ^1H MAS NMR but identified $\text{Mg}(\text{OH})_2$ clusters in the samples next to defect sites in LDH's prepared by co-precipitation with subsequent hydrothermal treatment to improve crystallinity [6, 11]. Cadars et al. identified $\text{MgAl}_2\text{-OH}$ environments, a signature of neighboring Al^{3+} ions, in MgAl LDH's obtained directly after co-precipitation and synthesized with the minimum Mg:Al ratio (2:1) theoretically possible[7]. These results were in agreement with earlier ^{27}Al NMR studies[8]. Given the detailed information obtained about MgAl LDH's from SSNMR it is of interest to investigate other LDHs to probe their local environments using this technique.

Here we report the results of a combined ^1H and ^{71}Ga SSNMR study of magnesium gallium (MgGa) LDH's with nitrate intercalated prepared using co-precipitation $[\text{Mg}_{1-x}\text{Ga}_x(\text{NO}_3)_x \cdot y\text{H}_2\text{O}]$ [19, 20]. Gallium has two NMR active isotopes, ^{69}Ga and ^{71}Ga , which are both quadrupolar nuclei ($I = 3/2$) with high Larmor frequencies of which the latter is generally preferred due to a smaller quadrupole moment. Similar to ^{27}Al NMR, the isotropic shift, $\delta_{\text{iso}}(^{71/69}\text{Ga})$, can be used to distinguish tetra-, penta- and octahedral Ga sites in the structure and the quadrupole coupling parameters provide insight into the symmetry of the coordination site. Moreover, ^{27}Al and $^{69,71}\text{Ga}$ NMR data obtained for isostructural compounds can be correlated [21]. Thus, MgGa LDH system is an obvious system to explore by SSNMR.

To our knowledge, only few SSNMR studies of the MgGa LDH's system have been reported [22-24]. Two types of -OH group were observed, but not quantified in ^1H MAS spectra[23] and a distorted ^{71}Ga MAS NMR spectrum reported [22, 24]. We take advantage of the advances in SSNMR equipment since then and have reinvestigated MgGa LDH's to probe the local structure in MgGa LDH's with emphasis on determination of Mg:Ga ratio, the ordering of Ga in these MgGa LDH's as well as the presence of defects.

2. Material and Methods

2.1. Synthesis:

The MgGa LDH's ($[\text{Mg}_{1-x}\text{Ga}_x(\text{OH})_2(\text{NO}_3)_x \cdot y\text{H}_2\text{O}]$) were prepared by the conventional co-precipitation method, 10 mL of an aqueous solution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ga}(\text{NO}_3)_3 \cdot 8\text{H}_2\text{O}$ with relative concentrations of 6:1 (MgGa-A), 4:1 (MgGa-B), and 2:1 (MgGa-C), respectively and a total cation ($\text{Mg}^{2+} + \text{Ga}^{3+}$) concentration of 1.4 M were slowly dripped into 10 mL of a 6 M NaOH solution. The water content of the gallium(III) nitrate starting material was verified by thermogravimetric analysis. After ageing at 60 °C overnight the gel was filtered, washed with decarbonized water and subsequently dried at 80 °C for 24 hrs. Carbonate impurities were minimized by the use of decarbonized water and nitrogen flow over the reaction. Only reflections from LDH phases were detected by powder X-ray diffraction and matched reported XRD data [25, 26].

2.2 Characterization by powder X-ray (pXRD) diffraction and IR:

The samples were characterized by PXRD using a Siemens Diffractometer D5000 (Cu $K\alpha$ radiation 1.5418 Å). The samples were scanned in the 2θ range from 5-70° using a step size of 0.02° and a step time of 1 s. The IR spectra (Figure S1, supporting information) were recorded on a Perkin-Elmer 1720 FTIR spectrometer. 1 mg of sample was mixed with KBr and disc prepared. The Mg and Ga content were determined by inductively coupled plasma chromatography (ICP).

2.3 Solid State NMR spectroscopy:

Single pulse ^1H MAS NMR spectra were recorded on a Varian VNMRs spectrometer with a medium-bore (63 mm) Oxford Instruments magnet operating at 21 T (900 MHz for ^1H). Single pulse ^{71}Ga MAS NMR spectra were recorded on a Varian INOVA 500 MHz NMR spectrometer using a 3.2 mm probe and 18 kHz spinning. The $\{^1\text{H}, ^{71}\text{Ga}\}$ HETCOR, 3QMAS and ^{71}Ga NMR experiments were performed on an Agilent DirectDrive 2 500 MHz NMR spectrometer using a 1.6 mm MAS probe and 35 kHz spinning.

HETCOR were obtained with contact times of 300 μ s and 2 ms contact times to probe short (Ga-OH) and longer ^1H - ^{71}Ga distances, respectively. The ^{71}Ga 3QMAS spectra were recorded using the z-filter sequence[27]. Standard shearing operation has been applied on 3QMAS spectrum and indirect dimension was referenced according to Amoureux et al. method[28, 29].

^1H and ^{71}Ga NMR spectra are referenced using H_2O ($\delta(^1\text{H}) = 4.6$ ppm) and 1 M solution of GaCl_3 ($\delta(^{71}\text{Ga}) = 0$ ppm). The magic angle was carefully set by minimizing the spinning side band lines shapes from the ^{23}Na resonance in NaNO_3 . Spectra were analyzed using SpinWorks developed by Kirk Marat[30] and STARS [31].

3. Results:

First the samples purity is investigated by pXRD. We then focus on the local Ga environment in MgGa LDH's obtained from ^{71}Ga single pulse and 3Q MAS NMR and compare this to the ^{27}Al NMR data for the MgAl LDH's. Following this, the local proton environments are assigned and quantified using high speed ^1H MAS and $\{^1\text{H}, ^{71}\text{Ga}\}$ HETCOR NMR. Subsequently, we discuss the information obtained in relation to the local structure in MgGa LDH and other LDH systems as well as compare this to earlier SSNMR studies of MgGa LDH's.

3.1 pXRD and IR

The three samples all have the characteristic powder XRD diffractogram of a LDH structure with very intense (003) and (006) reflections, as illustrated in Figure 2. No impurities from crystalline phases could be detected in the pXRD diffractograms. The unit cell parameters were determined using a hexagonal cell setting. Table 1 reports the a and c parameters, which provide information on the M-M distance and interlayer separation, respectively. These were determined from the position of the (110) and (003) reflections. The c spacing falls with the range 24.14-21.21 Å

reported for MgGa LDH with primarily nitrate intercalated [25]. Only small variations in the a parameter is observed. IR spectra (Supplementary information) showed the incorporation of nitrate ions. However, vibrations from nitrate and carbonate ion are very close [4] and small amounts of carbonate may be present.

3.2 Solid state NMR spectroscopy

3.2.1 ^{71}Ga solid state NMR spectroscopy

^{71}Ga 3QMAS NMR probes the sample purity with respect to Ga phases and identifies the number of possible Ga sites present, as illustrated for MgGa-C in Figure 3. The projection on the isotropic dimension (F1) shows a single peak in the region for octahedral Ga, i.e. a single site, as is expected for MgGa LDH's [26]. The line shape in the anisotropic (F2) dimension is distorted in the 3QMAS spectrum due to the fairly large quadrupole interaction.

Figure 4 shows the ^{71}Ga MAS NMR spectra of three MgGa LDH's, which are very similar and display the distinct quadrupolar broadened line shape for a Ga site with a fairly large quadrupole interaction. Line shape analysis show that the experimental spectra can be simulated by a single ^{71}Ga site (Figure 4), characterized by $C_Q = 5.35(10)$, $\eta_Q = 0.05(10)$, and $\delta_{\text{iso}}(^{71}\text{Ga}) = 40(2)$ ppm. The low frequency “horn” and “shoulder” are blurred due to a small distribution in mainly C_Q . This distribution is caused by the presence of different local environments in the 2nd cation coordination sphere and possibly stacking disorder, an inherent property of LDH's.

The ^{71}Ga NMR parameters can be related to the ^{27}Al NMR parameters reported for the isostructural MgAl LDH's using correlations established between ^{27}Al and ^{71}Ga NMR parameters from studies of inorganic materials by Massiot et al. [21].

$$\delta_{\text{iso}}(^{71}\text{Ga}) = 2.84(8)\delta_{\text{iso}}(^{27}\text{Al}) - 1(4) \text{ [ppm]} \quad (1)$$

$$C_Q(^{71}\text{Ga})/C_Q(^{27}\text{Al}) = 3.11(13) \quad (2)$$

We employ $C_Q(^{27}\text{Al}) = 1.55$ MHz and $\delta_{\text{iso}}(^{27}\text{Al}) = 11.8$ ppm reported by Sideris et al. [11] for this comparison. A $C_Q(^{71}\text{Ga}) = 4.9(2)$ MHz is predicted for ^{71}Ga in MgGa LDH's, which agrees fairly well with the 5.3 MHz determined experimentally in this work. $\delta_{\text{iso}}(^{71}\text{Ga}) = 35(5)$ ppm is obtained in good agreement 40(2) ppm determined experimentally.

3.2.2 The ordering of Ga and determination of the Mg:Ga ratio using ^1H MAS NMR.

The ^1H MAS NMR spectra of the three MgGa LDH samples (Figure 5) all contain three resonances centered at $\delta(^1\text{H}) = 4.6$, 2.4-2.7, and 0.5-0.6 ppm with different relative concentrations. These three sites are well-resolved due to a high magnetic field (21.1 T, 900 MHz) and fast spinning. The spectra can be assigned using $\{^1\text{H}, ^{71}\text{Ga}\}$ HETCOR experiments, which at a short (300 μs) contact time, show a single cross peak between Ga and the $\delta(^1\text{H}) = 2.7$ ppm resonance (Figure 6a). The first cross peaks expected to appear are between the $-\text{OH}$ directly bonded to the single Ga and the unique Ga site, i.e., identifying the $\text{Mg}_2\text{Ga}-\text{OH}$ group. As the contact time is increased to 2 ms, the $\delta(^1\text{H}) = 0.8$ ppm cross peak appears which originates from hydrogen further away (Figure 6b), and belong to the Mg_3-OH groups. Its isotropic chemical shift is in accordance with that reported for brucite ($\text{Mg}(\text{OH})_2$) [32]. The last resonance at $\delta(^1\text{H}) = 4.6$ ppm has a chemical shift typical for water molecules and belongs to the intergallery water [6]. Closer inspection of Figure 5 shows that $\delta(^1\text{H})$ for the $\text{Mg}_2\text{Ga}-\text{OH}$ resonance shifts from 2.4 to 2.7 ppm as the Ga content increases from 13 to 20 %, a trend also observed for the MgAl LDH's with increasing Al concentration [6].

Our assignment is in full agreement with that observed for the isostructural MgAl LDH's, where the Mg_3-OH group had the smallest shift and is similar to that found in brucite ($\text{Mg}(\text{OH})_2$) [6].

The observation of only two different hydroxy groups implies Ga ordering in our MgGa LDH's.

Deconvolution of the ^1H MAS NMR provides information about the Mg:Ga ratio. For an LDH with ordering of the Ga (M(III)), the percentage of Ga(III) ions can be determined from the relative intensity of the $\text{Mg}_2\text{Ga-OH}$ groups[6]:

$$x = \frac{I(\text{Mg}_2\text{Ga-OH})}{3} \quad (3)$$

For MgGa-C the Ga content determined from the ^1H MAS NMR and ICP are in agreement with the ratio of the reactants (Table 2). However, the Mg:Ga ratio determined from ^1H NMR does not agree with the Mg:Ga ratio of the reactants for MgGa-B and MgGa-C c.f. Table 2. For example, an ordered sample with a 2:1 Mg:Ga ratio will only contain $\text{Mg}_2\text{Ga-OH}$ sites and intergallery water. In contrast, 41 % $\text{Mg}_2\text{Ga-OH}$ and 59 % $\text{Mg}_3\text{-OH}$ are observed in a sample prepared with a 2:1 Mg:Ga ratio (MgGa-C, Table 2). These concentrations correspond to 20 % Ga in the layer, i.e., a 4:1 ratio of Mg:Ga. The Mg:Ga ratios derived from ^1H MAS NMR are in excellent agreement with that determined from ICP within the experimental uncertainties c.f. Table 2. ICP reports the bulk composition of the sample, whereas ^1H NMR reflects the Mg:Ga ratio for the LDH phase. Thus, the correct Mg:Ga ratio is obtained from ^1H MAS NMR and the presence of impurities (if any) is less than 1-2 %. The origin of this deviation will be discussed below in Section 4.

4. Discussion

^1H and ^{71}Ga SSNMR show the presence of a single phase in our three samples and thereby ordering of Ga in the brucite layer, but the Ga content is lower than expected based on the Mg:Ga ratio of the reactants. It has earlier been reported that MgGa-LDHs rarely have the same Mg:Ga ratio as the solution from which it was prepared, and incorporation of high concentrations of Ga in MgGa-LDH's is difficult [25, 33, 34]. The depletion of Ga in the MgGa LDH product compared to the starting materials has been proposed to stem from either formation of a gallium oxy hydroxide (GaOOH) phase, possibly amorphous since undetected by p-XRD, or soluble Ga

complexes such as $[\text{Ga}(\text{OH})_4]^-$. Our SSNMR and ICP results show that formation of soluble Ga complexes is the explanation for Ga depletion in the MgGa LDH's, as no impurity phases were detected in ^1H and ^{71}Ga , which could stem from such impurities. This observation is in excellent agreement with the fact that soluble $[\text{Ga}(\text{OH})_4]^-$ complexes are the predominant Ga species above pH 10 [35], the pH range in which the samples were prepared. We note that the presence of magnesium containing impurities would result in a smaller Mg:Ga ratio.

Our results show that the earlier SSNMR studies were performed using MAS speeds (4-5 kHz) at moderate field (7.1-9.4 T) insufficient for suppression of the strong ^1H dipolar coupling and observation of undistorted 2nd order quadrupolar line shape for the ^{71}Ga site [22-24]. Simulation of the ^{71}Ga central transition using the ^{71}Ga NMR parameters determined here shows that spinning speeds above 16 kHz are needed in contrast to the 5 kHz employed in the previous study [22]. The earlier ^1H MAS NMR study observed at two peaks with $\delta(^1\text{H}) = -1.1$ and 3.2 ppm assigned to $\text{Mg}(\text{OH})_2$ -like and OH groups coordinated to Ga, respectively but no quantification of was reported due to severe overlap of these resonances and multiple spinning side bands. These ^1H data agrees well with the high-resolution data obtained in this study. However, fast MAS and fairly high field is clearly needed to suppress the ^1H - ^1H dipolar interaction and obtain quantitative information.

There is evidence of M(III)-rich regions with Al-O-Al connectivities in MgAl LDH's, which has been reported from ^1H and ^{27}Al SSNMR,[7, 8] but not observed by Sideris et al.[6, 9-11]. It is of interest to see if similar Ga rich regions can be found in the MgGa LDH. Even close inspection of the ^1H NMR spectra (Figure 4) does not reveal any resonances over the detection limit of our ^1H NMR spectra (ca 1%) with $\delta(^1\text{H}) > 5$ ppm, where $\text{MgGa}_2\text{-OH}$ and $\text{Ga}_3\text{-OH}$ resonances would be expected for our MgGa LDH's. However, such environments should mainly be abundant for samples with a higher Ga content than those investigated here, based on the results in this paper and earlier observed for MgAl LDHs [7, 11].

5. Conclusions:

We have demonstrated that SSNMR gives detailed insight into the molecular level structure of MgGa LDH's. Our MgGa LDHs prepared using co-precipitation exhibits Ga ordering and are Ga depleted due to formation of soluble Ga complexes in solution resulting in significantly higher Mg:Ga ratios. The ^{71}Ga NMR parameters determined for the single Ga site correlates well with those reported for the isostructural MgAl LDH's. Moreover, the ^1H NMR data shows three sites from $\text{Mg}_3\text{-OH}$, $\text{Mg}_2\text{Ga-OH}$ and intergallery water, which were quantified and allowed for determination of the Mg:Ga ratio. Our results show many similarities between the MgGa and MgAl LDH's. Understanding the molecular level structure of LDH's will facilitate the studies of interaction between LDH's and the intercalated anions thereby achieving a detailed understanding of the function of LDH's.

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Tables:

Table 1: Unit cell parameters determined for the MgGa LDH samples from pXRD.

	a [Å]	c [Å]
MgGa-A	3.116(2)	24.2(3)
MgGa-B	3.112(2)	24.2(3)
MgGa-C	3.106(2)	23.9(3)

Table 2: The relative concentration of the different –OH groups in the MgGA LDH's determined from the ^1H NMR spectra in Figure 5 along with the Ga content (atomic %) of the parent solution (% Ga reactants) as well as the Ga content in the LDH's determined from ICP (% Ga ICP) and ^1H NMR (% Ga NMR).

Sample	$\delta(\text{Mg}_3\text{-OH})$ [ppm]	$\delta(\text{Mg}_2\text{Ga-OH})$ [ppm]	$\delta(\text{H}_2\text{O})$ [ppm]	$\text{Mg}_3\text{-OH}$ (%)	$\text{Mg}_2\text{Ga-OH}$ (%)	% Ga Reac- tants	% Ga ICP	% Ga NMR¹
MgGa-A	0.5(1)	2.4(1)	4.6(1)	59(1)	41(1)	14	13(1)	14(1)
MgGa-B	0.6(1)	2.5(1)	4.7(1)	52(1)	48(1)	20	17(1)	16(1)
MgGa-C	0.6(1)	2.6(1)	4.7(1)	41(1)	59(1)	33	20(1)	20(1)

¹ The Ga content is one third the concentration of $\text{Mg}_2\text{Ga-OH}$ ($c(\text{Mg}_2\text{Ga-OH})/3$) for an ordered LDH[11], see discussion in text.

Figure 1: The structure of a LDH illustrating the layered structure.[26] The concentration of anions (blue) in the interlayer is linked to M(III) concentration in the brucite layer (red). The intergallery water molecules are not shown for clarity. Each O(H) is coordinated to three different metal ions giving rise to four possible types of OH environments, which may be distinguished by ^1H NMR.

Figure 2: pXRD diffractograms of the three MgGa samples investigated with the characteristic reflections are indexed (hkl).[33] No crystalline impurities could be detected in the pXRD except for a single, weak reflection for MgGa-C, which is indicated by an asterisk

Figure 3: ^{71}Ga 3QMAS NMR spectrum of MgGa-C recorded at 11.7 T. The spectrum is shown as a contour plot with projections on the F1 (isotropic) and F2 (anisotropic) dimension. .

Figure 4: ^{71}Ga NMR of the MgGa LDH's at 11.7 T using 18 kHz spinning. $C_Q = 5.35$, $\eta_Q = 0.05$, and $\delta_{\text{iso}}(^{71}\text{Ga}) = 40$ ppm were employed in used in the simulation shown at the top.

Figure 5: ^1H MAS NMR spectra recorded at 900 MHz using 35 kHz spinning speed. The results from analysis of these spectra are summarized in Table 1.

Figure 6: $\{^1\text{H}, ^{71}\text{Ga}\}$ HETCOR experiment of MgGa-C using a) $300\ \mu\text{s}$ and b) $2\ \text{ms}$ contact time.

At short distances (a) only the hydrogen with $\delta(^1\text{H}) = 2.7\ \text{ppm}$ from the $\text{Mg}_2\text{Ga-OH}$ group is

observed. When the contact times is increased (b) the $\text{Mg}_3\text{-OH}$ groups at $\delta(^1\text{H}) = 0.8\ \text{ppm}$ appears.

Graphical Abstract

References:

- [1] F.P. Bonina, M.L. Giannossi, L. Medici, C. Puglia, V. Summa, F. Tateo, *Appl. Clay Sci.* 41 (2008) 165-171.
- [2] U. Costantino, V. Ambrogio, M. Nocchetti, L. Perioli, *Microporous and Mesoporous Mater.* 107 (2008) 149-160.
- [3] C. Forano, T. Hibino, F. Leroux, C. Taviot-Guého, B.K.G.T. Faïza Bergaya, L. Gerhard, *Developments in Clay Science*, Elsevier, 2006, pp. 1021-1095.
- [4] K.H. Goh, T.T. Lim, Z. Dong, *Water Res.* 42 (2008) 1343-1368.
- [5] D.G. Evans, R.C.T. Slade, in: X. Duan, D.G. Evans, (Eds.), *Layered Double Hydroxides*, 2006, pp. 1-87.
- [6] P.J. Sideris, U.G. Nielsen, Z.H. Gan, C.P. Grey, *Science* 321 (2008) 113-117.
- [7] S. Cadars, G. Layrac, C. Gérardin, M. Deschamps, J.R. Yates, D. Tichit, D. Massiot, *Chem.Mater.* 23 (2011) 2821-2831.
- [8] A. Vyalikh, F.R. Costa, U. Wagenknecht, G. Heinrich, D. Massiot, U. Scheler, *J. Phys. Chem. C* 113 (2009) 21308-21313.
- [9] G. Yu, M. Shen, M. Wang, L. Shen, W. Dong, S. Tang, L. Zhao, Z. Qi, N. Xue, X. Guo, W. Ding, B. Hu, L. Peng, *J. Phys. Chem. Lett.* 5 (2014) 363-369.
- [10] L. Zhao, Z. Qi, F. Blanc, G. Yu, M. Wang, N. Xue, X. Ke, X. Guo, W. Ding, C.P. Grey, L. Peng, *Adv. Funct. Mater.* 24 (2013) 1696-1702.
- [11] P.J. Sideris, F. Blanc, Z. Gan, C.P. Grey, *Chem.Mater.* 24 (2012) 2449-2461.
- [12] X. Hou, J.R. Kirkpatrick, P. Yu, D. Moore, Y. Kim, *Am. Miner.* 85 (2000) 173-180.
- [13] X. Hou, R.J. Kirkpatrick, *Chem. Mater.* 12 (2000) 1890-1897.
- [14] A.G. Kalinichev, P. Padma Kumar, R. James Kirkpatrick, *Philosophical Magazine* 90 (2010) 2475 - 2488.
- [15] P.P. Kumar, A.G. Kalinichev, R.J. Kirkpatrick, *J. Phys. Chem. B* 110 (2006) 3841-3844.
- [16] Q. Li, R.J. Kirkpatrick, *Am. Miner.* 92 (2007) 397-402.
- [17] M.X. Reinholdt, P.K. Babu, R.J. Kirkpatrick, *J. Phys. Chem. C* 113 (2009) 3378-3381.
- [18] J.W. Wang, A.G. Kalinichev, R.J. Kirkpatrick, *Geochimica Et Cosmochimica Acta* 70 (2006) 562-582.
- [19] M.R. Weir, J. Moore, R.A. Kydd, *Chem.Mater.* 9 (1997) 1686-1690.
- [20] E. LopezSalinas, M. GarciaSanchez, M.E. LlanosSerrano, J. NavarreteBolanoz, *J. Phy. Chem. B* 101 (1997) 5112-5117.
- [21] D. Massiot, T. Vosegaard, N. Magneron, D. Trumeau, V. Montouillout, P. Berthet, T. Loiseau, B. Bujoli, *Solid State Nucl. Magn. Reson.* 15 (1999) 159-169.
- [22] M.A. Aramendia, Y. Aviles, J.A. Benitez, V. Borau, C. Jimenez, J.M. Marinas, J.R. Ruiz, F.J. Urbano, *Microporous and Mesoporous Mater.* 29 (1999) 319-328.
- [23] M.a.A. Aramendia, V. Borau, C. Jiménez, J.M. Marinas, J.R. Ruiz, F.J. Urbano, *Mater. Lett.* 46 (2000) 309-314.
- [24] R. Prihod'ko, M. Sychev, I. Kolomitsyn, P.J. Stobbelaar, E.J.M. Hensen, R.A. van Santen, *Microporous and Mesoporous Materials* 56 (2002) 241-255.
- [25] F. Prinetto, D. Tichit, R. Teissier, B. Coq, *Catal. Today* 55 (2000) 103-116.
- [26] G.V. Manohara, P.V. Kamath, *Bull. Mater. Sci.* 33 (2010) 325-331.
- [27] D. Massiot, B. Touzo, D. Trumeau, J.P. Coutures, J. Virlet, P. Florian, P.J. Grandinetti, *Solid State Nucl. Magn. Reson.* 6 (1996) 73-83.
- [28] J.P. Amoureux, C. Fernandez, *Solid State Nucl. Magn. Reson.* 10 (1998) 211-223.
- [29] J.P. Amoureux, C. Fernandez, *Solid State Nucl. Magn. Reson. Resonance* 16 (2000) 339-343.
- [30] K. Marat, <http://home.cc.umanitoba.ca/~wolowiec/spinworks/>.
- [31] J. Skibsted, N.C. Nielsen, H. Bildsøe, H.J. Jakobsen, *J. Magn. Reson.* 95 (1991) 88-117.
- [32] X. Xue, M. Kanzaki, *J. Am. Ceram. Soc.* 92 (2009) 2803-2830.
- [33] G.S. Thomas, P.V. Kamath, *Mater. Res. Bull.* 40 (2005) 671-681.
- [34] U. Unal, *J. Solid State Chemi.* 180 (2007) 2525-2533.
- [35] B. Hacht, *Bull. Korean Chem. Soc.* 29 (2008) 372-376.