# Preparation and Characterization of Transparent, Photoluminescent MgAl$_2$O$_4$:Eu$^{2+}$ Ceramics

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The influence of 0.1 mol-% Eu$^{2+}$ doping in a transparent MgAl$_2$O$_4$ ceramic on the optical properties has been investigated. The goal was to prepare first an Eu$^{3+}$-doped spinel by a conventional sintering process for a transparent ceramic followed by a reductive densification step yielding an Eu$^{2+}$-doped product. Commercially available spinel powder was doped with 0.1 mol-% europium using a nitrate salt and afterwards compacted into green bodies. In the following process the specimens were pre-sintered and post-densified using hot isostatic pressing (HIP) in an argon atmosphere. The transparency of the disks was measured optically using UV/Vis and fluorescence spectroscopy. After optimization of the sintering conditions the resulting Eu$^{2+}$-doped spinel showed a transparency of 77.4 % and a conversion of the UV light with a wavelength of 260 nm into blue light with a wavelength of 450 nm.

*Key words:* Optical Ceramic, Transparent Ceramic, Spinel, Photoluminescence, Ceramic

## Introduction

In search for optical materials with light-converting properties, the focus of research has shifted from single crystals to transparent ceramics because of the possibility to process polycrystalline materials with a significant transparency and higher doping level for optical application with the simultaneous benefit of high mechanical strength [1]. In contrast to the preparation of single crystals, the sintering of transparent ceramics allows to decrease remarkably the process temperature as well as the production time whilst the possibility to manufacture larger ceramic parts arises. In order to achieve a high transparency in polycrystalline ceramics, critical parameters such as purity, grain size, porosity and second phases have to be controlled carefully [4].

The classical spinel, the cubic magnesium aluminate MgAl$_2$O$_4$, is formed in the system MgO-Al$_2$O$_3$ with a stoichiometric ratio of MgO : Al$_2$O$_3$ of 1 : 1 at temperatures above 1100 °C and can be synthesized as a polycrystalline, transparent ceramic [2]. It crystallizes in the cubic crystal system with the spinel-type structure in the space group $Fd\bar{3}m$ (no. 227) [3]. The unit cell consists of eight formula units with 32 anion and 24 cation sites. Whereas the Bravais lattice is face-centered cubic (fcc), the oxygen anion substructure is close-packed in a pseudo-cubic arrangement (ccp). Only 24 of the 96 interstices are occupied by cations. In the ideal structure the tetrahedral sites are occupied to 1/8 by Mg, and one half of the octahedral sites by Al. The real structure of thermally treated MgAl$_2$O$_4$ shows 39 % degree of inversion (*i. e.* Al$^{[6]}$ and Mg$^{[4]}$ change atomic positions) [4]. The wide stability range of MgAl$_2$O$_4$ is based on the large number of unoccupied sites in the structure and opens the possibility to solute not only a higher content of aluminum but also dopants such as rare-earth metals into the structure. Nowadays, polycrystalline spinel ceramics show transparencies of above 80 % over the spectral range of wavelengths between 200 to 5500 nm, which is almost the theoretical limit with 87 % of this material [5]. Be-

cause of its optical and mechanical properties, transparent spinel is used for transparent shielding of sensitive analytical equipment such as infrared (IR) domes or as transparent armor [6].

Highly transparent, polycrystalline spinel ceramic can be prepared by two different processing pathways, hot pressing or pre-sintering plus a hot isostatic pressing step. In case of hot pressing (HP), sintering additives such as LiF are often used to densify the MgAl$_2$O$_4$ powder as well as powder mixtures of MgO and Al$_2$O$_3$ [7, 8]. Hot isostatic pressing (HIP) of already hot-pressed specimens leads to a transparency near the theoretical limit, but is closely connected to an extreme increase of the grain size (200 – 300 $\mu$m) [9]. Hot pressing combined with fast heating rates, short holding times (some minutes) and lower temperatures ($< 1400\,^\circ$C) inhibit the grain growth as realized using spark plasma sintering techniques of nanosized spinel powders [10].

The second way is the pre-sintering in air of uniaxial dry-pressed powders, designated as green bodies, which are composed of MgAl$_2$O$_4$ or a mixture of MgO and Al$_2$O$_3$ with a low porosity and hence a relative density of 96 – 98 %, followed by hot isostatic pressing (HIP) as a second densification and heating step. Depending on the particle size of the powders and the sintering conditions, highly transparent, fine-grained spinel ceramic can be fabricated [5, 11, 12].

For optically activated MgAl$_2$O$_4$ ceramics it is known from the literature that polycrystalline spinel doped with transition metals (*e. g.* V or Mn) [13, 14] or rare-earth metals (*e. g.* Ce) [15] can be prepared highly transparent by hot pressing. These ceramics convert UV light into visible light of wavelengths in the range of blue and green. Wiglusz *et al.* prepared a translucent Eu$^{3+}$-doped MgAl$_2$O$_4$ ceramic by hot pressing that can be used as a red light-emitting optically activated ceramic [16]. The red emission with a wavelength maximum at 612.5 nm was assigned to the $^5$D$_0 \rightarrow$ $^7$F$_2$ transition of Eu$^{3+}$. In this case of hot-pressed Eu-doped spinel, the europium was not reduced due to the conditions during the sintering process and remained in the 3+ oxidation state.

In this work, the goal was to prepare an Eu$^{2+}$-doped, transparent polycrystalline spinel ceramic by pre-sintering in air and a following hot isostatic pressing (HIP) step to form transparent bulk ceramics with the property to convert UV light to blue light for optical applications.

## Results and Discussion

After milling and calcination at a temperature of 1100 $^\circ$C the spinel MgAl$_2$O$_4$ powder doped with 0.1 mol-% europium was examined with powder X-ray diffraction (XRD) in order to check the stability and insertion of the europium into the structure. Fig. 1 displays the XRD pattern of this Eu-doped MgAl$_2$O$_4$ powder after the milling and calcination step in comparison to the Bragg reflections (PDF 01-070-5187 [17]) of spinel structure type magnesium aluminate. The measured reflections do not show any shifts in position or additional phases in the sample, indicating that the europium was inserted completely into the structure.

In order to verify the doping of the europium ions into the structure, the doped spinel was excited ($\lambda =$ 260 nm) and the emission spectra recorded after calcination in air and after hot isostatic pressing (HIP) under reductive atmosphere (*vide infra*) (Fig. 2). The calcined powder emitted red light with bands at 577, 591, 598, 655 and a maximum at 618 nm. These bands are typical for the transitions of Eu$^{3+}$ ions and were also observed by Wiglusz *et al.* under excitation at a wavelength 266 nm of an Eu$^{3+}$-doped, translucent spinel ceramic, that had been hot-pressed keeping the Eu$^{3+}$ ions in their oxidation state [16]. After the processing of the doped powders they were pre-sintered in air at two different temperatures (1480 and 1500 $^\circ$C) and afterwards subjected to HIP at $T = 1500\,^\circ$C under argon pressure to decrease the residual porosity in the
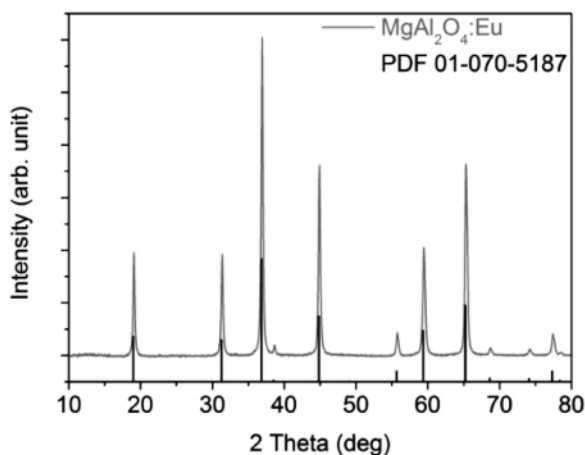


Fig. 1. X-Ray diffraction pattern of MgAl$_2$O$_4$ powder doped with 0.1 mol-% Eu after calcinations at $T = 1100\,^\circ$C for 5 h in air.
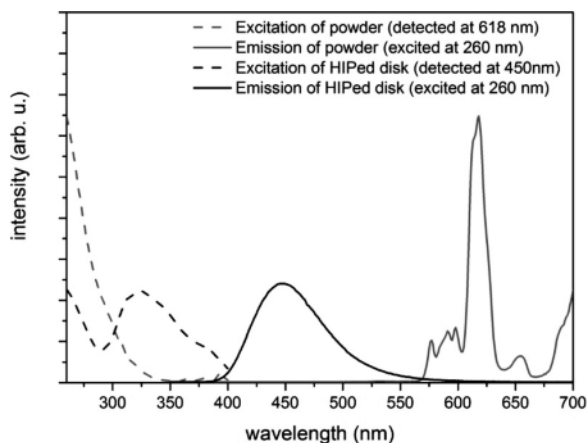
Fig. 2. Excitation and emission spectrum of MgAl$_2$O$_4$ powder doped with 0.1 mol-% Eu after calcination in air. The spectra were obtained on transparent disks made of this powder after hot isostatic pressing (HIP).
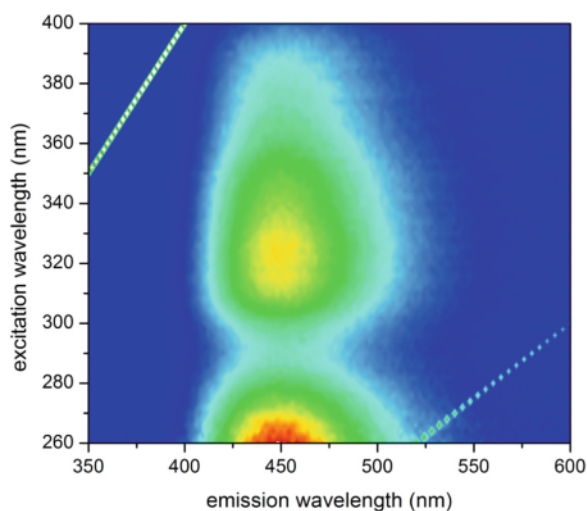


Fig. 3 (color online). Excitation-emission map of a transparent disk made of MgAl$_2$O$_4$ powder doped with 0.1 mol-% Eu after HIP.



Fig. 4. $^{27}$Al MAS NMR spectra of the MgAl$_2$O$_4$ powder doped with 0.1 mol-% Eu (MgAl$_2$O$_4$:Eu$^{3+}$) and of a pulverized, transparent disk made of this powder (MgAl$_2$O$_4$:Eu$^{2+}$) compared to undoped MgAl$_2$O$_4$ powder.

bulk disks. Our hot isostatically pressed samples exhibit a broad blue emission band near the wavelength of 450 nm without an emission in the red wavelength range after excitation at 260 nm (Figs. 2 and 3). The reductive atmosphere (*vide infra*) at the high pressure during the HIP process seems to reduce the Eu$^{3+}$ ion to a blue-emitting Eu$^{2+}$ ion in the spinel structure.

In order to analyze the reduction and the changes in the structure during the HIP process, the adjacent surroundings of the Al cations were checked using $^{27}$Al
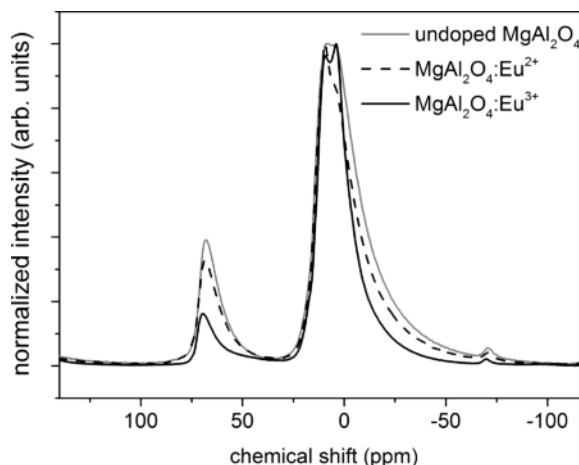
magic angle spinning (MAS) NMR spectroscopy. In the ideal cubic MgAl$_2$O$_4$ structure the Mg$^{2+}$ ions occupy the tetrahedral sites and the Al$^{3+}$ the octahedral sites [3], while the real spinel structure of MgAl$_2$O$_4$ shows a degree of inversion of about 39 % after heat treatment [4]. The distribution of the Al$^{3+}$ ions on both sites can be measured using $^{27}$Al MAS NMR spectroscopy. This method was used to compare the Eu$^{3+}$-doped powder and the grinded Eu$^{2+}$-doped ceramic with an undoped spinel powder (Fig. 4, Table 1). The chemical shift of all three samples near 0 ppm (calibrated to a 1 M AlCl$_3$ solution) corresponds to the octahedral sites of Al$^{3+}$, and a small signal near 70 ppm to the tetrahedral sites. The position and shape of the signals are consistent with those of previous studies and display due to the second order quadrupole interaction a broadening to the lower frequency side in comparison to the isotropical shift position [4, 17, 18]. Maekawa *et al.* [18] suggested that this corresponds to a broad distribution of nuclear quadrupole coupling constants and the asymmetry of the environments of the six-fold coordinated Al atoms. The intensities of the NMR signals were normalized to the octahedral site signal, for a better comparison of the differences to the intensities of the signals of the tetrahedrally coordinated aluminum atoms. The content of Al on tetrahedrally or octahedrally coordinated sites was determined by calculating the integrated area of the signals at 0 ppm and at 70 ppm. In the undoped and Eu$^{3+}$-doped powders,

Table 1. $^{27}$Al MAS NMR data of undoped and 0.1 mol-% Eu-doped $MgAl_2O_4$ powders after calcination in air or HIP under reductive atmosphere.

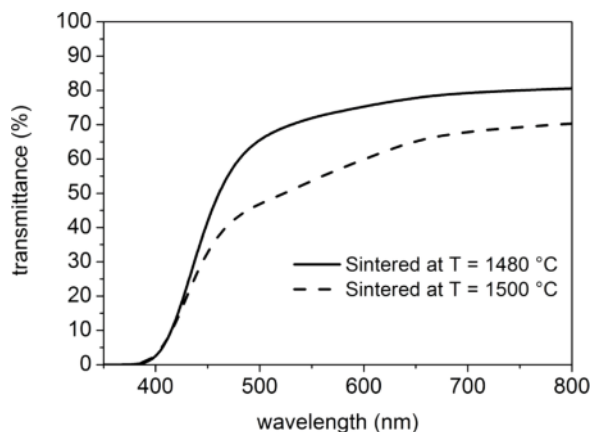| | Chemical shift (ppm) | Al content of $AlO_4$ site (%) | Al content of $AlO_6$ site (%) |
|---|---|---|---|
| Undoped $MgAl_2O_4$ | 9.27 ($AlO_6$) 68.15 ($AlO_4$) | 20 | 80 |
| Calcined $Eu^{3+}$-doped $MgAl_2O_4$ | 7.57 ($AlO_6$) 67.62 ($AlO_4$) | 19 | 81 |
| HIPed $Eu^{2+}$-doped $MgAl_2O_4$ | 3.70, 9.05 ($AlO_6$) 69.19 ($AlO_4$) | 11 | 89 |



Fig. 5. Optical transmittance spectra in a wavelength range of 300 to 800 nm of polished, 4 mm thick disks made of $MgAl_2O_4$ powder doped with 0.1 mol-% Eu after pre-sintering at different temperatures and post-HIP at 1500 °C for 15 h.

about 20% of the tetrahedral sites are occupied by Al. This value is comparable to 20.6% inversion of stoichiometric $MgAl_2O_4$ reported by Ito *et al.* [17].

In the $Eu^{2+}$-doped powder only 11% of this type of interstices are occupied by aluminum atoms. In contrast to undoped and $Eu^{3+}$-doped powders, the $Eu^{2+}$-doped ceramic has the lowest content of $Al^{3+}$ on tetrahedrally coordinated sites, and this is a hint to the occupation of tetrahedral sites by $Eu^{2+}$. In conclusion, the luminescence and NMR data indicate that $Eu^{3+}$ in the spinel structure not only undergoes a reduction to $Eu^{2+}$ but also exchanges the octahedral for the tetrahedral site during the HIP process. As compared to the hot-pressed spinel with $Eu^{3+}$ described by Wiglusz *et al.* [15], our HIP conditions with high argon gas pressure ($> 180$ MPa) in combination with an atmosphere produced by the graphite heater lead to the reduction of $Eu^{3+}$ to $Eu^{2+}$ with concomitant exchange of sites in the spinel structure, although the very nature of the reducing agent still has to be established. This rearrangement in the spinel structure can also be determined by a change of the lattice parameters (Table 2). The substitution of large ions such as $Ga^{3+}$ [17] or $Eu^{3+}$ [16] on the octahedral sites increases the lattice parameter, whereas the occupation of additional tetrahedral sites (*e. g.* by $Al^{3+}$ in Al-rich spinel) leads to a decrease of the lattice parameter $a_0$ [12]. Here, the lattice parameter of the $Eu^{3+}$-

doped $MgAl_2O_4$ powder ($a_0 = 0.80851 \pm 0.00003$ nm) is comparable to that of undoped $MgAl_2O_4$ ($a_0 = 0.80858$ nm [17]). In contrast to this, the $Eu^{2+}$-doped spinel ceramic (after HIP) has a lower lattice parameter $a_0 = 0.80764 \pm 0.00002$ nm, compared to the undoped spinel with $a_0 = 0.80858$ nm [17]. This decrease of the lattice parameter correlates with the occupation of tetrahedral sites by additional $Al^{3+}$ known from Al-rich spinel [12] and is another hint of the occupation of the tetrahedral sites by the $Eu^{2+}$ ions.

The polished, transparent disks of $MgAl_2O_4$:$Eu^{2+}$ show defects which are observable macroscopically and may be due to inhomogenities, residual porosity or absorption sites. Fig. 5 and Table 3 display the transmittance of HIPed specimens depending on the pre-sintering state. Assuming that the sintered bodies have closed porosity, the first sample (sintered at $T = 1480$ °C) has a lower pre-sintering density of 3.41 g cm$^{-3}$ (96%) compared to the second sample (sintered at $T = 1500$ °C) with 3.55 g cm$^{-3}$ (99%). In this case, the difference of $\Delta T = 20$ K influences extremely the densification in the third sintering stage.

| Sample | Material | Position | Lattice parameter (nm) |
|---|---|---|---|
| Single crystal [17] | $MgAl_2O_4$ | | 0.80858 |
| $Ga^{3+}$-doped crystal [17] | $MgAl_{1.62}Ga_{0.38}O_4$ | ($AlO_6$) | 0.81151 |
| 2% $Eu^{3+}$-doped ceramic [15] | $MgAl_2O_4$:$Eu^{3+}$ | ($AlO_6$) | 0.80975 |
| 0.1% $Eu^{3+}$-doped ceramic | $MgAl_2O_4$:$Eu^{3+}$ | ($AlO_6$) | $0.80851 \pm 0.00003$ |
| Al-rich, transparent ceramic [11] | $MgAl_{2.06}O_4$ | ($AlO_4$) | 0.80759 |
| 0.1% $Eu^{2+}$-doped ceramic | $MgAl_2O_4$:$Eu^{2+}$ | ($AlO_4$) | $0.80764 \pm 0.00002$ |

Table 2. Lattice parameters of $Eu^{2+}$-doped $MgAl_2O_4$ ceramics compared to literature data of undoped, $Ga^{3+}$- and $Eu^{3+}$-doped spinel.

Table 3. Pre-sintering temperature and density, HIP temperature and density as well as transmittance of two polished ceramic disks (with 4 mm thickness) made of 0.1 mol-% Eu-doped MgAl$_2$O$_4$.

|  | Pre-sintering temperature (°C) | Pre-sintering density (g cm$^{-3}$) | HIP temperature (°C) | HIP density (g cm$^{-3}$) | Transmittance at 640 nm wavelength (%) |
|---|---|---|---|---|---|
| Sample 1 | 1480 | 3.41 | 1500 | 3.57 | 77.4 |
| Sample 2 | 1500 | 3.55 | 1500 | 3.57 | 64.3 |

The lower density of pre-sintered bodies is due to pores between grains (*inter*-granular pores). Whereas the higher pre-sintering temperature activates the grain growth, this is followed by an inclosing of the pores into these larger grains (*intra*-granular pores). In contrast to the *inter*-granular pores, the enclosed, *intra*-granular pores cannot be eliminated during HIP, and the residual porosity is reducing the transmittance by scattering of light at pores because of different refractive indices. Therefore, the goal of pre-sintering is to achieve closed porosity to inhibit the infiltration of argon gas during HIP but also to obtain a pre-sintering density of about 96 % without *intra*-granular pores. That is the reason why sample 1 with lower pre-sintering density exhibits the higher transmittance of 77.4 % after HIP at the same temperature of 1500 °C for both samples. And on the other hand, the higher pre-sintering density of sample 2 leads to the lower transmittance of 64.3 %.

## Conclusion

Eu$^{3+}$-doped MgAl$_2$O$_4$ powder was fabricated successfully by calcination of commercially available spinel powder and Eu$^{3+}$ nitrate in air and exhibits the typical red luminescence of Eu$^{3+}$. Starting with this powder, Eu$^{2+}$-doped spinel ceramic with a transparency about 77 % was prepared by shaping the powder to disks, pre-sintering in air and hot isostatic pressing under argon atmosphere at a temperature of 1500 °C and a gas pressure of above 180 MPa. Compared to hot-pressed, translucent and Eu$^{3+}$-doped spinel ceramic known from the literature [16], the here presented Eu$^{2+}$-doped ceramic shows high transparency for visible light (77.4 % at 640 nm wavelength with 4 mm thickness) and emits blue light at about 450 nm after excitation at 260 nm wavelength. Solid-state NMR spectroscopy data and lattice parameters from powder XRD patterns indicate that the Eu$^{2+}$ ions may occupy the tetrahedral sites in the spinel structure.

## Experimental Section

MgAl$_2$O$_4$ powder with a specific surface of about 14 m$^2$ g$^{-1}$ was added to a solution of 0.1 mol-% europium nitrate pentahydrate in pure ethyl alcohol. This suspension was milled for two hours in a 250-mL polyethylene bottle filled with high-purity alumina balls. The advantages of using ethyl alcohol compared to water are the lower vapor pressure for drying by evaporation and the constant viscosity of the suspension during the whole milling process. According to experience, the usage of water for milling MgAl$_2$O$_4$ powder leads to an increase of viscosity. After milling, the slurry was dried by evaporation of ethyl alcohol, and the resulting powder was sieved ($< 250\,\mu$m). The powder was calcined at a temperature of 1100 °C for five hours and dispersed again by ball-milling for two hours with ethyl alcohol and polyethyleneglycol as a pressing agent. After drying the powder again by evaporation, the doped spinel powder was formed in cylindrical disks in two steps: At first by uniaxial pressing at a pressure of 50 MPa and afterwards by cold isostatic pressing (CIP) at about 700 MPa. The polyethyleneglycol was burned out carefully at a temperature of 800 °C, and after this a green density (*i. e.* the density of shaped bodies of loose packed powder before sintering) of about 55 % (compared to the theoretical density of MgAl$_2$O$_4$ crystals) was determined. The spinel disks were pre-sintered in air up to closed porosity (*i. e.* the closed surface of a sintered body also named as sintered skin) with a relative density of the body between 95 and 99 %. The closed porosity is a requirement for the following hot isostatic pressing (HIP) in argon at a temperature of 1500 °C for 15 h under a pressure of about 180 MPa. The sintered skin inhibits the infiltration with argon, so that during HIP the pores can be eliminated and highest densification is reached. The resulting bulk disks were grinded and polished to a thickness of 4 mm.

The phase of the calcined powder was identified, and the lattice parameters were determined using powder X-ray diffraction on a D8 Advance and with TOPAS software of Bruker Corp. The green density was measured geometrically by determination of thickness, diameter and weight, and the density of sintered disks was determined using the Archimedes method. Optical transmittance (with a wavelength range between 300 and 800 nm) of the 4 mm thick samples was measured with a Cary 4000 spectrometer (Var-

ian Inc.) with an aperture angle of 5°. The fluorescence data were obtained in air using a FS920 of an Edinburgh Instruments spectrometer with a xenon arc lamp as light source. The emission spectra in a wavelength range of 350 to 700 nm were measured with an excitation at a wavelength of 260 nm, while the excitation spectra between 260 and 400 nm were obtained by emission wavelengths of 450 or 618 nm. The emission-excitation map was measured by detecting the emission between wavelengths of 350 to 600 nm and scanning of the excitation wavelength between 260 and 400 nm with a step width of 2 nm and without filter. Solid-state $^{27}$Al MAS NMR (magic-angle spinning nuclear mag-netic resonance spectroscopy) spectra were recorded using an Advance$^{TM}$ 400 MHz WB spectrometer (Bruker Corp.) and used to determine the position of the Al ions in the spinel lattice. The chemical shift with 0 ppm was measured against 1 M AlCl$_3$ solution and determined with a magnetic flux density of 9.4 T and a frequency of 104.3 MHz.

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