$Sr_4Al_{14}O_{25}$: Formation, Stability, and ^{27}Al High-Resolution NMR Characterization

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$Sr_4Al_{14}O_{25}$ was synthesized from an aqueous solution of aluminum and strontium nitrates by using a spray-drying process. Its formation was studied by differential scanning calorimetry (DSC) at 5 °C/min and X-ray diffraction (XRD). The amorphous precursor crystallized first, through a sharp exothermic peak at 923 °C, into a mixture of two solid solutions: γ-Al_2O_3 stabilized by strontium, and $SrAl_2O_4$ in its hexagonal form stabilized with excess aluminum atoms. These two solid solutions reacted together through a second exothermic peak at 1134 °C to yield the pure $Sr_4Al_{14}O_{25}$ phase. This compound was found to be stable up to 1500 °C, and decomposed at higher temperatures into $SrAl_2O_4$ and $SrAl_4O_7$, and then into $SrAl_2O_4$ and $SrAl_{12}O_{19}$. The $Sr_4Al_{14}O_{25}$ local structure was characterized using ^{27}Al magic angle spinning (MAS) and multiple quantum magic angle spinning (MQ-MAS) NMR techniques.

I. Introduction

Strontium aluminates, doped with rare-earth metal ions, have been studied for a long time for their excellent properties such as high quantum efficiency[1] and long persistence of phosphorescence.[2] Besides the well-known strontium monoaluminate $SrAl_2O_4$, it was reported that Eu^{2+} doped $2SrO\cdot3Al_2O_3$ and $4SrO\cdot7Al_2O_3$ were even more efficient.[1] However it has been shown that $2SrO\cdot3Al_2O_3$ was in fact a mixture of two phases: $SrAl_2O_4$ and $Sr_4Al_{14}O_{25}$ ($4SrO\cdot7Al_2O_3$).[3] The crystal structure of $Sr_4Al_{14}O_{25}$ has been described by Wong et al. from powder X-ray diffraction.[4,5] They determined an orthorhombic structure with the *Pmma* space group, very similar to that found by Nadezhina et al.[6] for a single-crystal synthesized by the hydrothermal method. By solid-state reaction between strontium carbonate $SrCO_3$ and aluminum hydroxide $Al(OH)_3$ and with boric acid acting as a flux, they showed that single phase $Sr_4Al_{14}O_{25}$ could be obtained at 1300 °C after some hours of thermal treatment, with the intermediary phases $Sr_3Al_2O_6$, $SrAl_2O_4$, and $SrAl_{12}O_{19}$. This solid-state synthesis was confirmed by Lin et al.[7] However this compound is not reported in the Al_2O_3−SrO phase diagram[8] and its temperature domain of stability remains unknown. The purpose of the present work is to bring some enlightenment on the formation of this compound and its domain of stability. The recent developments in nuclear magnetic resonance (NMR) technology, such as high applied magnetic field, very fast magic angle spinning (MAS), and multiple quantum magic angle spinning (MQ-MAS) NMR[9] have also been used to characterize the local environment of the different aluminum sites in the structure.

II. Experimental Section

II.1. Synthesis. A spray-drying and calcination process was used to synthesize an amorphous powder precursor of $Sr_4Al_{14}O_{25}$. For this, an aqueous solution of aluminum and strontium nitrates was spray-dried using a laboratory apparatus (Büchi, Flawil, Switzerland, 190 mini spray-drier equipped with a 0.5-mm nozzle). The drying air was heated at 200−210 °C. The powder was collected in a cyclone and then heated in a ventilated furnace, at 5 °C/min, to 700 °C for 1 h in order to completely decompose the nitrates, resulting in an amorphous precursor.

II.2. Characterization. Data from thermogravimetric analysis (TGA) for the decomposition of the nitrates, and differential scanning calorimetry (DSC) for the crystallization of the powder, were collected using a 5 °C/min heating rate under air atmosphere (Setaram, Caluire, France). X-ray diffraction (XRD) at room temperature (Cu $K\alpha$ radiation, Philips PW1729 diffractometer, Eindhoven, The Netherlands) was used to identify the crystalline phases.

The ^{27}Al magic angle spinning (MAS) NMR experiments were carried out on Bruker DSX400 (9.4*T*) and DRX600 (14.1*T*) spectrometers operating at ^{27}Al Larmor frequencies 104.3 and 156.4 MHz respectively, using 4-mm MAS and 2.5-mm high-speed MAS probeheads. The ^{27}Al MAS NMR spectra were recorded using a single pulse acquisition with small pulse angle ($\pi/12$) to ensure a quantitative excitation of the central transition[10] and recycle delay of 5 s. The ^{27}Al multiple quantum MAS[9] (MQ-MAS) spectrum was recorded at 9.4*T* while spinning at 15 kHz using the shifted-echo sequence.[11] To avoid

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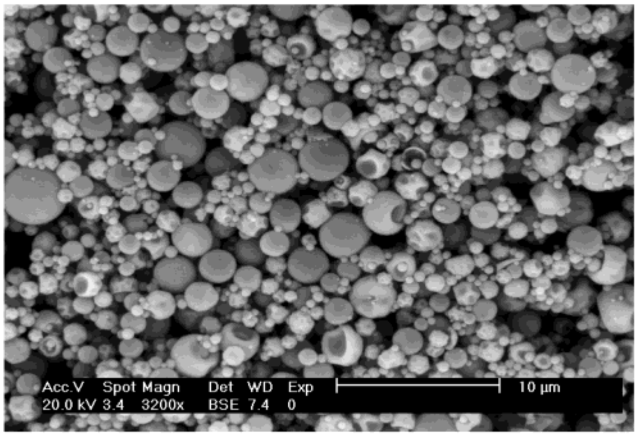

Figure 1. Scanning electron micrograph of a spray-dried powder precursor of $Sr_4Al_{14}O_{25}$ heat-treated at 700 °C for 1 h.

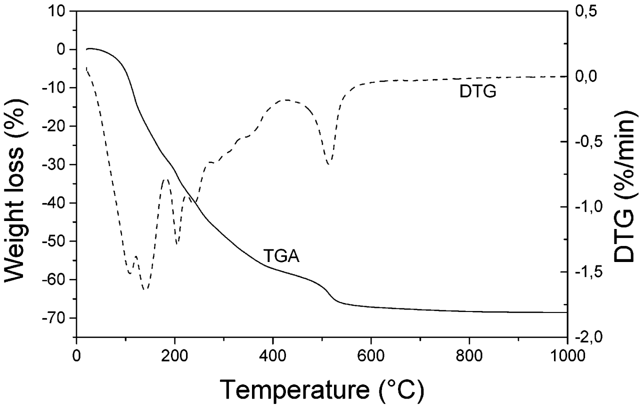

Figure 2. TGA curve of the spray-dried powder precursor of $Sr_4Al_{14}O_{25}$; heating rate 5 °C/min.

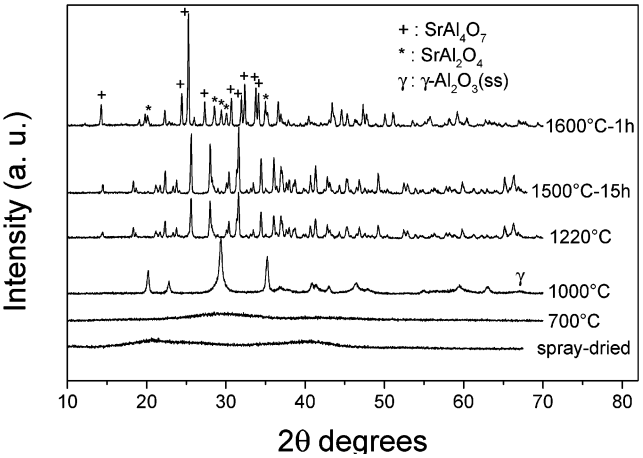

Figure 3. XRD patterns showing the formation of $Sr_4Al_{14}O_{25}$ via $SrAl_2O_4$ and γ-Al_2O_3 solid solutions and its decomposition at higher temperature.

sidebands in the ω_1 dimension and improve the sensitivity, the t_1 time increment was synchronized with the rotor period.[12] The two-dimensional pure absorption phase spectrum was obtained using the hypercomplex method.[13] The ^{27}Al NMR spectra were referenced at 0 ppm relative to a 1 M $Al(NO_3)_3$ aqueous solution.

III. Results and Discussion

III.1. Synthesis of $Sr_4Al_{14}O_{25}$ Precursor. The amorphous precursor powder was obtained by a simple aqueous process, which has been shown to be very efficient in the preparation of chemically very homogeneous aluminosilicate powders, such as mullite and cordierite,[14−16] and alkaline-earth aluminates.[17,18] The starting solution of strontium and aluminum nitrates was rapidly transformed into a powder by spray drying. This process is well-known in ceramic powder synthesis.[19] It usually yields hollow spheres due to rapid supersaturation and precipitation of the salts at the droplet surface, followed by an increase of the inside solvent pressure, and then a disintegration of the hollow spheres leading to shell fragments and second generation smaller particles. Figure 1 shows a typical micrograph for a precursor powder of $Sr_4Al_{14}O_{25}$ calcined at 700 °C. The mean particle size ranges from 0.5 to 4 μm. The spray-dried powder, being slightly hygroscopic, was further calcined in order to completely decompose the nitrates. This decomposition was studied by thermal analysis.

The TGA curve of the spray-dried powder (Figure 2) shows that the decomposition takes place between ambient temperature and 600 °C. This curve may be easily interpreted knowing the individual behaviors of aluminum and strontium nitrates at the same heating rate. Similarly spray-dried aluminum nitrate was partially decomposed by spray drying, and by further heating, was completely decomposed between 100° and 350 °C, with two maxima for the weight loss rate at 145 °C and 265 °C.[17] Strontium nitrate was decomposed between 535 and 720 °C, with a strong maximum at 703 °C. In Figure 2, the weight loss between ambient and about 400 °C traduces the release of adsorbed water (maximum at 108 °C) and the completion of the decomposition of aluminum oxynitrate, with the two maxima at 140 and 205 °C. The weight loss at about 500 °C (maximum at 514 °C) is due to the decomposition of strontium nitrate. As in the case of synthesis of calcium aluminate precursors[17] the decomposition of aluminum nitrate is shifted to lower temperatures in the presence of intimately mixed strontium nitrate, and conversely the decomposition of strontium nitrate is lowered in such mixtures, by nearly 200 °C in the case of $4SrO\cdot 7Al_2O_3$.

III.2. Intermediary Solid Solutions. The spray-dried powder, after decomposition of the strontium nitrate and heating to 700 °C for 1 h, was amorphous (Figure 3). The crystallization has been studied by DSC, at a 5 °C/min heating rate (Figure 4). The DSC trace exhibits two exotherms: a sharp one at 923 °C, and a second one, wider, at 1134 °C. The XRD diagram of the spray-dried powder heated to 1000 °C (Figure 3) shows that the first exothermic event is due to the crystalliza-

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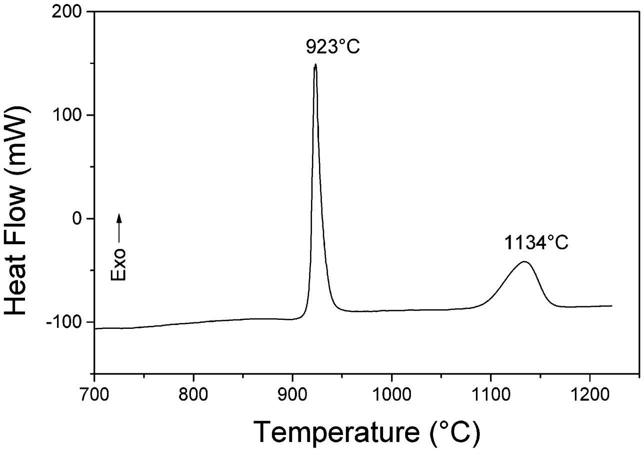

Figure 4. DSC curve of the amorphous powder precursor of $Sr_4Al_{14}O_{25}$; heating rate 5 °C/min.

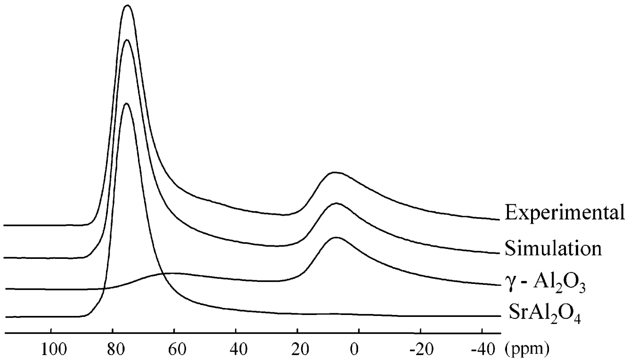

Figure 5. ^{27}Al MAS NMR spectrum of the mixture of solid solutions after heating to 1000 °C.

tion of strontium monoaluminate $SrAl_2O_4$ in its hexagonal structure (JCPDS file 31-1336), that is its high-temperature modification.[20] Usually this polymorph is not stable at room temperature and transforms to the monoclinic structure by cooling below 650 °C.[20] Studies in our laboratory have shown that the hexagonal structure may be stabilized at room temperature after firing to 1000−1300 °C as solid solution with excess aluminum content or calcium or silicon atoms. The presence, scarcely discernible, of a weak bump at 67° 2θ on this XRD diagram, indicates that a part of the powder has crystallized into a high defect transition alumina solid solution (of γ-Al_2O_3 type). As in the CaO−Al_2O_3 system[17] all the alumina-rich precursors synthesized by this process crystallize first into γ-Al_2O_3 solid solution, at least partly. After heating to the first exotherm, the powder is thus a mixture of two solid solutions: $SrAl_2O_4$ (high temperature form) and γ-Al_2O_3.

The presence of these two solid solutions was confirmed by ^{27}Al MAS NMR experiments at 9.4T. As shown in Figure 5, the ^{27}Al MAS NMR spectrum of the spray-dried powder heated to 1000 °C exhibits two overlapping AlO_4 resonances and one AlO_6 resonance. It may be easily simulated as a combination of the experimental spectra of $SrAl_2O_4$ and γ-Al_2O_3 solid solutions synthesized separately under the same conditions. In the $SrAl_2O_4$ structure all the aluminum atoms are located into AlO_4 tetrahedra, whereas in the γ-Al_2O_3 solid solution there are both tetra- and hexa-coordinated aluminum environments. As these two solid solutions are stabilized by excess aluminum atoms for $SrAl_2O_4$ and excess strontium atoms for γ-Al_2O_3, their exact respective compositions remain unknown and cannot be simply determined from this MAS NMR spectrum. It should be noted that the observed ^{27}Al line shapes are characteristic of a distribution of ^{27}Al chemical shift and quadrupolar coupling constant as expected for these disordered solid solutions.

Table 1. $Sr_4Al_{14}O_{25}$ Cell Parameters

	a (Å)	b (Å)	c (Å)
Nadezinha et al. (ref 6)	24.785	8.487	4.866
Wang et al. (ref 5)	24.7451(2)	8.4735(6)	4.8808(1)
this work	24.7751(6)	8.4826(5)	4.8838(1)

III.3. $Sr_4Al_{14}O_{25}$. After heating beyond the second exotherm (1220 °C, Figure 4) only $Sr_4Al_{14}O_{25}$ was found on the XRD diagram (Figure 3). In some preparations it may happen that little amounts of $SrAl_2O_4$ and $SrAl_4O_7$ are present in addition to $Sr_4Al_{14}O_{25}$ just after the second exothermic peak, but these phases react easily together by further heating to yield pure $Sr_4Al_{14}O_{25}$. This phase is stable up to 1500 °C (at least 15 h at this temperature) and decomposes at 1600 °C into $SrAl_2O_4$ (monoclinic form at room temperature) and $SrAl_4O_7$. The latter compound, being not stable at this temperature, decomposes into a mixture of $SrAl_2O_4$ and $SrAl_{12}O_{19}$ but this decomposition is slow at this temperature.[21]

The whole process of formation−decomposition may thus be summarized as follows: (a) 923 °C, crystallization into $SrAl_2O_4$ (hexagonal) and γ-Al_2O_3 solid solutions; (b) 1134 °C, formation of $Sr_4Al_{14}O_{25}$ by combination of the two solid solutions; (c) up to 1500 °C, $Sr_4Al_{14}O_{25}$ is stable; and (d) 1600 °C, decomposition into $SrAl_2O_4$ and $SrAl_4O_7$.

Studies in our laboratory[22] have shown that $SrAl_4O_7$ and $Sr_4Al_{14}O_{25}$, having close compositions, should not coexist. Their respective domains of stability exclude each other. $SrAl_4O_7$ may be obtained as a pure phase by the same process of synthesis in the 900−1000 °C temperature range, but with a low kinetics of formation, either via the two $SrAl_2O_4$ and γ-Al_2O_3 solid solutions or directly. On the other hand, at temperatures higher than about 1100 °C, $Sr_4Al_{14}O_{25}$ is preferentially formed and $SrAl_4O_7$ can no more be crystallized, except in another range of temperature close to its melting point (~1830 °C). $SrAl_4O_7$ is not stable in the temperature domain of stability of $Sr_4Al_{14}O_{25}$ and its decomposition by prolonged heating at 1400 °C into $SrAl_2O_4$ and $SrAl_{12}O_{19}$, strontium mono- and hexa-aluminates, has already been reported.[21]

By Rietveld refinement, using the Fullprof whole pattern fitting program[23] on the sample heated to 1500 °C for 15 h, the orthorhombic structure reported by Nadezhina et al.[6] and Wang et al.[5] was confirmed for our $Sr_4Al_{14}O_{25}$ sample, with space group $Pmma$ and cell parameters close to those already reported in the literature (Table 1).

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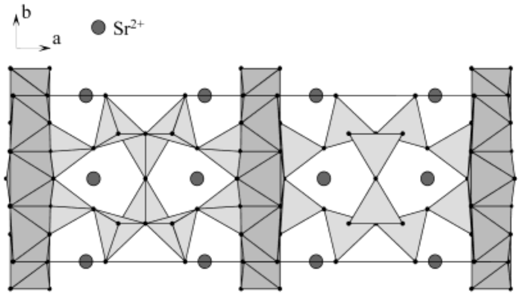

Figure 6. Projection of the structure of $Sr_4Al_{14}O_{25}$ on the ab plane.

To confirm the structural description previously proposed,[5,6] we have characterized the local environment of aluminum in $Sr_4Al_{14}O_{25}$ using high-resolution ^{27}Al NMR spectroscopy. The structure of orthorhombic $Sr_4Al_{14}O_{25}$ consists of layers made up of AlO_6 octahedra chains interconnected by a double layer of AlO_4 tetrahedra chains[5,6] (Figure 6). The octahedra are connected together by sharing one edge, whereas the tetrahedra are connected by corner sharing, two by two or three by three, resulting in the presence of tricoordinated oxygen atoms and tetrahedra triclusters such as in $CaAl_4O_7$,[24] $SrAl_4O_7$,[25] and mullite.[26] There are six different crystallographic sites for the aluminum atoms in the structure: three AlO_6 octahedral sites and three AlO_4 tetrahedral sites.

The ^{27}Al MAS NMR spectra of $Sr_4Al_{14}O_{25}$ obtained at two different applied magnetic fields (9.4 and 14.1T) are shown in Figure 7. The observed change in line shape with the applied magnetic field indicates that the broadening of the spectra is due to second-order quadrupolar interaction, as expected for ^{27}Al. These spectra evidence the presence of several AlO_4 overlapping resonances in the frequency range 40 to 90 ppm, in addition to one narrow and two broader AlO_6 resonances as clearly indicated by the well-defined discontinuities in the frequency range 10 to −70 ppm. Despite the use of high magnetic field and very fast spinning rate, the different overlapping AlO_4 contributions are not resolved in these spectra. To obtain a ^{27}Al NMR spectrum with improved resolution, we have used the two-dimensional multiple quantum MAS technique that allows us to average out the second-order quadrupolar broadening.[9,11] As shown in Figure 8, three distinct AlO_4 resonances and the narrowest AlO_6 resonance are clearly resolved in the isotropic ω_1 dimension of the MQ-MAS spectrum recorded at 9.4T. The two other broader AlO_6 sites with larger quadrupolar coupling are not detected in this MQ-MAS spectrum due to loss of efficiency of the triple quantum excitation with limited radio frequency field strength.[27] The whole set of one-dimensional MAS and two-dimensional MQ-MAS spectra can be modeled using the parameters reported in Table 2[28] where quantitation is derived from the MAS spectrum obtained at 14.1T.

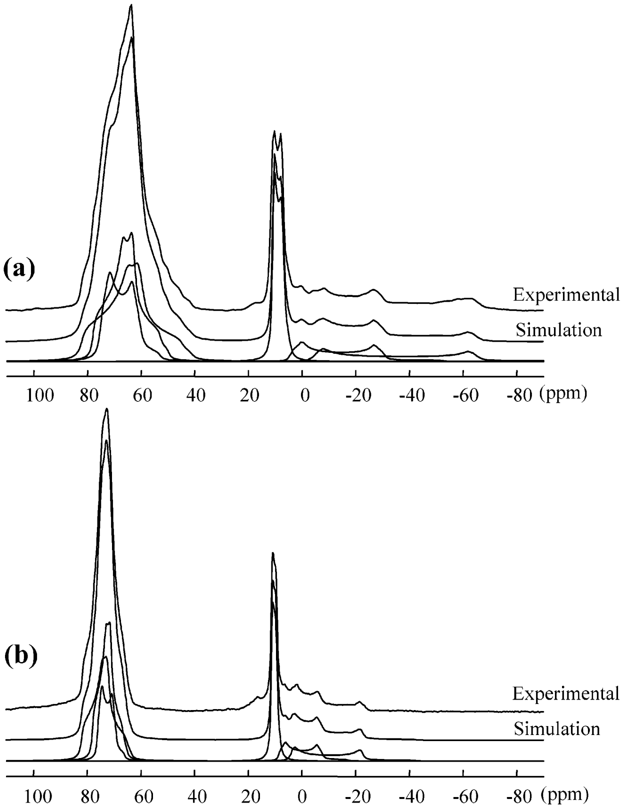

Figure 7. Experimental ^{27}Al MAS NMR spectra of $Sr_4Al_{14}O_{25}$ obtained at (a) 9.4T (14 kHz spinning rate) and (b) 14.1T (35 kHz spinning rate) and their simulations.

The assignment of these different ^{27}Al resonances to the different crystallographic sites of the structure can be realized on the basis of their relative intensities and according to their chemical shift and quadrupolar parameters that are related to the nature and geometry of the ^{27}Al local environments. The three AlO_6 resonances show relative intensities in the ratio 2:1:1 in good agreement with the multiplicities of the Al(4), Al(5), and Al(6) crystallographic sites. The resonance with the highest intensity (δ_{ISO} = 11.7 ppm, C_Q = 2.4 MHz, η_Q = 0.1) is thus unambiguously attributed to the crystallographic Al(4) site. The distinction between the two other AlO_6 contributions (in the intensity ratio 1:1) is made by considering the quadrupolar asymmetry parameter η_Q which measures the deviation from axial symmetry. The resonance with the lower asymmetry parameter (δ_{ISO} = 10.9 ppm, C_Q = 9.3 MHz, η_Q = 0) is attributed to the Al(6) crystallographic site which is close to axial symmetry with the higher contrast between equatorial and apical distances (leading to the higher quadrupolar coupling constant C_Q value), while the remaining contribution (δ_{ISO} = 11.5 ppm, C_Q = 6.8 MHz, η_Q = 0.15) is assigned to the Al(5) site. The relative intensities of the three AlO_4 resonances are in the ratio 2:2:1 in agreement with the multiplicities of the Al(1), Al(2), and Al(3) crystallographic sites. In the $Sr_4Al_{14}O_{25}$ structure, Al(3) and Al(1) are associated in tricluster units while the Al(2) is connected to the double octahedra chains. Previous NMR studies of $CaAl_4O_7$[29] and mullite[30,31] have shown that these tricluster units

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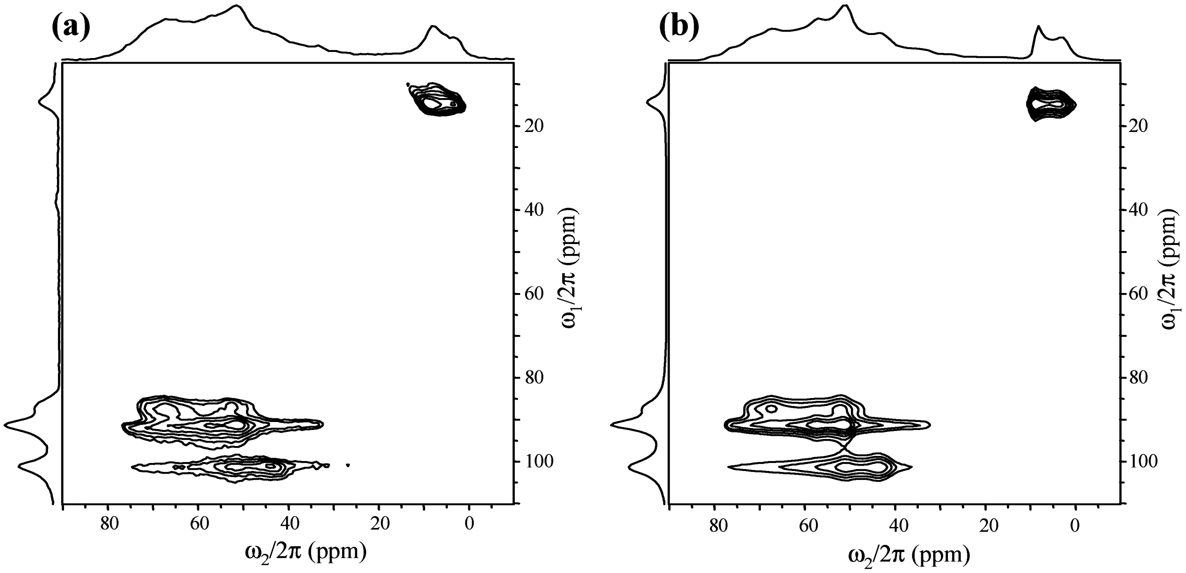

Figure 8. Experimental ^{27}Al MQ-MAS NMR spectrum $Sr_4Al_{14}O_{25}$ obtained at 9.4*T* (a) and its simulation (b).

Table 2. ^{27}Al Isotropic Chemical Shift, Quadrupolar Parameters, and Relative Intensities Obtained from the Simulation of the ^{27}Al MAS and MQ-MAS Spectra of $Sr_4Al_{14}O_{25}$

Al site	Wyckoff position	δ_{ISO} (ppm)	C_Q (MHz)	η_Q	intensity (%) NMR	intensity (%) XRD
Al(1)	8f	78.1 ± 0.2	4.4 ± 0.1	0.75 ± 0.02	29.1	28.6
Al(2)	8f	82.3 ± 0.2	5.2 ± 0.1	0.80 ± 0.02	29.7	28.6
Al(3)	4k	76.9 ± 0.0.2	4.2 ± 0.1	0.25 ± 0.02	14.1	14.3
Al(4)	4g	11.7 ± 0.2	2.4 ± 0.1	0.10 ± 0.02	13.1	14.3
Al(5)	2c	11.5 ± 0.2	6.8 ± 0.1	0.15 ± 0.02	6.9	7.1
Al(6)	2b	10.9 ± 0.2	9.3 ± 0.1	0.00 ± 0.02	7.1	7.1

exhibit significantly lower ^{27}Al isotropic chemical shifts. According to this criterion and to the site multiplicities, the resonances with ^{27}Al isotropic chemical shifts of 76.9 and 78.1 ppm can be assigned to the Al(3) and Al(1) sites respectively, whereas the remaining resonance ($\delta_{ISO} =$ 82.3 ppm, $C_Q = 5.2$ MHz, $\eta_Q = 0.8$) is attributed to the Al(2) site.

IV. Conclusion

$Sr_4Al_{14}O_{25}$ is easily formed at about 1100 °C from an amorphous precursor via metastable solid solutions of $SrAl_2O_4$ and γ-Al_2O_3. It is stable between 1100 and 1500 °C. Its crystallographic structure has been confirmed. The ^{27}Al MAS and MQ-MAS studies allow the characterization of the six different aluminum sites which can be assigned to the different crystallographic positions. This compound gives a good example of aluminum tetrahedral sites in triclusters, the occurrence of which is a matter of debate in related glasses.

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