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The system $Ga_2O_3(Al_2O_3)$–$GeO_2(SiO_2)$ studied by NMR, XRD, IR and DTA

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The formation of germanate phases with the mullite structure [$Ga_6Ge_2O_{13}$, $Al_6Ge_2O_{13}$ and $(Ga,Al)_6Ge_2O_{13}$] from oxide mixtures and hybrid sol–gel precursors was studied by thermal analysis, XRD, IR spectroscopy and multinuclear MAS NMR. The course of the thermal reactions in all the Ga-containing oxide mixtures, irrespective of the starting composition, is dominated by the intermediate formation below 1150 °C of α- and β-Ga_4GeO_8 and by the volatilization of GeO_2 at higher temperatures. In oxide mixtures containing alumina, Ga incorporation in the mullite-type phase occurs only above 1150 °C. IR spectroscopy confirms the incorporation of both Al and Ga into the mullite-type structure at higher temperature. No reaction with Ga_2O_3 occurred where the GeO_2 was replaced by SiO_2.

Thermal treatment of gel precursors produces intermediate amorphous phases in which the Al is in typical sites with a ^{27}Al MAS NMR resonance at 33 ppm, in addition to tetrahedral and octahedral sites. Crystallization of the amorphous intermediates below 1300 °C produces mixtures of the mullite phase and Ga_4GeO_8. Many of the ^{71}Ga MAS NMR spectra are dominated by the quadrupolar lineshape of β-Ga_2O_3 from the structural units of α-Ga_4GeO_8 or unreacted starting material. The ^{71}Ga MAS NMR spectrum of $Ga_6Ge_2O_{13}$ is broad and featureless, as are the ^{69}Ga MAS NMR spectra of these systems. The ^{17}O NMR spectra of an isotopically enriched gel and its reaction products are also reported.

Introduction

Within the Al_2O_3–SiO_2 system, the aluminosilicate mullite has attracted interest because of its favorable high temperature properties, *i.e.* low thermal expansion and conductivity and low creep resistance up to 1400 °C.[1] Mullite is a nonstoichiometric compound with a defect structure and a composition ranging from 3 : 2 to 2 : 1 $Al_2O_3 : SiO_2$, the former produced by sinter processes and the latter crystallizing from the melt. The 1 : 1 composition, Al_2SiO_5, exists in three different structural forms, sillimanite,[2] kyanite and andalusite.[3] Aluminosilicates can be prepared by various methods, ranging from the dehydroxylation of kaolinite clay (which has been studied by solid state NMR)[4] to sol–gel syntheses. The latter have been used for the preparation of mullite and have the advantages of lower temperature of formation and greater purity and homogeneity of the product.[5] The thermal evolution of mullite precursor gels has been studied by solid state NMR,[6] which indicated that the high temperature transformation to mullite can be affected by the previous thermal treatment. The ^{27}Al MAS NMR spectra of the gels show the presence of a peak near 30 ppm with intensity increasing with temperature from 250 °C until just prior to mullite crystallization. This peak is conventionally assigned to 5-coordinate Al, though it bears little resemblance to peaks in crystalline compounds with known 5-coordinate Al environments. The nature of the species giving rise to this peak and its transformation into mullite are of considerable interest as it occurs in many aluminosilicate systems.

Gallium and germanium analogues of the aluminosilicates also exist, as do mixed gallium and aluminium germanates. Schneider and Werner[7] studied the high temperature reactions of GeO_2, Al_2O_3 and Ga_2O_3, finding that andalusite-type germanates were favored at lower temperatures and Al contents, while higher temperatures and Al contents favored 3 : 2 mullite-type germanates. Phase equilibrium studies in the GeO_2–Al_2O_3 system predict only germanium–mullite ($3Al_2O_3{\cdot}2GeO_2$ or $Al_6Ge_2O_{13}$),[8] but two other Al–Ge–O phases are also known. These are Al_2GeO_5, which has the kyanite structure[9] and the digermanate $Al_2Ge_2O_7$, which, unlike thortveitite ($Sc_2Ge_2O_7$),[10] contains AlO_5 bipyramids. Its ^{27}Al MAS NMR spectrum has been reported to have a quadrupolar coupling constant of 8.8 MHz, an asymmetry parameter of 0.4 and an isotropic shift of 36 ppm[10] but with a quadrupolar lineshape giving an entirely different NMR spectrum to the broad 30 ppm peak.

The Ga_2O_3–GeO_2 and Al_2O_3–GeO_2 phase diagrams have been investigated[11,12] and the crystal structures of some of the phases determined.[9] Within these systems, three compounds have been identified: Ga_2GeO_5, Ga_4GeO_8 and $Ga_4Ge_3O_{12}$. Of these, Ga_2GeO_5 is reported[13] to exist in two polymorphic forms, one isostructural with andalusite (below 1300 °C), the other with mullite. However, the 1 : 1 composition suggested by these authors[13] for the mullite-type phase is based on the composition of the starting mixture, with an arbitrary adjustment for the loss of GeO_2; a more likely stoichiometry based on the 3 : 2 composition would be $Ga_6Ge_2O_{13}$. Ga_4GeO_8 also exists in two polymorphic forms, related to the Ga_2O_3–TiO_2 system;[14] the α-form, stable below 1300 K consists of intergrowths of octahedral rutile-type GeO_2 in a β-Ga_2O_3 network, with large hexagonal tunnels at the junction of both lattices. The Ga is located in both tetrahedral and octahedral sites. The high-temperature form, β-Ga_4GeO_8, is similar to metastable Al_4GeO_8 and is isostructural with $Fe_3Ge_2O_8$. $Ga_4Ge_3O_{12}$ appears to be derived from α-Ga_4GeO_8 by insertion of more rutile-type structural elements. No homologues of Ga_2O_3–GeO_2 have been reported in the system Ga_2O_3–SiO_2.

The aim of this work was to systematically explore the formation and structure of compounds formed within the $Ga_2O_3(Al_2O_3)$–$GeO_2(SiO_2)$ systems by sol–gel synthesis, and, for comparison, by solid-state oxide reaction. The reaction products were characterized by multinuclear MAS NMR, IR spectroscopy and X-ray powder diffraction.

Experimental

A series of solid-state reaction mixtures was prepared by blending the appropriate amounts of the various reagent-grade oxides (α-Al_2O_3, Ga_2O_3 (Aldrich), GeO_2 and SiO_2 as appropriate), grinding under ethanol, drying and heating in air at the selected temperature for 1 h. The compositions of the oxide-based preparations (designated O1–O8) are shown in Table 1. A well-crystallized Ga–Ge mullite (O8) was prepared by heating a mixture of Ga and Ge oxides with 43 mol% GeO_2 at 1360 °C for 2 h.

A series of sol–gel preparations (S1–S6) were made by dissolving anhydrous $GaCl_3$ or $AlCl_3$ in dry toluene and adding to ethanolic solutions of $Ge(OC_2H_5)_4$ or $Si(OC_2H_5)_4$ which had been prehydrolysed by heating with 1 mol water per g-atom of Ge or Si. The compositions of these gels are also shown in Table 1.

After reaction at room temperature for 72 h most of the residual solvent was removed by warming (samples S1 and S2 go brown or black, S3 and S4 are white and S5 and S6 form clear gels). The gels were then heated at 350 °C for 1 h (S1 then becomes black, S2 grey and the others white). The gel samples were subsequently heated sequentially for 1 h at selected temperatures. The prehydrolysis of $Ge(OC_2H_5)_4$ was carried out with water enriched with 20% ^{17}O (Isotec) and the solution refluxed for 1 h.

Room-temperature MAS NMR spectra were obtained at 11.7 T using a Varian Unity 500 spectrometer and a 5 mm Doty MAS probe with sample spinning at 10–14 kHz. The ^{27}Al, ^{69}Ga, ^{71}Ga and ^{17}O spectra were obtained using an echo pulse sequence with 16-step phase recycling[15] and 1 μs pulses with 0.1 s recycle delays. The echo delay was set to synchronize with the sample rotation; for a spinning speed of 14 kHz a delay of 71 μs was used. These spectra were referenced to aqueous $Al(NO_3)_3$, $Ga(NO_3)_3$ solutions and water, respectively. The ^{29}Si spectra were obtained using a Bloch decay pulse sequence with 4 μs pulses and 30 s recycle delays, the spectra being referenced to tetramethylsilane (TMS).

X-Ray powder diffraction patterns were obtained using a Philips PW 1700 computer-controlled diffractometer with a graphite monochromator and Co-Kα radiation. TG/DSC measurements of oxides were made using a Rheometric Scientific STA 1500H thermal analyzer with a heating rate of 10 °C min^{-1} in air.

Results

Thermal analysis

A selection of DSC traces of the oxide mixtures and gel samples is shown in Fig. 1.

All the oxide mixtures show broad, weak endotherms in the region 400–640 °C (Fig. 1a–c), with sharper, more distinct endotherms at 1107–1111 °C. The only mass change in the oxide mixtures is a small loss starting at about 1320 °C due to the onset of GeO_2 volatilization. Based on the published phase diagram[9] and the XRD results (Table 1), these events in O2 and O4 may correspond to the formation of α-Ga_4GeO_8, which converts at 1053 °C to the (high temperature) β-form. A

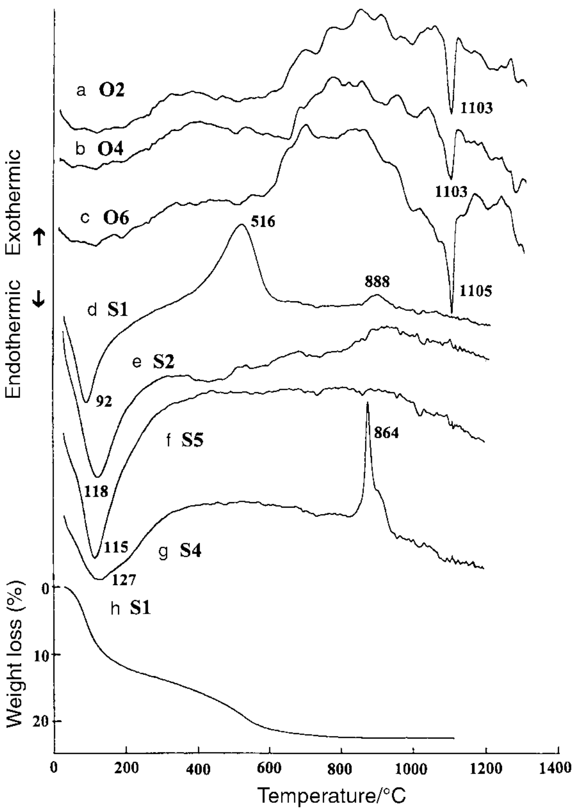

Fig. 1 (a–g) DSC curves for selected oxide mixtures and sol–gel precursors in air, heating rate 10 °C min^{-1}. (h) TG curve for sample S1 under the same conditions.

Table 1 Sample composition and X-ray powder diffraction data

	Mol fraction of oxide					XRD phases observed after heating	
Sample	Ga_2O_3	Al_2O_3	GeO_2	SiO_2	Nominal composition	1150 °C	1370 °C
O1	1.5	—	1	—	$Ga_6Ge_2O_{13}$	α- + β-Ga_4GeO_8	Ga_2O_3 + $Ga_6Ge_2O_{13}$ (tr)
O2	1	—	1	—	Ga_2GeO_5	α- + β-Ga_4GeO_8	$Ga_6Ga_2O_{13}$ + Ga_2O_3
O3	0.75	0.25	1	—	$Ga_3AlGe_2O_{10}$	β- + α-Ga_4GeO_8 + Al_2O_3	amor + $(Ga,Al)_6Ge_2O_{13}$ + Ga_2O_3
O4	0.5	0.5	1	—	$GaAlGeO_5$	β- + α-Ga_4GeO_8 + Al_2O_3	$(Ga,Al)_6Ge_2O_{13}$
O5	0.25	0.75	1	—	$GaAl_3Ge_2O_{10}$	amor + Ga_2O_3 + Al_2O_3 + GeO_2	$(Ga,Al)_6Ge_2O_{13}$
O6	0	1	1	—	Al_2GeO_5	$Al_6Ge_2O_{13}$ + Al_2O_3	$Al_6Ge_2O_{13}$
O7	0.1	0.9	—	1	$(Al,Ga)_2SiO_5$	Ga_2O_3 + Al_2O_3 + SiO_2	Ga_2O_3 + Al_2O_3 + SiO_2
O8	1.3	—	1	—	$Ga_6Ge_2O_{13}$	—	$Ga_6Ge_2O_{13}$
						800 °C	1300 °C
S1	1.5	—	1	—	$Ga_6Ge_2O_{13}$	amor + GeO_2 + ?	β-Ga_4GeO_8 + $Ga_6Ge_2O_{13}$
S2	0.75	0.75	1	—	$Ga_3Al_3Ge_2O_{13}$	amor + GeO_2	$(Ga,Al)_6Ge_2O_{13}$ + β-Ga_4GeO_8
S3	—	1.5	1	—	$Al_6Ge_2O_{13}$	amor + ?	$Al_6Ge_2O_{13}$ + ?
S4	—	1	1	—	Al_2GeO_5	amor + GeO_2	$Al_6Ge_2O_{13}$
S5	0.75	0.75	—	1	$Ga_3Al_3Si_2O_{13}$	amor	Ga_2O_3 + $Al_6Si_2O_{13}$(tr)
S6	1	—	—	1	Ga_2SiO_5	amor + ?	Ga_2O_3 + SiO_2

amor = amorphous phase. ? = unidentified phase.

subsequent weak exotherm at 1220–1250 °C in O2 and O4 (Fig. 1a,b) may correspond to the conversion of β-Ga_4GeO_8 to the mullite-type phase $(Ga,Al)_6Ge_2O_{13}$, which is reported[9] to occur above 1300 °C for the pure Ga compound, this temperature decreasing as the proportion of Al in the sample increases. On this basis, the pure aluminium germanate mullite could have already formed in mixture O6 at the temperature of the 1111 °C endotherm (Fig. 1c); XRD (Table 1) shows this to be the case.

The sol–gel samples S1, S2, S4 and S5 (Fig. 1d–g) all show broad endotherms at 90–110 °C with continuing mass loss up to 600 °C of up to 20% (in S1), despite pre-heating at 350 °C for 1 h. In sample S1 (composition $Ga_6Ge_2O_{13}$), this mass loss (Fig. 1h) encompassed an additional exotherm at 516 °C (Fig. 1d). These losses, which were complete in all the gel samples by 600 °C, are associated with the removal of absorbed moisture (at lower temperatures) and, in the case of S1, the exothermic removal of tightly-bound residual solvent or unhydrolysed alkoxy groups which are not removed by thermal treatment at 350 °C. Gels S1 and S4 show higher-temperature exotherms at 888 and 864 °C, respectively (Fig. 1d,g); a corresponding but broader and poorly-defined feature may also be discerned in S2 (Fig. 1e). In common with the oxide mixtures shown in Fig. 1, these gel samples have mullite-type phases as their high-temperature crystallization products (Table 1), yet the DSC results indicate differing thermal behavior. XRD (Table 1) indicates that at 800 °C all the gel samples are still X-ray amorphous, but some contain phase-separated GeO_2. By 1300 °C, all but S6 have crystallized to form a mullite-type phase. As with the oxide mixtures, the reaction in S1 and S2 involves Ga_4GeO_8 as either an unreacted intermediate or a co-product. The exotherm in S4 (Fig. 1g) must be related to the formation of the mullite-type phase $Al_6Ge_2O_{13}$, since this is the sole product of this gel. By contrast with the formation of this compound in the oxide mixture O6 (Fig. 1c), this exotherm is sharper and occurs about 400 °C lower, similar to the differences between gel and oxide syntheses of aluminosilicate mullite.

Powder X-ray diffraction

Reactions in the oxide mixtures. The XRD results (Table 1) indicate that in the oxide mixtures containing Ga_2O_3, GeO_2 and varying amounts of Al_2O_3, the reaction proceeds, irrespective of the starting composition, *via* the formation of α- and β-Ga_4GeO_8 (PDF numbers 36-290 and 4-235) which is complete by 1150 °C. At this temperature, the alumina addition has still not reacted. In all these cases, the final product, formed by 1370 °C, shows the typical mullite-type XRD pattern of $Al_6Ge_2O_{13}$ (PDF no. 19-15), which is similar to that of another phase described as mullite-type, Ga_2GeO_7 (PDF no. 35-387). As discussed in the introduction, the latter is more likely to have a composition nearer to 3 : 2 mullite ($Ga_6Ge_2O_{13}$) rather than its nominal starting composition, due to volatilization of its oxide constituents during thermal reaction.

In mixture O6, containing no Ga_2O_3, the mullite-structure $Al_6Ge_2O_{13}$ is formed by 1150 °C. No crystalline reaction product is formed in the system Ga_2O_3–Al_2O_3–SiO_2.

Consideration of the reaction stoichiometry in the oxide mixtures in the light of Table 1 shows that, in all cases, the results can be understood in terms of the stability of the intermediate phase Ga_4GeO_8 and the volatilization of excess GeO_2. Thus, the reactions in mixture O1 can be written:

$$2Ga_2O_3 + 1.33GeO_2 \rightarrow Ga_4GeO_8 + 0.33GeO_2\uparrow \qquad (1)$$

The composition Ga_4GeO_8 also corresponds to a mullite of 2 : 1 stoichiometry, which could adopt the mullite structure at higher temperatures by atomic rearrangement, without further loss of GeO_2. However, the formation in air of a conventional 3 : 2 mullite composition would require the loss of further GeO_2:

$$3Ga_4GeO_8 + 2O_2 \rightarrow 2Ga_6Ge_2O_{13} + GeO_2\uparrow \qquad (2)$$

A similar reaction can be written for the equimolar mixture O2, in which case the loss of 1 mol of GeO_2 is predicted in the formation step of Ga_4GeO_8. The presence of excess Ga_2O_3 in both these mixtures heated to 1370 °C (Table 1) is consistent with the high-temperature loss of additional GeO_2, detected by TG.

When increasing amounts of Al_2O_3 are introduced, as in mixtures O3–O5, the alumina does not participate in the initial stage of the reaction, as with mixture O4:

$$2Ga_2O_3 + 2Al_2O_3 + 4GeO_2 \rightarrow Ga_4GeO_8 + 3GeO_2\uparrow + 2Al_2O_3 \quad (3)$$

The alumina is incorporated during the formation of the mullite-type phase at higher temperatures:

$$Ga_4GeO_8 + 2Al_2O_3 + 1.67GeO_2 \rightarrow 1.33Ga_3Al_3Ge_2O_{13} \quad (4)$$

In the alumina-rich composition O5, insufficient Ga_2O_3 is present to form the intermediate phase Ga_4GeO_8 and, in the absence of an Al analogue, the mullite-type phase is formed directly at higher temperature:

$$0.75Ga_2O_3 + 2.25Al_2O_3 + GeO_2 \rightarrow Ga_{1.5}Al_{4.5}Ge_2O_{13} + GeO_2 \quad (5)$$

In the absence of Ga_2O_3 (mixture O6), the mullite-type phase is formed directly at 1150 °C:

$$3Al_2O_3 + 3GeO_2 \rightarrow Al_6Ge_2O_{13} + GeO_2\uparrow \qquad (6)$$

The presence of unreacted Al_2O_3 at 1150 °C suggests that this reaction proceeds *via* a Ge-rich composition which assumes the final stoichiometry by the further loss of a small amount of GeO_2 at higher temperatures.

Reactions in the gels. Even after heating to 800 °C, all the gel compositions retain a considerable proportion of X-ray amorphous material: in samples S1, S2 and S4 this is a material from which some GeO_2 has crystallized, whereas in S1, S3 and S6, the material is another poorly developed phase showing two peaks which are too diffuse to permit identification. By 1300 °C, these amorphous phases have crystallized to identifiable products for which the following equations may be written:

$$\text{Gel S1.}\ 5Ga_2O_3 + 3.33GeO_2 \rightarrow Ga_4GeO_8 + Ga_6Ge_2O_{13} + 0.33GeO_2\uparrow \quad (7)$$

$$\text{Gel S2.}\ 3Ga_2O_3 + 3Al_2O_3 + 4GeO_2 \rightarrow 1.33Ga_{1.5}Al_{4.5}Ge_2O_{13} + Ga_4GeO_8 + 0.33GeO_2\uparrow \quad (8)$$

The only identifiable crystalline phase in gel S3 is a small amount of $Al_6Ge_2O_{13}$; the major crystalline phase could not be identified, although the phase diagram[9] predicts Al_2GeO_5. The stoichiometry of gel S4 indicates that its formation of very pure crystalline mullite-type $Al_6Ge_2O_{13}$ is described by eqn. (6). The two Si-containing gels S5 and S6 are very unreactive, as was found with mixture O7; both contain unreacted Ga_2O_3 but the Al-containing gel S5 produced a small amount of mullite. The latter is presumed to be $Al_6Si_2O_{13}$, since no evidence of a Ga-containing silicate mullite has been found amongst the other Si-containing compositions.

To summarize, the formation of germanate mullite-type phases in the gel samples containing Ga proceeds with the co-formation of Ga_4GeO_8. The persistence of the latter at 1300 °C may indicate a difficulty in producing monophases from such gels. By contrast, Al-germanate gels readily produce pure germanate mullite at 1300 °C. Gels containing Si are unreactive.

IR spectroscopy

The FTIR spectra of the oxide mixtures heated at 1370 °C are shown in Fig. 2. All the spectra of mixtures containing Ga (Fig. 2a–d) show bands at 668 and 460 cm^{-1}, corresponding to characteristic Ga–O vibrations which are also present in Ga_2O_3. The germanate phases in the mixtures are responsible for bands near 1040 and 750 cm^{-1}, the frequencies of which change essentially linearly with the degree of Al-for-Ga substitution (Fig. 3).

The strength of these bands in the pure Al germanate (Fig. 2e) indicates that in this material they are associated with Al–O–Ge vibrations; their change in frequency with Ga substitution is consistent with a close association of both Ga and Al in the same germanate phase. The observed increase of the 1040 cm^{-1} vibration frequency as the average mass of the M^{3+} cation decreases (Fig. 3) is as predicted for Ga-for-Al substitution at a common (tetrahedral) site in the same germanate phase.

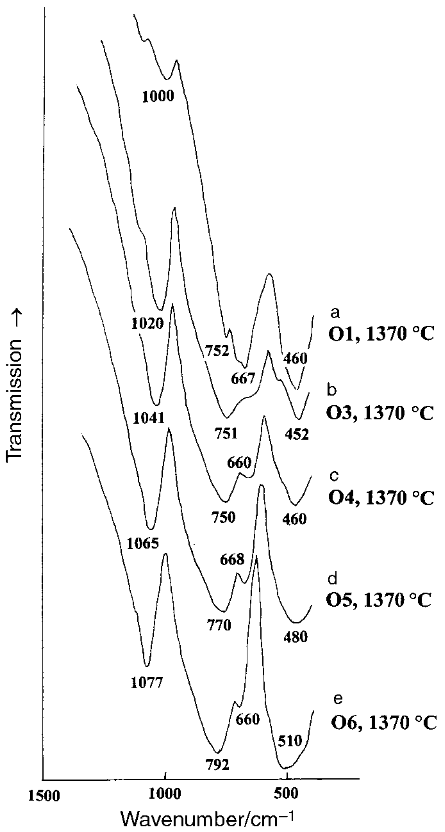

Fig. 2 FTIR spectra of oxide mixtures heated at 1370 °C.

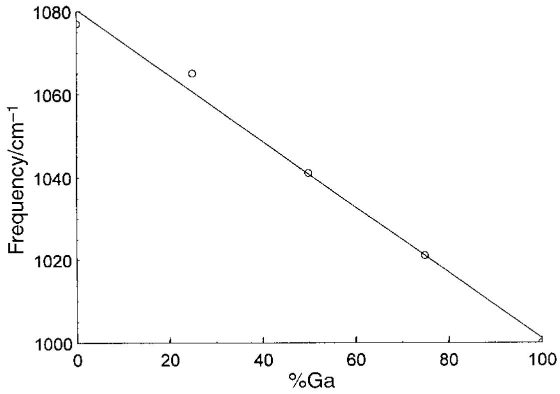

Fig. 3 Change in infrared frequency with Ga content in (Ga, Al) germanates derived from oxide mixtures heated at 1370 °C.

MAS NMR

^{27}Al spectra. A selection of room-temperature ^{27}Al MAS NMR spectra of the various Al-containing oxide mixtures heated at 1150 and 1370 °C is shown in Fig. 4. The NMR spectra show that, irrespective of the starting composition, the Al configuration after heating these oxide mixtures at 1150 °C is very similar, with octahedral and tetrahedral sites indicated by the peaks at 14 and 55 ppm, respectively. The 14 ppm peak is characteristic of the unreacted α-alumina seen by XRD. In samples heated to 1370 °C, the presence of the 14 ppm peak indicates the persistence of some unreacted α-alumina (undetected by XRD), but the formation of Ge–mullite in these samples has the effect of moving the main octahedral peak upfield by an amount depending on the degree of Ga-for-Al substitution. In the sample containing no Ga (O6, Fig. 4e), the octahedral peak is at 4 ppm, whereas in the sample containing 75% Ga substitution (O3, Fig. 4h), the peak has moved to 7 ppm. The upfield tail on the main octahedral resonance is indicative of a range of electric field gradients (EFGs) due to disorder. All these samples contain a large tetrahedral resonance at 58 ppm; their spectra closely resemble that of Al–Si mullite, and appear to be insensitive to composition, apart from the small changes in the position of the octahedral peak.

The ^{27}Al spectra of the Al-containing gel samples heated at three different temperatures are shown in Fig. 5. The spectra of gel S2 (initial composition $Ga_3Al_3Ge_2O_{13}$) indicate that, after heating at 350 °C it contains predominantly octahedral Al, with only a trace of tetrahedral Al detectable (Fig. 5c). Heating to 800 °C, at which temperature the aluminate component is still amorphous, produces a typical aluminate gel spectrum (Fig. 5b) containing tetrahedral and octahedral peaks at 61 and 11 ppm respectively, and a central peak at 32 ppm which is often assigned to five-coordinate Al. The 32 ppm peak is lost on formation of the mullite-type phase at 1350 °C (Fig. 5a), but the proportion of tetrahedral Al (47%) is less than in the corresponding oxide-derived sample O4 (Fig. 4g).

For gel S3 (initial composition $Al_6Ge_2O_{13}$), the typical three-peak amorphous aluminate spectrum is already developed at

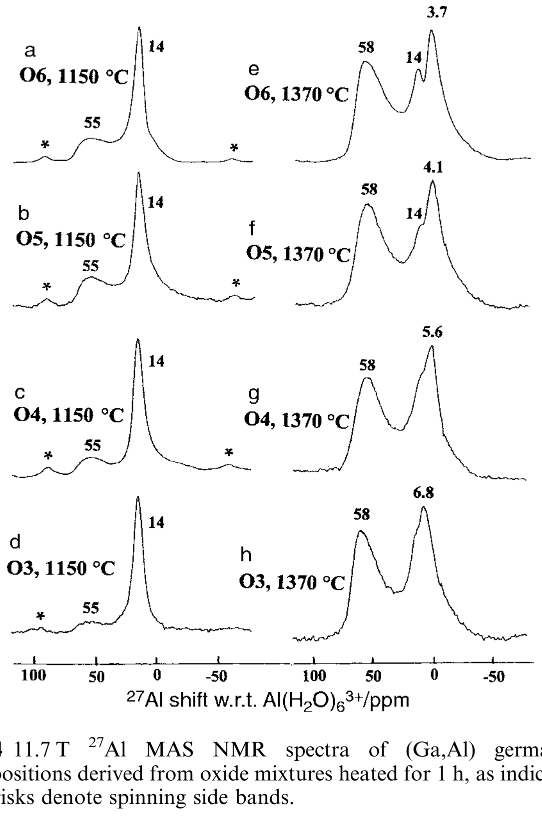

Fig. 4 11.7 T ^{27}Al MAS NMR spectra of (Ga,Al) germanate compositions derived from oxide mixtures heated for 1 h, as indicated. Asterisks denote spinning side bands.

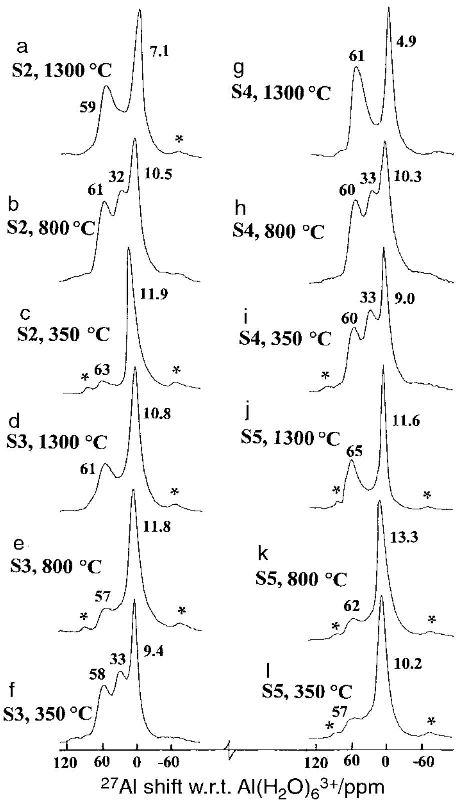

Fig. 5 11.7 T ^{27}Al MAS NMR spectra of sol–gel (Ga,Al) germanate preparations heated for 1 h, as indicated. Asterisks denote spinning side bands.

350 °C (Fig. 5f); by 800 °C the 33 ppm peak has disappeared, the phase assemblage at this temperature containing only octahedral and tetrahedral Al. The proportion of tetrahedral Al increases to 39% on heating at 1300 °C (Fig. 5d) but never reaches the proportion found in the analogous oxide mixture O6 (Fig. 4e).

Gel S4 (containing 0.5 mol less Al_2O_3 than S3) shows a similar early development of the three-peak aluminate spectrum (Fig. 5i), but this, however, persists beyond 800 °C. The spectrum of the final $Al_6Ge_2O_3$ product (Fig. 5g) is more like that of the corresponding oxide-derived phase, containing a higher proportion of tetrahedral Al (62%) than the mullite products of the other gels. The spectrum of S4 differs from that of O6 in showing slightly sharper peaks, which are also shifted downfield, suggesting less disorder. The absence of α-alumina in S4 also indicates a greater degree of homogeneity than in O6.

Gel S5 (the silicate analogue of S2) is the only composition which shows no three-peak spectrum at any stage of heating (Fig. 5j–l), suggesting that this gel is less homogeneous than its Ge-containing analogue. Little difference in the tetrahedral/octahedral Al ratio is induced by heating the gel to 800 °C, but although the octahedral peak shifts to 13 ppm, close to the value for α-alumina, the sample remains X-ray amorphous. The formation of some $Al_6Si_2O_{13}$ at 1300 °C is accompanied, as expected, by an increase in the proportion of tetrahedral Al to 47%. The shoulder at about 73 ppm has also been reported in $Al_2Ge_2O_7$, in which it was attributed to the tetrahedral site in a transitional aluminium oxide impurity.[11]

In summary, the substitution of Ga for Al in the heated oxide mixtures has no effect on the tetrahedral Al sites and produces only a small downfield shift in the octahedral Al resonance with increasing Ga content.

In the gel samples, the development of the amorphous aluminate site at 33 ppm is delayed by the substitution of Ga for Al, but its thermal stability is unaffected. The ^{71}Ga signal is very weak in this sample heated at 800 and 1300 °C (see below), raising the possibility that 5-coordinated Ga is also favored in this system.

A smaller proportion of tetrahedral Al is seen in the fully-reacted gel samples, by comparison with the analogous oxide mixtures. This may indicate a predominance of the tetragonal form of mullite, which contains less tetrahedral Al than the higher-temperature orthorhombic form. The preferred formation of tetragonal mullite in the gel samples could result either from the lower processing temperature or from some templating effect inherited from the gel synthesis.

^{71}Ga and ^{69}Ga spectra. A selection of ^{71}Ga spectra are shown in Fig. 6. The spectra are generally broad, with widths of 50–90 kHz, but in some instances show quadrupolar fine structure arising from several environments. Magic angle spinning removed residual dipolar broadening and produced a slight sharpening of the fine structure.

Gel S6 heated at 1300 °C contains only unreacted $Ga_2O_3 + SiO_2$; its spectrum (Fig. 6a) is as reported[16] for β-Ga_2O_3, containing Ga in both octahedral and tetrahedral sites with large electric field gradients (EFGs). Similar spectra were recorded for gel S1 heated at 1300 °C and for the oxide mixtures O1–O5 heated at 1150 °C. These oxide mixtures all contain α-Ga_4GeO_8, the structure of which consists of β-Ga_2O_3 into which rutile-type GeO_2 chains are inserted. The similarity of their spectra to that of β-Ga_2O_3 suggests that the presence of the rutile-like chains has little effect on the EFGs experienced by the Ga. The oxide mixture O7, in which the Ga_2O_3 remains unreacted even at 1370 °C, also shows a typical Ga_2O_3 spectrum, as in Fig. 6a in the 1150 and 1370 °C samples.

Many of the other ^{71}Ga spectra are broad and featureless, but show some changes on heating, possibly due to the effects of disorder. Thus the spectrum of oxide mixture O3 heated at 1150 °C displays the features of the β-Ga_2O_3 units of α-Ga_4GeO_2 (Fig. 6a) but at 1200 °C this structure is lost (Fig. 6d). On further heating, the broad featureless peak shifts downfield

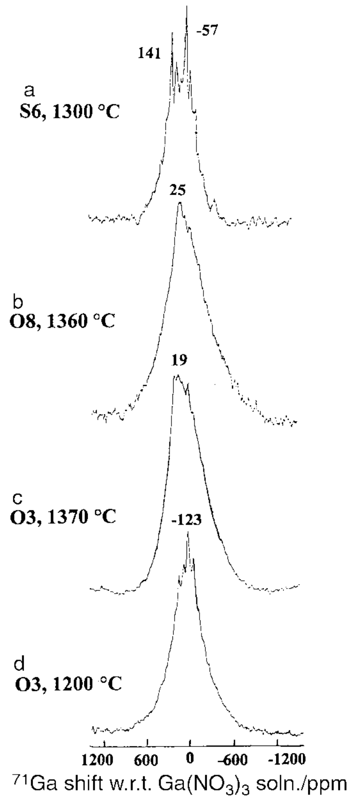

Fig. 6 Typical 11.7 T ^{71}Ga MAS NMR spectra of (Ga,Al) germanates derived from sol–gel precursors and oxide mixtures.

(Fig. 6c), approaching the position and asymmetric shape of crystalline $Ga_6Ge_2O_{13}$, as typified by O8 (Fig. 6b). The broadness and shape of the latter may arise from the presence of disorder and an associated range of EFGs.

The presence of large EFGs may also be the reason for a major loss of ^{71}Ga signal intensity observed in gel S2 when heated at 800–1300 °C. XRD indicates that the products are $Al_6Ge_2O_{13}$ and a small amount of Ga_4GeO_8 (which may be the source of the small residual ^{71}Ga NMR signal), plus another amorphous or highly distorted phase. If the latter contains Ga in 5-coordinate sites or in other highly distorted environments, the resulting EFGs may be sufficient to broaden the Ga signal beyond detection.

^{69}Ga spectra were also acquired from these samples; they all showed a broad peak at about 120 ppm, but they provided no additional information because of their large halfwidths (about 110 kHz) resulting from the high quadrupole moment of this nuclide and the presence of large EFGs.

^{29}Si spectra. Fig. 7 shows the ^{29}Si spectra of the two Si-containing gels S5 and S6 heated at different temperatures. All the Si-containing compositions were particularly unreactive, as evidenced by these spectra, which show peaks at −106 to −109 ppm, characteristic of uncombined SiO_2. The exception is S5 heated at 1300 °C (Fig. 7c), which contains an additional peak at −86 ppm arising from the small quantity of aluminosilicate mullite detected by XRD in this sample. The broadness of the SiO_2 peaks in the lower-temperature spectra is consistent with amorphous silica; on heating S6 at 1300 °C the SiO_2 crystallizes to cristobalite, with a concomitant sharpening of the resonance (Fig. 7e).

^{17}O spectra. Fig. 7 also shows the ^{17}O spectra of gel sample S1 (initial composition $Ga_6Ge_2O_{13}$) prepared with ^{17}O-enriched water and heated to various temperatures. All the spectra contain at least two resonances corresponding to distinctive oxygen environments; a broad peak near 25 ppm (narrowing slightly on heating), and a sharp peak appearing at 98 ppm at 800 and 1300 °C. At 350 °C (below crystallization), there may be a shoulder at 74 ppm. This resembles previously-reported ^{17}O NMR spectra of mullite during its evolution from aluminosilicate gels,[17] which at 1300 °C showed a broad peak near 30 ppm and a shoulder near 68 ppm.

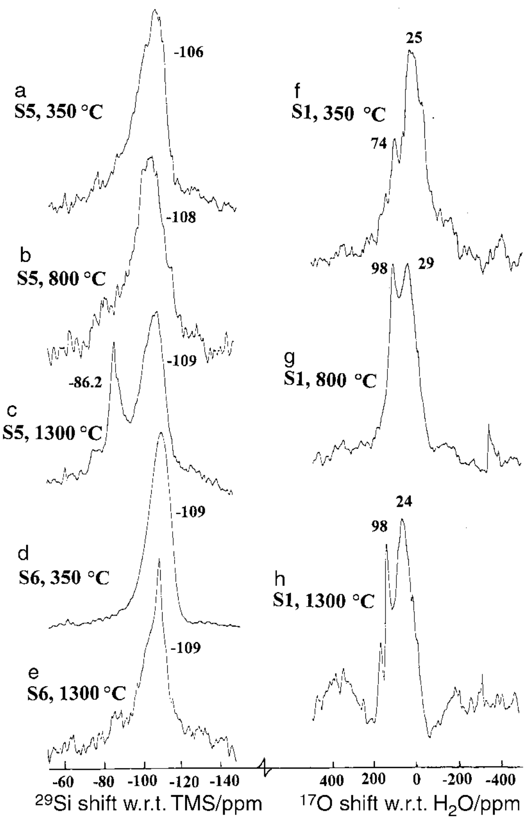

Fig. 7 (a–e) 11.7 T ^{29}Si MAS NMR spectra of (Ga,Al) silicate mixtures from sol–gel precursors. (f–h) 11.7 T ^{17}O MAS NMR spectra of ^{17}O-enriched sol–gel-derived $Ga_6Ge_2O_{13}$ heated for 1 h, as indicated.

^{17}O studies of zeolites[18] and aluminas[19] indicate that the isotropic shift of Si–O–Al, Si–O–Si and OAl_4 units occurs at 31–34, 44–50 and 70–75 ppm, respectively. Substitution of Al by Ga makes virtually no difference to the isotropic chemical shift in zeolites, the value for Ga–O–Si being 28–29 ppm,[20] though the value of the nuclear quadrupole coupling constant χ for the Ga linkage is 4.0 MHz compared to 3.18 MHz for the Al linkage. In a series of isostructural titanates and zirconates (ABO_3) with the same cation, the ^{17}O shifts are constant in the inverse ratio of the metal polarising power;[21] a similar effect has been found for hafnium and zirconium.[22] The ratio of Ga/Al polarising power (proportional to the square of the cation radius) is 1.34, predicting that the Ga–O shifts should differ from those of Al–O by a factor of 0.75.

An indication of the effect on the ^{17}O chemical shift resulting from the substitution of Ge for Si may be gained from studies of $Li_2TiOSiO_4$ in which the Si–O–Ti linkages show a peak at 150 ppm (with $\chi = 3.05$ MHz, $\eta = 0.35$, $\delta_{iso} = 157$). Substitution of Si by Ge in this compound shifts the peak upfield (near 105 ppm) and increases the quadrupolar broadening ($\chi = 4.80$ MHz, $\eta = 0.22$, $\delta_{iso} = 148$).[23] In studies of HfO_2–SiO_2 and HfO_2–GeO_2 gels,[22] OHf_3 and OHf_4 resonances were reported at 343–330 and 252–240 ppm, respectively, analogous to the effect of coordination number in Al oxides. The resonances of Hf–O–Si and Hf–O–Ge occur at 139 and 115 ppm, respectively, with the latter showing larger electric field gradient (EFG) effects ($\chi = 5.2$ MHz, $\eta = 0.65$, $\delta_{iso} = 185$). Thus ^{17}O shifts tend upfield with increasing oxygen coordination number, cation radius and covalent character of the metal–oxygen bond (increased EFG also leading to broadening).[24] These effects would also be expected with the isostructural substitution of Ga for Al and Ge for Si.

A tentative explanation of the ^{17}O spectra of the Ga–Ge mullite-forming system may be made on the basis of the oxygen coordination in the aluminosilicate mullite structure, taking into account the changes in peak positions due to atomic substitutions, as discussed above. In the present gel S1 the broad peak at 25 ppm is approximately 4 ppm upfield from the value for aluminosilicate mullite; although this change is small, it is in the direction expected for Ga substitution of Al, as observed in zeolites. The width of this peak reflects the increase in EFG caused by Ge-for-Si substitution and (probably primarily) by substitutional disorder in the (Si,Al) tetrahedron. The area of the peak implies that most of the oxygens contribute. In the aluminosilicate mullite structure,[25] there are four distinct oxygens, three of which are coordinated to four cations. The other oxygen (O*) is associated with the oxygen tricluster vacancy and is coordinated to only three cations. The coordinating cations may be tetrahedral (T), octahedral (O) or associated with the tetrahedral tricluster vacancy (T*). The coordination environment of the T* cation is asymmetric, leading to two distinct variations of this cation, one with a longer Al–O bond than the other. All oxygens except O* are coordinated to two Al^* cations and either two T sites or 1 T and 1 O cation. This range of tetrahedral coordination types will have an associated range of isotropic shifts and EFGs which give rise to the broad peak at 25 ppm.

The origin of the sharp 98 ppm peak is less clear; it could be a single sharp peak or the downfield component of a quadrupolar lineshape of which the upfield component is obscured by the larger, broader 26 ppm peak. The O* site is only 3-coordinate and is therefore expected to be considerably downfield of the 4-coordinate sites. The occupation of O* is predicted from the mullite structure to be 0.14, by comparison with 2.59 for the other three regular O sites taken together. The much lower area of the 98 ppm peak relative to 26 ppm might suggest the identification of the O* site with the 98 ppm resonance. However, the substitution of Ga and Ge for Al and Si would be expected to lead to an upfield isotropic and EFG shift, whereas the aluminosilicate mullite peak occurs at approximately 68 ppm. Since this downfield shift in the gallium germanate is in the direction expected for shorter M–O bond lengths, this resonance could only arise from an O* site of slightly different geometry to that of aluminosilicate mullite. Alternatively, the origin of the 98 ppm peak may be an impurity phase, such as Ga_4GeO_8, which is present at both 800 and 1300 °C.

Conclusions

Mullite-structure Ga and Al germanate phases and analogues containing various proportions of (Ga,Al) were synthesized from both sol–gel precursors and oxide mixtures.

In the Ga-containing oxide mixtures, the formation of the mullite-type phase proceeds *via* α- and β-Ga_4GeO_8, irrespective of the starting composition, but the formation of the β-form of the intermediate is favored by the presence of alumina, which does not however react with the mixture until the mullite phase is formed above 1150 °C. Pure Al–Ge mullite $Al_6Ge_2O_{13}$ is formed from the oxides at 1150 °C without an intermediate phase, but the presence of Ga increases the formation temperature of the mullite. Systematic changes in the infrared spectra on Al-for-Ga substitution are consistent with the incorporation of both ions into the mullite structure. Volatilization of GeO_2 at higher temperatures can influence the phase composition of the final product, resulting in the presence of unreacted Ga_2O_3 in some mixtures. No reaction was found in mixtures containing Ga_2O_3 and SiO_2.

The formation of mullite-type germanates by thermal treatment of sol–gel precursors proceeds *via* amorphous phases which crystallize below 1300 °C, but the co-existence of Ga_4GeO_8 at 1300 °C may limit the usefulness of these precursors in the production of a monophase product. The ^{27}Al MAS NMR spectra of the Al-containing precursors heated at 350–800 °C show the presence of a site with a characteristic resonance at 33 ppm, typical of amorphous aluminates. The formation temperature of this site is increased by the presence of Ga but its thermal stability at higher temperatures increases with increasing Al content.

The ^{27}Al MAS NMR spectra of the crystallized products are similar to that of aluminosilicate mullite; the smaller proportion of tetrahedral Al in the gel-derived samples by comparison with those prepared from the oxide mixtures may reflect a higher proportion of lower-temperature tetragonal mullite in the former. The thermal behavior of an ^{17}O-labelled $Ga_6Ge_2O_{13}$ gel is also similar to that reported in an aluminosilicate mullite gel precursor, suggesting the involvement of similar oxide units. In many of the samples, the ^{71}Ga MAS NMR spectra are dominated by the characteristic Ga_2O_3 quadrupolar lineshape arising either from unreacted Ga_2O_3 or from the presence of α-Ga_4GeO_8 which contains β-Ga_2O_3 structural units. The ^{71}Ga MAS NMR spectrum of $Ga_6Ge_2O_{13}$ is broad and featureless, suggesting the presence of disordered sites with an associated range of large EFGs which also render the ^{69}Ga MAS NMR spectra too broad and featureless to provide additional information.

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