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Evolution of crystalline aluminates from hybrid gel-derived precursors studied by XRD and multinuclear solid-state MAS NMR

II. Yttrium–aluminium garnet, $Y_3Al_5O_{12}$

K.J.D. MacKenzie[1,*], T. Kemmitt

New Zealand Institute for Industrial Research and Development, P.O. Box 31-310 Lower Hutt, New Zealand

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Abstract

The thermal evolution of structure in a hybrid gel of YAG composition ($Y_3Al_5O_{12}$) prepared from aluminum alkoxide and yttrium acetate was studied up to 1250°C. XRD indicates that the gels are amorphous <900°C, when they abruptly crystallize to YAG and hexagonal $YAlO_3$. The latter exists only briefly, being fully converted to YAG by 1000°C. ^{27}Al MAS NMR shows that after the loss of volatiles at 375°C, the Al occupies three types of sites in the amorphous gel (tetrahedral, octahedral and a site characterized by an NMR resonance at 38 ppm). The distribution of Al over these sites progressively changes during heating <980°C but ^{89}Y MAS NMR suggests that the Y is comparatively less mobile within the gel, achieving its final YAG environment only after the YAG crystal structure has been established. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Yttrium aluminate, $Y_3Al_5O_{12}$, one of the best known of the compounds in the yttria–alumina system crystallises with a cubic garnet structure, leading to the name yttrium–aluminium garnet (YAG). The electronic properties of single-crystal YAG make it suitable as a laser host material, but its high-temperature strength, low creep and thermal expansion compatibility and lack of reaction with alumina also suggest engineering ceramic applications, in monolithic form, as a coating or as fibres for reinforcing ceramic composites. Since solid-state synthesis of YAG from the oxides requires temperatures of ≈1600°C [1], soft chemical methods are an attractive proposition. Recently, Hay [2] and Liu et al. [3] reported syntheses involving the co-hydrolysis of Al and Y alkoxides, whereas Gowda [4] and Manalert and Rahaman [5] have used a hybrid (organic/inorganic) sol–gel synthesis from aluminium tri-sec butoxide and yttrium acetate, in the latter case followed by supercritical CO_2 drying [5]. The hybrid gels are reported to crystallise to YAG at 800–900°C [4,5], but the nature of the interatomic movements which may precede crystallisation in the amorphous precursor is unknown. In this paper, we seek such information by the use of ^{27}Al and ^{89}Y MAS NMR spectroscopy.

Both, the ^{27}Al and ^{89}Y MAS NMR spectra of YAG have previously been reported; the ^{27}Al spectrum [6] showed evidence of octahedral and tetrahedral sites, but not in the expected ratio, possibly because not all

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*Corresponding author. Tel.: +44 18652 73742; fax: +44 18652 73783; e-mail: kenneth.mackenzie@materials.ox.ac.uk

[1] Present address: Department of Materials, University of Oxford, OX1 3PH, UK

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the Al was detected [6]. The ^{89}Y MAS NMR spectrum of YAG [7] shows a relatively broad resonance at 222 ppm (w.r.t. 1 M YCl_3 solution), the broadness of this feature being attributed to residual unaveraged nuclear interactions [7]. The MAS NMR spectra of gels in the Y_2O_3–Al_2O_3 system have not previously been reported, but the technique is used here in conjunction with thermal analysis and X-ray powder diffraction to monitor the processes leading up to the formation of crystalline YAG from a hybrid gel.

2. Experimental

The gel studied here was prepared by the method of Gowda [4] using Al-sec-butoxide dissolved in dry isobutanol added dropwise to a stirred aqueous solution of yttrium acetate at 85°C. After drying at a room temperature, the gel was crushed and examined by thermal analysis in flowing air (50 ml/min) at heating rate of 10°C/min using a Rheometrics STA 1500 thermoanalyser. Samples of the crushed gel were heated in air in platinum crucibles at 600–1250°C for 15 min and examined by powder XRD (Philips PW1700 automatic goniometer with graphite monochromator and CoK_α radiation) and by ^{27}Al and ^{89}Y MAS NMR at 11.7 T (Varian Unity 500 spectrometer with a high-speed 5-mm Doty MAS probe spun at 10–12 kKz). The spectrum acquisition conditions were:

> ^{27}Al: Spectrometer frequency 130.245 MHz, 15° pulse of 1 μs, recycle delay 1 s, referenced to $Al(H_2O)_6^{3+}$.
>
> ^{89}Y: Spectrometer frequency 24.5 MHz, spectra acquired using a Hahn spin-echo pulse sequence with 16-step phase recycling and a refocusing interval of 20 μs. Since the relaxation times of some ^{89}Y compounds are reported to be long in the absence of deliberately introduced paramagnetic species [7], a recycle delay of 3000 s was used here, with typically 58–60 transients acquired. The spectra were baseline-corrected and referenced to aqueous YCl_3 solution.

3. Results and discussion

The thermal analysis traces of the YAG gel are shown in Fig. 1.

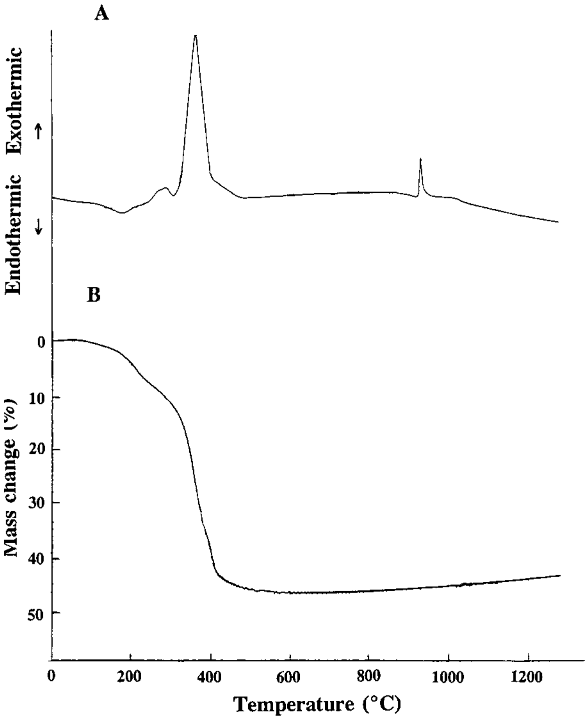

Fig. 1. Thermal analysis curves for hybrid YAG gel in flowing air (50 ml min^{-1}), heating rate 10°C min^{-1}. A. DSC curve, and B, TG curve.

The two exothermic events, at 324° and 375°C are accompanied by mass losses of ca. 10 and 35%, respectively, and represent the removal of gel constituents (water and trapped alcohol). The unheated gel has an X-ray amorphous character, with a broad major feature at ca. 13 Å (Fig. 2(A)), reminiscent of hydrated aluminosilicate gels such as allophanes. The positions of the other baseline humps in the XRD pattern of this gel (3.6 Å, 2.2 Å, 1.8 Å) are approximately similar to those of allophanes, those at 2.2 and 1.8 Å also approximately corresponding to the 2.4 and 1.9 Å reflections of γ-Al_2O_3. After the thermal removal of the volatile constituents, the broad baseline humps of the unheated material shift to become a broad feature in the approximate position of the major YAG reflection at d=2.69 Å (Fig. 2(B)). This XRD pattern persists to >800°C, but at 930°C a small, sharp exothermic event signals the abrupt crystallisation of YAG, which is evident in the XRD trace of all samples heated >1000°C (Fig. 2(D)). In samples heated at 900°C, representing the situation close to the

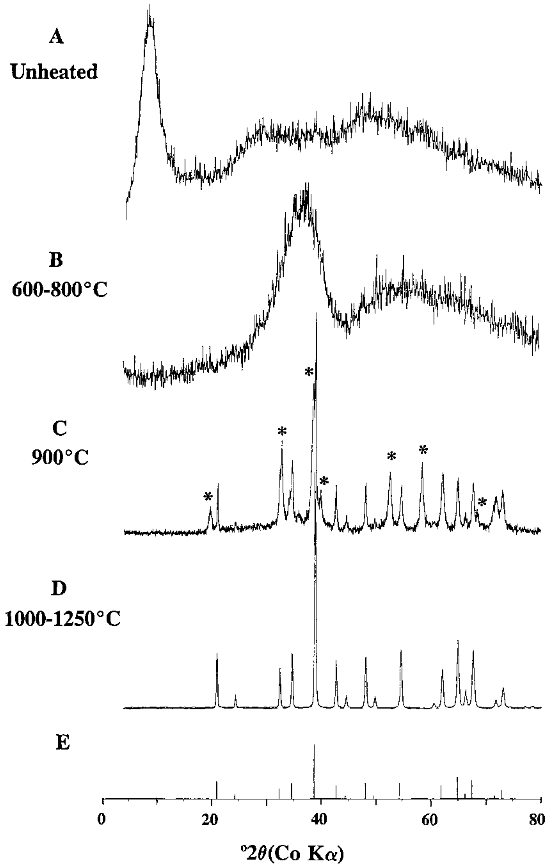

Fig. 2. XRD traces of hybrid YAG gel heated in air at the indicated temperatures for 15 min. E. PDF powder pattern 33–40, $Y_3Al_5O_{12}$. Asterisks indicate reflections of hexagonal $YAlO_3$ (PDF No. 16-219).

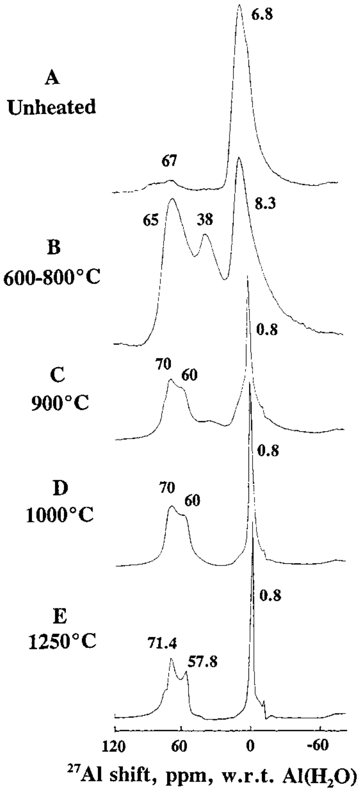

Fig. 3. 11.7 *T* ^{27}Al MAS NMR spectra of hybrid YAG gel heated in air at the indicated temperatures for 15 min.

exothermic event, the XRD trace (Fig. 2(C)) shows, in addition to the crystallizing YAG, evidence of hexagonal $YAlO_3$ formation (PDF 16–219); this phase is a transient intermediate, however, and is fully converted to YAG by 1000°C.

Fig. 3 shows the ^{27}Al NMR spectra of the YAG gels at various stages of thermal treatment.

The major resonance in the spectrum of the unheated gel (Fig. 3(A)) occurs in the position of octahedrally coordinated Al, and shows evidence of a shoulder upfield of the main peak. A much smaller feature at ca. 67 ppm indicates a small proportion of the Al in the initial gel is located in tetrahedral sites. Elimination of the residual volatiles by heating to 600°C produces a large increase in this tetrahedral resonance, and the appearance of a significant resonance at 38 ppm, in addition to the original octahedral resonance, which has broadened and shifted slightly (Fig. 3(B)). This spectrum resembles the ^{27}Al spectra of a number of X-ray amorphous Al-containing materials such as monophasic aluminosilicate gels [8], lanthanum hexaluminate gels (to be published) and mechanically amorphised Al compounds (mullite [9], oxide mixtures [10], gibbsite (to be published)). The shifts of all three resonances are 8–10 ppm more positive than reported in the aluminosilicates and gibbsite, suggesting that all three types of Al site in the present gels are less shielded, possibly resulting from the proximity of the large yttrium ion. The similar effect of a rare earth ion may also be operating in lanthanum hexaluminate gels, in which the ^{27}Al resonances occur at ca. 64, 37 and 7 ppm (to be published).

The ^{27}Al NMR resonance in an intermediate position between the octahedral and tetrahedral regions is

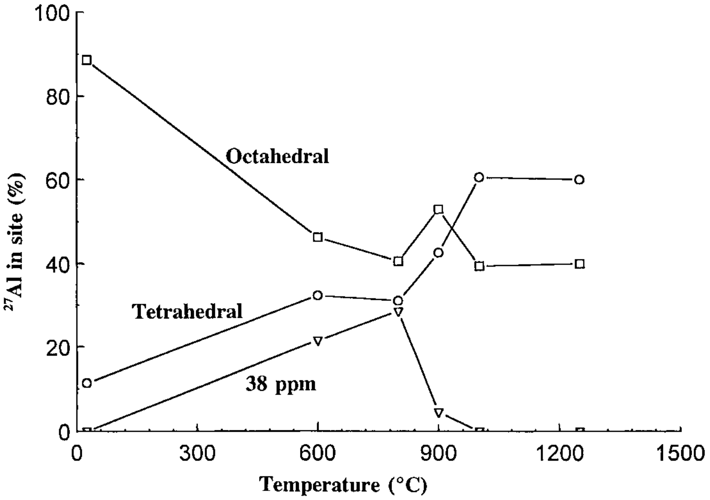

Fig. 4. Distribution of ^{27}Al over the sites in hybrid YAG gel as a function of the heating temperature.

often ascribed to Al in a five-fold coordination, but alternatively, it may arise from tetrahedral sites which have been distorted by the presence of oxygen defects such as those occurring in mullite [8]. Such defects normally have a charge-balancing role, e.g. where Si is substituted by Al; large cations such as Y are unlikely to be involved in such substitutions, and probably act as network modifiers in an irregularly cross-linked amorphous network. The evolution and subsequent disappearance of the sites giving rise to this resonance are plotted in Fig. 4, in which the relative ^{27}Al site occupancies were estimated from the spectra by curve-fitting procedures.

Fig. 4 shows that the increase in the number of both tetrahedral and 38 ppm sites occurs up to 800°C at the expense of the octahedral sites. The intensity of the 38 ppm reaches a maximum just before the exothermic crystallisation of YAG at 930°C, but they rapidly disappear when YAG is formed, with a concomitant increase in the tetrahedral sites and a brief increase in the octahedral site occupancy. The latter may reflect the transient formation of $YAlO_3$ noted at this temperature by XRD (Fig. 2(C)); the reported ^{27}Al spectrum of this phase [6] consists of a principal resonance at 9.4 ppm, visible at 900°C (Fig. 3(C)) as a shoulder on the narrow YAG resonance at 0.8 ppm. Above 900°C, the ^{27}Al spectrum (Fig. 3(D and E)) takes on the characteristics of a typical YAG spectrum [6], containing a narrow octahedral resonance at 0.8 ppm and a tetrahedral resonance with a distinctive quadrupolar lineshape arising from a significant electric field gradient (EFG) at this site. As the crystallinity of the YAG improves with increased heating temperature, the diagnostic YAG spectrum becomes more distinct (Fig. 3(E)) and at 1000–1250°C the ^{27}Al tetrahedral/octahedral ratio (deduced by curve-fitting) becomes 1.5, in excellent agreement with the ratio expected from the crystal structure of this phase [6]. The quadrupolar lineshape of the tetrahedral site (Fig. 3(E)) was satisfactorily simulated by setting the nuclear quadrupole coupling constant χ and the asymmetry parameter η to 6 MHz and 0, respectively, these being the parameters used by Dupree et al. [6] and Brog et al. [11]. Applying a Gaussian line broadening of 5 ppm, the tetrahedral isotropic chemical shift (the true shift in the absence of an electric field gradient) is 76.4 ppm, in satisfactory agreement with the value of 74 ppm calculated by Dupree et al. [6]. A similar spectral simulation of the octahedral YAG resonance using the parameters of Dupree et al. [6] and Brog et al. [11] (χ=0.06 MHz, η=0) yields a narrow octahedral resonance with an isotropic chemical shift of 0.85 ppm, again in satisfactory agreement with the value of $\approx$1 ppm calculated by Dupree et al. [6].

The ^{89}Y MAS NMR spectra of the heated gels are shown in Fig. 5.

The spectra of samples heated <1000°C are all broad, consistent with an amorphous material in which the Y occurs in a number of slightly different envir-

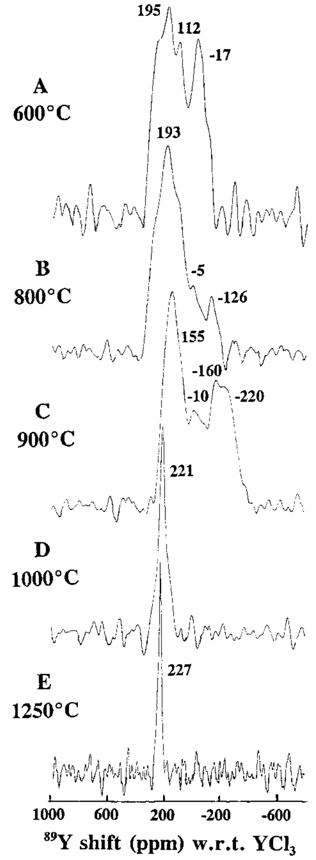

Fig. 5. 11.7 T ^{89}Y MAS NMR spectra of hybrid YAG gels heated in air at the indicated temperatures for 15 min.

onments. The centre-of-gravity (COG) of these broad resonances is considerably more negative than in the few Y oxide and aluminate phases for which NMR shifts have been reported [7], suggesting that the Y sites in the gel are more shielded (more highly coordinated) than in crystalline YAG. The COG becomes progressively more negative (i.e. the effective coordination of the Y environment increases) as the gel is heated up to the YAG recrystallization temperature. At 900°C, the ^{89}Y spectrum is too broad to show evidence of the YAlO$_3$ known from XRD and ^{27}Al NMR to be coexisting with YAG at this temperature. The narrow ^{89}Y resonance of YAlO$_3$ which is reported to occur at 214.5 ppm [7] could, however, be masked by the broad spectral envelope (Fig. 5(C)), the persistence of which suggests that even when the long-range ordering of the crystalline aluminates has been established the large Y ions attain final environment sluggishly. By 1000°C, the ^{89}Y resonance has abruptly sharpened and assumed a position similar to that reported for YAG (222 ppm [7]). The ^{89}Y spectra give no indication of the formation of other Y-containing intermediates such as Y_2O_3, which has even more positive shifts (314 and 272.5 ppm [7]).

Both the ^{27}Al and ^{89}Y NMR spectra suggest that, after the elimination of the volatiles, the present gel is fairly homogeneous, showing typical characteristics of a monophasic aluminate gel, but with the positions of all the Al resonances influenced to a similar degree by proximity of the Y-ion. Progressive heating of the gel <800°C causes some of the Al, initially in octahedral sites, to increasingly enter tetrahedral sites, and the other site which may be either penta-coordinated or a highly distorted tetrahedral. Although there is no XRD evidence of the establishment of long-range atomic order <800°C, it is worth noting that a lower temperature hexagonal form of YAlO$_3$ which exists below ca. 1000°C is thought to contain Al in a distorted penta-coordinated environment [6], but its ^{27}Al NMR spectrum has not been reported. The crystalline YAlO$_3$ which appears in addition to YAG in the present gels over a short temperature range at ca. 900°C is of the hexagonal type (PDF 16–219); however, in the ^{27}Al NMR spectrum of this sample (Fig. 3(C)) the 38 ppm peak is barely discernable. There is, thus, evidence in this spectrum of a broad octahedral shoulder in the position which has been reported by Dupree et al. [6] for the high-temperature orthorhombic form of YAlO$_3$; these authors were unable to prepare the phase-pure hexagonal form. Thus, the crystalline hexagonal YAlO$_3$, known by XRD to be present at 900°C, is apparently associated with an NMR spectrum characteristic of the orthorhombic form which, according to XRD, is not present. More work is needed to resolve this apparent inconsistency before the 38 ppm ^{27}Al resonance in the present gels could be confidently attributed to penta-coordinated Al in an uncrystallized precursor of hexagonal YAlO$_3$.

The appearance of an intermediate phase at the crystallization temperature is unusual in gel-derived samples of YAG composition. Manalert and Rahaman [5] reported that hybrid gels, prepared in the same way as the present gels but dried by supercritical CO_2 extraction, crystallise directly to YAG at ca. 900°C, and a similar observation was made by Gowda [4] for a hybrid YAG gel dried conventionally. Liu et al. [3], working with mixtures of the metal isobutyrates, reported direct crystallisation to YAG at ca. 910°C without any conclusive evidence of phase separation or formation of intermediates. However, Hay [2], working with diphasic metal isopropoxide gels of YAG composition, observed by XRD the intermediate appearance of monoclinic $Y_4Al_2O_9$ at 800–850°C. TEM observations on films of the same material [2] suggested the transient formation of metastable $YAlO_3$, subsequent to the appearance of $Y_4Al_2O_9$. The brief presence of $YAlO_3$ in the present samples may, therefore, indicate a degree of inhomogeneity, namely the presence of Y-rich regions with more nearly 1 : 1 molar composition. The single exotherm at 935°C suggests that the crystallisation of these regions to $YAlO_3$ occurs simultaneously with the crystallisation of YAG with which it coexists at 900°C. Further reaction with amorphous Al_2O_3 occurs below 1000°C:

$$3YAlO_3 + Al_2O_3 \rightarrow Y_3Al_5O_{12} \tag{1}$$

Hay [2] has suggested that the formation and conversion of the intermediate phase are controlled by diffusion of Al and O, and that the Y is relatively immobile. This is confirmed by the present ^{89}Y spectra, which indicate that the Y does not achieve its final environment until XRD and ^{27}Al MAS NMR indicates that the $YAlO_3$ and YAG lattices are well established.

4. Conclusions

1. After the loss of volatile components at ca. 375°C, hybrid gels of YAG composition remain X-ray amorphous, and contain Al in tetrahedral and octahedral sites, and in another site with a 38 ppm ^{27}Al MAS NMR resonance typical of amorphous aluminates. This 38 ppm resonance may arise either from a distorted tetrahedral site associated with charge-balancing structural defects in the gel, or from a penta-coordinated Al site possibly associated with Al-poor regions which later give rise to transient hexagonal $YAlO_3$.
2. Changes in the gel on heating are related to the mobility of the Al; at temperatures <900°C, the occupation of the tetrahedral and 38 ppm Al sites progressively increases at the expense of the octahedral sites.
3. At about the temperature of the 935°C exothermic event, $YAlO_3$ and YAG crystallise, as evidence by the XRD and ^{27}Al NMR data, but the ^{89}Y MAS NMR data indicate that the Y achieves its characteristic YAG environment more sluggishly. Between 900° and 1000°C, further diffusion of Al into the $YAlO_3$ brings about its conversion to YAG.

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