

# Coprecipitation of Yttrium and Aluminium Hydroxide for Preparation of Yttrium Aluminium Garnet

J. W. G. A. Vrolijk, J. W. M. M. Willems & R. Metselaar

Centre for Technical Ceramics, Eindhoven University of Technology,  
P.O. Box 513, 5600 MB Eindhoven, The Netherlands

(Received 27 December 1989; revised version received 19 February 1990; accepted 20 February 1990)

## Abstract

Coprecipitation of yttrium and aluminium hydroxide for the preparation of pure yttrium aluminium garnet (YAG) powder with small grain size is the subject of this study. Starting materials are sulphates and chlorides of yttrium and aluminium. To obtain pure YAG ( $Y_3Al_5O_{12}$ ), the pH during flocculation of the precursor must be chosen carefully. The presence of water increases the degree of agglomeration. To minimize agglomeration, the influence of dispersion liquids has been studied, leading to optimized conditions for precipitation.

*Das Thema dieser Arbeit ist die Kopräzitation von Yttrium und Aluminium zur Darstellung von reinem Yttrium–Aluminium–Granat-Pulver mit kleiner Korngröße. Ausgangsmaterialien sind die Sulfate und Chloride von Yttrium und Aluminium. Um reines YAG ( $Y_3Al_5O_{12}$ ) zu erhalten muss der pH-Wert während der Fällung des Zwischenproduktes sorgfältig gewählt werden. Die Anwesenheit von Wasser hat einen nachteiligen Effekt auf den Grad der Agglomeration. Um diesen nachteiligen Effekt beseitigen zu können wird der Einfluß verschiedener Dispersionsflüssigkeiten untersucht. Damit ist es möglich geworden die optimale Bedingungen für die Fällung festzustellen.*

*On décrit la coprécipitation d'yttrium et d'aluminium pour obtenir une poudre d'yttrium aluminate très fine et de haute pureté. Comme matériaux de départ sont employés des sulfates et des chlorures d'yttrium et d'aluminium. La préparation de YAG ( $Y_3Al_5O_{12}$ ) pur demande un choix précis du pH pendant la*

*floculation de produit intermédiaire. En ce qui concerne l'hydrolyse, la quantité relative d'eau détermine le degré d'agglomération. L'influence des liquides de dispersion différentes est étudiée ce qui a conduit aux conditions optimisées pour la floculation.*

## 1 Introduction

Polycrystalline yttrium aluminium garnet (YAG,  $Y_3Al_5O_{12}$ ) sintered to full density, has interesting optical<sup>1</sup> and mechanical<sup>2</sup> properties. As it has a cubic crystallographic structure there are no birefringence effects and thermal expansion is isotropic. Moreover YAG has a good resistance to corrosion from alkali metals.<sup>3</sup> Sintering behaviour is largely determined by precursor powder characteristics. The latter depend on the conversion steps in the powder preparation process. In a wet chemical synthesis precipitation, calcination and conversion into garnet will contribute to the properties of the resulting powder. Agglomerates, formed during precipitation and remaining in the powder compact after calcination, are disastrous for sintering to full density.<sup>4,5</sup> To optimize process conditions the influence of the dispersion medium on the agglomeration of precursor particles during precipitation has been studied. Furthermore, to obtain a stoichiometric precipitate in the quasi-binary system it is important to take into account the dependence on pH for precipitation of Y and Al hydroxide. The present paper describes the circumstances for obtaining an ultrafine precursor powder of the proper stoichiometry. Conversion into YAG and sintering behaviour will be discussed in a following paper.

## 2 Phase Diagram

The system yttria–alumina has been studied intensively. Cockayne<sup>6</sup> presented the chronological development of the phase diagram. Most recently Adylov *et al.*<sup>7</sup> investigated this system. In all cases the three possible compounds  $Y_3Al_5O_{12}$  (YAG—garnet structure),  $YAlO_3$  (YAP—perovskite structure) as well as  $Y_4Al_2O_9$  (YAM—monoclinic crystal structure) are given to be line compounds, so any deviation of the YAG stoichiometry will result in a two-phase system containing  $Al_2O_3$  or YAP besides YAG. To obtain pure YAG from the precursor, pH during coprecipitation of Y and Al hydroxide has to be carefully chosen. For this reason titration curves of Y and Al salt solutions with sodium hydroxide were measured as described in the next section.

## 3 Experimental

Yttria (99.99%, Rare Earth Products Ltd, UK) was dissolved under reflux in sulphuric acid. Aluminium sulphate solution was obtained by dissolving metallic aluminium (99.95%, Merck, FRG) in the same manner. Moreover, nitrogen gas was introduced to dilute and remove the hydrogen gas evolved. In both cases there was an excess of sulphuric acid. Titration of these solutions with sodium hydroxide and simultaneous measuring of pH provides the graph of Fig. 1. Precipitation of aluminium hydroxide is completed at pH 5; on the other hand, precipitation of yttrium hydroxide occurs at pH > 7. In the same way mixtures of yttrium and aluminium sulphate (Y/Al = 1 and Y/Al = 0.6) were titrated. The results are given in Fig. 2. It is evident that Al hydroxide precipitates before Y hydroxide, so that under these circumstances a homogeneous mixture of the precipitates cannot be expected. To examine the Y and Al content in the precipitate as a function of pH, mixtures of Y and Al sulphate (Y/Al = 1 as well as Y/Al = 0.6) were titrated at a range of pH values, filtered, dried and analysed (EDX-Jeol 840). In the

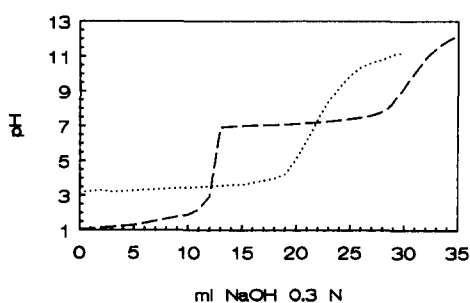


Fig. 1. Titration curves of 0.3N NaOH added to 50 ml of sulphate solutions of Y (----) and Al (.....) respectively.

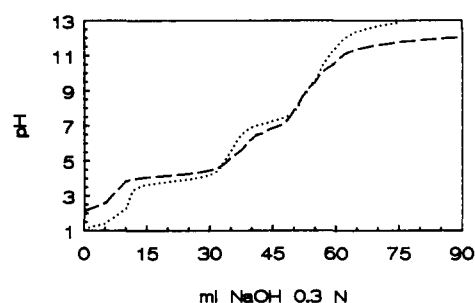


Fig. 2. Titration curves of 0.3N NaOH added to 50 ml of mixed Y and Al sulphate solutions. Y/Al = 1 (.....) and Y/Al = 0.6 (----).

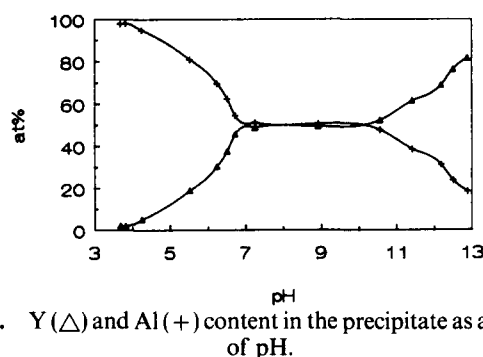


Fig. 3. Y ( $\Delta$ ) and Al (+) content in the precipitate as a function of pH.

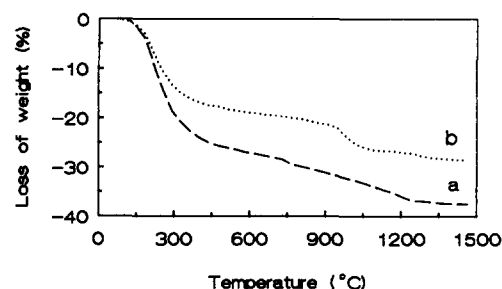


Fig. 4. Thermogravimetric analysis of YAG precursor. Line a, sulphate solution added to NaOH solution (---); line b, NaOH solution added to sulphate solution (.....).

precipitate the ratio Y/Al = 0.6 is reached between pH 7 and pH 11. In Fig. 3 it is demonstrated that for Y/Al = 1 the same holds. To obtain a stoichiometric precipitate further reactions were carried out at pH 9, using an automatic titration apparatus to keep the pH constant. To ensure homogeneous precipitation the salt solution was added dropwise into the alkaline medium. Furthermore a stirrer supplied with two oppositely rotating propellers was employed during flocculation.

Thermogravimetric analysis (Netzsch Simultaneous Thermal Analyzer STA 409,  $\Delta T = 5 \text{ K min}^{-1}$ ) of the precipitate obtained by adding Y and Al sulphate solution into the alkaline medium shows a more or less continuous loss of weight (Fig. 4, line a). The product obtained by adding NaOH solution to the bulk of Y and Al sulphate solution shows a slightly different behaviour (Fig. 4, line b). A precipitate obtained by the IPAA method, as described in the next section, shows a much better result. In this case the loss of weight (Fig. 5) is nearly complete at

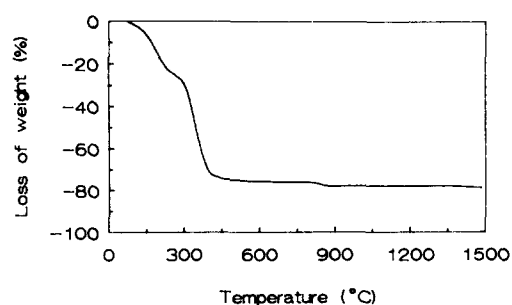


Fig. 5. Thermogravimetric analysis of YAG precursor obtained by the IPAA method.

400°C. SIMS analysis of precipitates heated at 600 and 1000°C respectively showed that the small bend near 800°C must be ascribed to dehydroxylation and dechlorination.

To avoid the relatively high temperature of decomposition the sulphates were replaced by chlorides. The procedure described gave identical results. Furthermore, instead of sodium hydroxide, ammonia was used for the precipitation. Ammonium chloride that is left after washing, is removed simply by heating at the temperature of sublimation (340°C).<sup>8</sup> The precipitate was separated by centrifugation, washed with a distilled water/ammonia (pH 9) mixture until no chlorides could be detected. Subsequently the precipitate was washed three times with ethanol to remove the attached free water and dried in a rotating evaporator. The powder was heated at 350°C to remove ammonium chloride, calcined at 650°C and then heated at 800°C to obtain garnet. XRD measurements proved that YAG was obtained.

#### 4 Agglomerates

The particles in the precipitate agglomerate. To obtain a powder with good sintering behaviour it was attempted to make a precipitate with small agglomerate size and weak bonding within the agglomerates. To diminish agglomeration the precipitate is usually washed with ethanol,<sup>9,10</sup> iso-

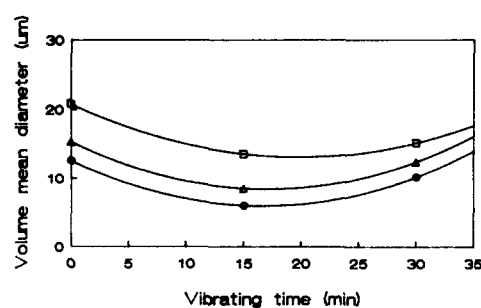


Fig. 6. Agglomerate sizes after washing and vibrating. Washing media are water (□), water followed by ethanol (△) and ethanol (○).

propanol<sup>11</sup> or acetone,<sup>12</sup> prior to drying. To check the influence on the precipitate of washing with water, with water followed by ethanol and directly with ethanol, each washing step was repeated three times. For more data on the effect, the precipitates were also vibrated ultrasonically (50 W, 50 kHz) for 15 and 30 min, respectively. The size distribution of the undried precursor particles was obtained from small angle light scattering (Malvern 2600). The results (Fig. 6) show that washing the precipitate right away with ethanol decreases the volume mean diameter of the agglomerates more than using ethanol after washing with water. Ultrasonic vibration gave a similar effect, but with a minimum at about 15 min. (The lines through the points in Fig. 6 are second-order polynomials.)

The maximum agglomerate sizes ( $d_{10}$ ,  $d_{50}$  and  $d_{90}$ ) below which 10, 50 and 90 wt% of the wet

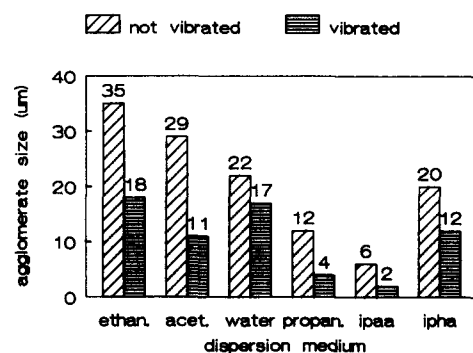
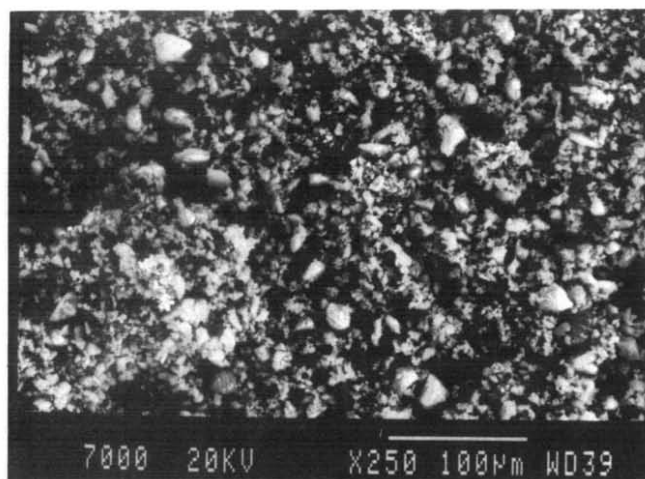


Fig. 7. Volume mean diameters of agglomerates precipitated in different dispersion media.

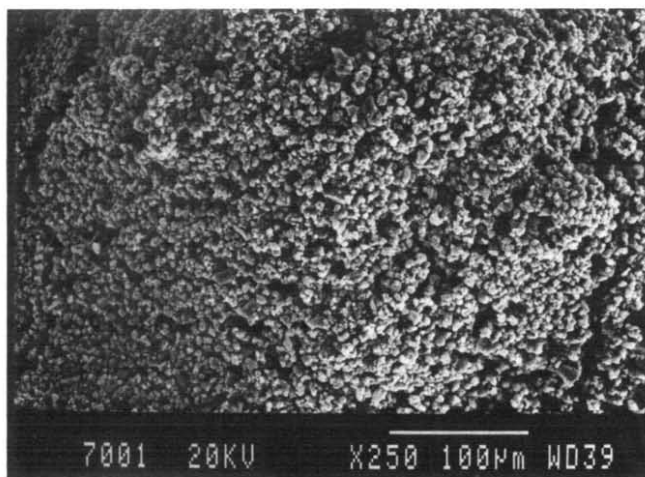
Table 1. Precipitates washed by water, water/ethanol or ethanol

	Water			Water/ethanol			Ethanol		
	a	b	c	a	b	c	a	b	c
$d_{10}$	8.3	3.1	2.8	8.0	2.1	1.6	7.0	2.6	2.4
$d_{50}$	15.2	8.1	15.2	14.0	4.1	6.7	11.6	4.0	4.3
$d_{90}$	33.1	32.5	29.2	23.1	27.3	30.8	18.8	12.0	27.9
Volume mean diameter	20.8	13.5	15.1	15.3	8.5	12.4	12.5	6.0	10.2

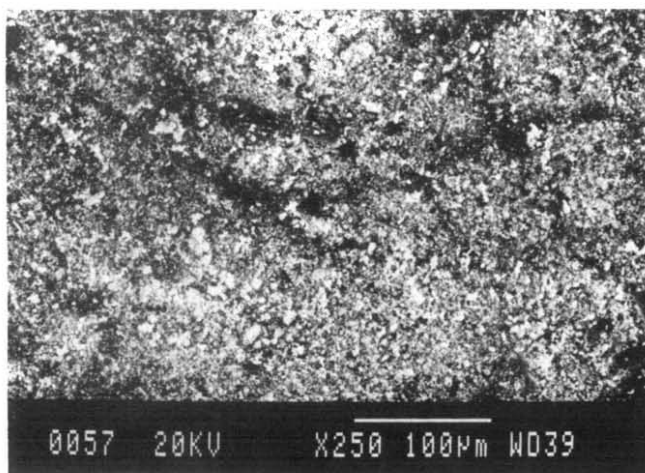
Maximum agglomerate sizes ( $d_{10}$ ,  $d_{50}$ ,  $d_{90}$  in  $\mu\text{m}$ ) below which 10, 50 and 90 wt.% of the undried precipitate are found. a, Not vibrated; b, ultrasonically vibrated for 15 min; c, ultrasonically vibrated for 30 min.



(a)



(b)



(c)

**Fig. 8.** SEM photographs of dried YAG precursor obtained (a) in acetone, (b) in isopropanol and (c) by the IPAA method.

precipitates are found, are given in Table 1. Thus it is demonstrated that presence of water must be avoided as far as possible in order to obtain small agglomerates. This led to the carrying out of precipitating the organic liquids already mentioned. Before precipitation ammonia was added until the

**Table 2.** Precipitates obtained in acetone or isopropanol

	Acetone		Isopropanol	
	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>
$d_{10}$	5.5	5.0	5.8	2.3
$d_{50}$	18.1	10.4	9.6	4.0
$d_{90}$	75.1	17.6	16.5	8.4
Volume mean mean	28.9	11.2	10.9	4.3

Maximum agglomerate sizes ( $d_{10}$ ,  $d_{50}$ ,  $d_{90}$  in  $\mu\text{m}$ ) below which 10, 50 and 90 wt.% of the undried precipitate are found. *a*, Not vibrated; *b*, ultrasonically vibrated for 5 min.

pH apparatus indicated pH 9. To diminish the water content due to the aqueous salt solution added the precipitate flocculated in isopropanol/ammonia was dissolved in acetic acid and flocculated again (referred to as IPAA method) in the isopropanol/ammonia mixture. For comparison the same procedure was followed, but the precipitate was dissolved in hydrochloric acid, referred to as the IPHA method. The decrease of volume mean diameter of the agglomerates in the order of ethanol > acetone > isopropanol as dispersion media, with that obtained using the IPAA method being the lowest, is convincing (Fig. 7, not vibrated). Figure 8 shows SEM photographs of the dried precipitate obtained (a) in acetone, (b) in isopropanol and (c) by the IPAA method. From the different media used for flocculation isopropanol leads to the smallest volume mean diameter and the most narrow distribution of agglomerate sizes. In Table 2 the results are given for acetone and isopropanol. The IPAA method gives still smaller agglomerates.

The undried precipitates were also vibrated ultrasonically. The decrease of volume mean diameter is dependent on the dispersion medium (Fig. 7, vibrated). It is expected that the ratio of decrease is a measure for the bond strength within the agglomerates. The greater the relative decrease in size the weaker the bonding. Following the IPAA method the smallest and weakest agglomerates are obtained.

## 5 Conclusions

- Stoichiometric YAG precursor can be obtained by precipitation from salt solutions at pH 9.
- To obtain small YAG precursor particles the best dispersion liquid during flocculation is an isopropanol/ammonia mixture.
- To diminish the size of the agglomerates in the precipitate the water content of the liquids used must be minimized. This can be done by

redissolving the precipitate in an isopropanol/acetic acid mixture and subsequently flocculating again the YAG precursor in a mixture of isopropanol and ammonia.

### Acknowledgements

The authors wish to thank G. J. Bezemer for performing TG/DTA analyses, T. Meijers for performing SIMS analyses, H. de Jonge Baas for XRD measurements and G. de With for helpful comments.

### References

1. De With, G. & Van Dijk, H. J. A., Translucent  $Y_3Al_5O_{12}$  ceramics. *Mat. Res. Bull.*, **19** (1984) 1669–74.
2. De With, G. & Parren, J. E. D., Translucent  $Y_3Al_5O_{12}$  ceramics: Mechanical properties. *Solid State Ionics*, **16** (1985) 87–93.
3. De With, G., Preparation, microstructure and properties of  $Y_3Al_5O_{12}$  ceramics. *Philips J. Res.*, **42** (1987) 119–30.
4. Rhodes, W. H., Agglomerate and particle size effects on sintering yttria-stabilized zirconia. *J. Am. Ceram. Soc.*, **64** (1981) 19–22.
5. Roosen, A. & Hausner, H., The influence of processing conditions on the sintering behaviour of coprecipitated calcia-stabilized zirconia powders. In *Ceramic Powders*, ed. P. Vincenzini. Elsevier Scientific Publishing Company, Amsterdam, 1983, pp. 773–82.
6. Cockayne, B., The uses and enigmas of the  $Al_2O_3$ – $Y_2O_3$  phase system. *J. Less-Common Metals*, **114** (1985) 199–206.
7. Adylov, G. T., Voronov, G. V., Mansurova, E. P., Sigalov, L. M. & Urazaeva, E. M., System  $Y_2O_3$ – $Al_2O_3$  above 1473 K. *Zh. Neorg. Khim.*, **33** (1988) 1867–9, in Russian.
8. Weast, R. C., Astle, M. J. & Beyer, W. H. (ed.), *Handbook of Chemistry and Physics*, 65th edn, The Chemical Rubber Company, Boca Raton, FL, 1984.
9. Pampuch, R. & Haberko, K., Agglomerates in ceramic micropowders and their behaviour on cold pressing and sintering. In *Ceramic Powders*, ed. P. Vincenzini. Elsevier Scientific Publishing Company, Amsterdam, 1983, pp. 623–34.
10. Winnubst, A. J. A., Van de Graaf, M. A. C. G., Keizer, K. & Burggraaf, A. J., Tetragonal  $ZrO_2$ – $Y_2O_3$ . Part I: Preparation methods and characterisation. *Journal de Physique* **47** (1986) 569–73.
11. Van de Graaff, M. A. C. G., Ter Maat, J. H. H. & Burggraaf, A. J., Microstructural development during pressing and sintering of ultra-fine zirconia powders. In *Ceramic Powders*, ed. P. Vincenzini. Elsevier Scientific Publishing Company, Amsterdam, 1983, pp. 783–94.
12. Dole, S. L., Scheidecker, R. W., Shiers, L. E., Berard, M. F. & Hunter, O. Jr, Technique for preparing highly sinterable oxide powders. *Mat. Sci. Eng.*, **32** (1978) 277–81.