

Homogeneous coprecipitation of precursor for preparation of yttrium aluminum garnet

Citation for published version (APA):

Vrolijk, J. W. G. A., & Metselaar, R. (1991). Homogeneous coprecipitation of precursor for preparation of yttrium aluminum garnet. In P. Vincenzini (Ed.), *Ceramics today - tomorrow's ceramics : proceedings, Montecatini, Terme, Italy, 24-30 June, 1990* (pp. 935-941). (Materials Science Monographs; Vol. 66B). Elsevier.

Document status and date:

Published: 01/01/1991

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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HOMOGENEOUS COPRECIPITATION OF PRECURSOR FOR PREPARATION OF YTTRIUM ALUMINUM GARNET

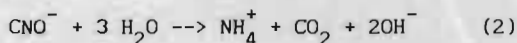
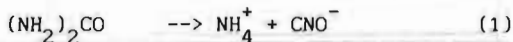
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Pure yttrium aluminium garnet powders were prepared by homogeneous coprecipitation of the precursor. Urea was added to an aqueous solution of yttrium sulphate and aluminium sulphate. Heating between 80 - 100 °C leads to a precipitate, consisting of ultra fine microspheres. After washing, drying and heating yttrium aluminium garnet powder was obtained.

1. INTRODUCTION

The precipitation of aluminium basic sulphate by urea has been investigated more than 50 years ago ¹. The reaction is based on the decomposition of urea that occurs homogeneously in the solution according to



At elevated temperatures ($T > 70$ °C) reaction (1) has a marked rate. A study of the decomposition of urea in water was presented in 1955 ². In general homogenous precipitation causes monodispersed and often spherical particles. Excellent examples are given by Matijevic' ³. Sordelet and Akinc investigated the preparation of spherical, monosized yttria precursor particles in detail ⁴.

The decomposition of urea in an aqueous solution is also usable for coprecipitation of a stoichiometric mixture ($\text{Y}/\text{Al} = .6$) of yttrium and aluminium compounds as precursor for preparation of yttrium aluminium garnet ($\text{Y}_3\text{Al}_5\text{O}_{12}$, YAG). In this case, however, the precursor is a complex precipitate inter alia consisting of hydroxysulphates and hydroxycarbonates. This mixture has to be calcined to form yttria and alumina, that next have to be converted into YAG. During these reactions the spherical particles can loose their shape and original size. The goal of this ongoing study is to obtain a well defined pure

YAG powder, having a good sintering behaviour.

2. EXPERIMENTAL

2.1. Coprecipitation

Yttria (99.99%, Rare Earth Products Ltd, UK) was dissolved in sulphuric acid by stirring several hours at room temperature. Metallic aluminium (99.95%, Merck, FRG) was dissolved under reflux in sulphuric acid. Nitrogen gas was introduced to dilute and remove the developed hydrogen gas. Those solutions were separately filled up in 1 liter measuring flasks, $[Y^{3+}]$ being .10188 M and $[Al^{3+}]$ 0.10186 M respectively. In 150 ml of a stoichiometric mixture ($Y/Al = .6$) the about twenty fold excess of urea was dissolved and 150 ml of twice distilled water was added. In this solution, magnetically stirred on a heating plate, the precipitation reaction occurred within approximately 1 hour in a temperature range of 80 °C up to boiling temperature. The precipitate was separated by centrifugation and washed with water and isopropanol by means of ultrasonic vibration, each washing step twice. From the well mixed dispersion a droplet was dried upon a brass sample holder and prepared for electron microscopy by sputtering a thin gold/palladium layer on it. Figure 1 shows a SEM photograph (Cambridge S200) of the precipitate. The diameter of the spherical particles is about 0.3 μm . Note the narrow size distribution of the particles.

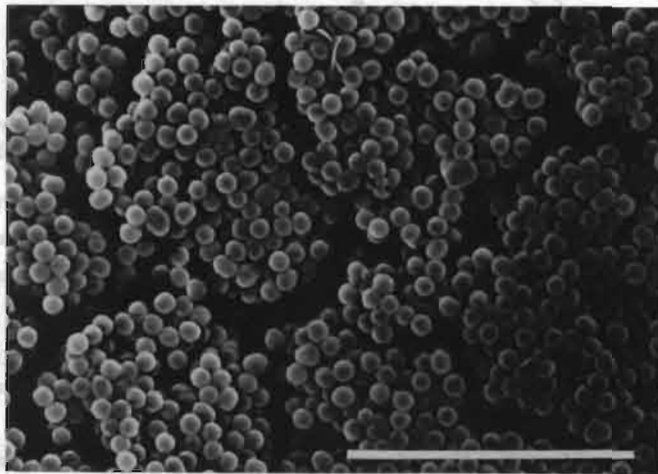


FIGURE 1

SEM photograph of precipitate obtained by heating an aqueous solution of urea containing sulphates of Y and Al. $[Y]/[Al] = .6$. Scale marker = 5 μm .

2.2. Details on the chemical reactions

As demonstrated in Figure 2 thermogravimetric analysis (Netzsch Simultaneous Thermal Analyzer STA 409) of the washed precipitate, i.e. YAG precursor, showed a loss in weight of 16 % between 800 °C and 1100 °C and a constant weight above 1100 °C.

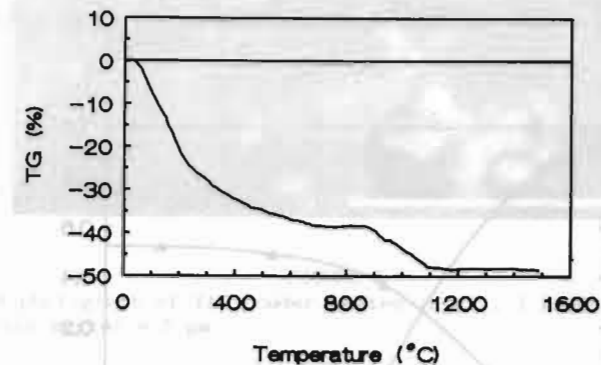


FIGURE 2

TGA graph of YAG precursor, heated in air at 2.5 K/min.

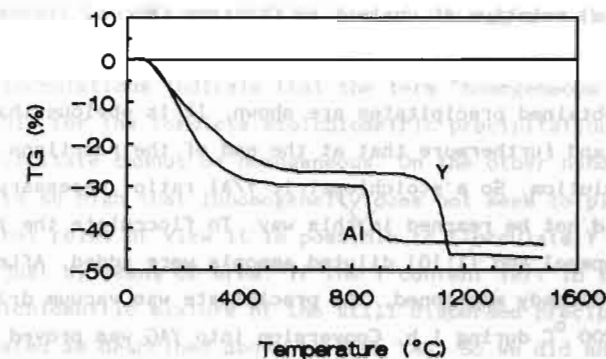


FIGURE 3

TGA graph of precipitates separately obtained from Al and Y sulphate solutions, respectively. Heated in air at 2.5 K/min.

Al sulphate and Y sulphate solutions were also flocculated separately as described above and the washed precipitates were analysed thermogravimetrically. Figure 3 shows the results. The Al as well as the Y precipitate decompose in two steps, in the second step losing 18.6 % and 26 % in weight, respectively. This can only be comprehended if the samples at 800 °C are complex.

To follow the coprecipitation the Al content of the solution was determined as a function of time. From the moment the first "bluish" tint appeared samples from the well mixed dispersion were taken. After centrifugation the Al content of the clear solutions were determined by atomic absorption (Perkin Elmer 3030). On the other hand the Y/Al ratio in the precipitates were determined by EDX (Jeol 840) measurements. For this purpose samples were prepared by sputtering a thin carbon layer on the powders. In figure 4 the traces of the relative Al content in the filtrates (i.e. $Al/Al_{initial}$) as well as the

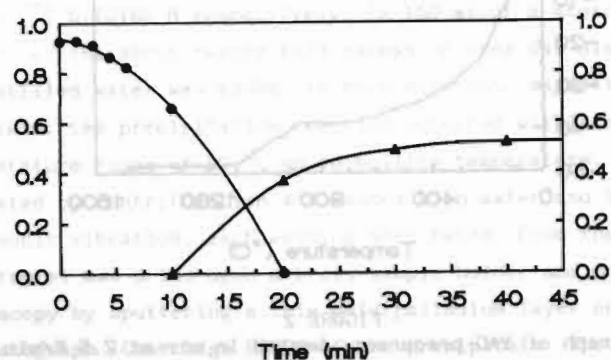


FIGURE 4
Time dependency of a) relative Al content in filtrate (●), b) [Y]/[Al] ratio in precipitate (▲).

Y/Al ratio in the obtained precipitates are shown. It is obvious that Al precipitated before Y and furthermore that at the end of the reactions some Y had been left in the solution. So a stoichiometric Y/Al ratio, necessary for the YAG precursor, could not be reached in this way. To flocculate the Y left in the solution isopropanol and (1:10) diluted ammonia were added. After the washing procedure, already mentioned, the precipitate was vacuum dried at 50 °C and heated at 1200 °C during 1 h. Conversion into YAG was proved by means of XRD patterns, obtained with a Rigaku diffractometer (Cu K α radiation, monochromator). A powder sample heated at 1400 °C during 1 h shows already considerable sintering (Figure 5). Therefore pre-fired powders have to be dis-agglomerated before pressing to pellets.

2.3. Size distribution of agglomerates

The size distribution of the agglomerates as they are formed by the precursor particles was obtained from small angle light scattering (Malvern 2600). From figure 6 it can be deduced that the agglomerates are very voluminous and almost monodispersed. Adding isopropanol to the clear filtrate causes precipi-

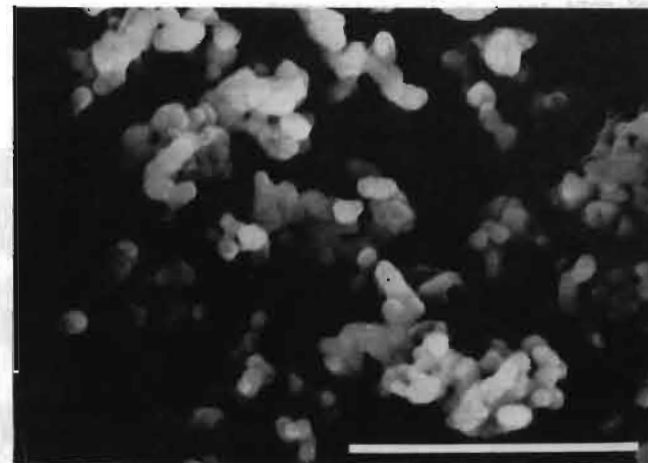


FIGURE 5
SEM photograph of YAG powder heated in air, 1 h at 1400 °C.
Scale marker = 5 μ m

tation of Y that is left in the solution after the reaction with urea. Figure 7 shows the agglomerate size distribution of this precipitate in the region up to 25 μ m. The peak at 4 μ m and the shoulder at 12 μ m are more pronounced. The peaks increase by adding diluted ammonia to the same filtrate, containing isopropanol already. So the size distribution of the agglomerates can be influenced in this way.

The latter flocculations indicate that the term "homogeneous coprecipitation" is not valuable for the complete stoichiometric precipitation. Above all, the obtained precipitate cannot be homogeneous. On the other hand the reactivity to form YAG is so high that inhomogeneity does not seem to play an important role. From that point of view it is possible to flocculate Y and Al precursor separately, just by means of urea. If the Y content left in the solution is known, a stoichiometric mixture of the still dispersed precipitates can be made and treated as described above to form YAG. So we did and this led to good results.

2.4. Pressing pellets and sintering

After conversion into YAG the powder was disagglomerated by ballmilling with agate in isopropanol and carefully dried in vacuum at room temperature. Manageable pellets were formed by uniaxial pressing under a pressure as low as possible. Those pellets, wrapped up in thin rubber, were cold isostatically pressed (400 MPa) and sintered in air at 1600 °C during 16 h. A partial beginning of translucency could be observed. Figure 8 shows a SEM photograph

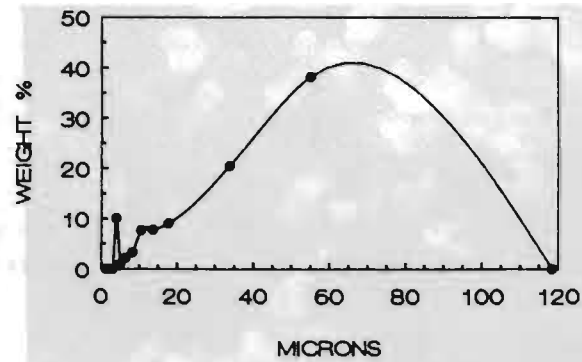


FIGURE 6

Agglomerate size distribution in the precipitate obtained by heating a solution containing urea, Y sulphate and Al sulphate. $[Y]/[Al] = .6$.

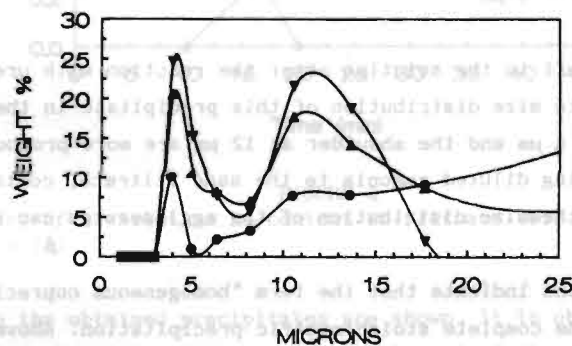


FIGURE 7

Agglomerate size distribution up to 25 μm . Precipitate obtained a) as original YAG precursor (urea) (●), b) by adding isopropanol to the clear filtrate (▲), c) by adding diluted ammonia to the suspension containing isopropanol (▼).

of such a part from the pellet. A translucent pellet of homogeneous density was obtained after sintering in air during 4 h at 1600 $^{\circ}\text{C}$, followed by 4 h at 1700 $^{\circ}\text{C}$.

3. CONCLUSIONS

Coprecipitation of precursor for preparation of yttrium aluminium garnet by means of urea is an easy and cheap route.

Precursor particles with a mean diameter of .3 μm are simply obtainable.

Well prepared pellets can be sintered in air to partial translucency at

1600 $^{\circ}\text{C}$ during 16 h. A sintering temperature of at least 1700 $^{\circ}\text{C}$ seems to be necessary to obtain a translucent pellet of homogeneous density.

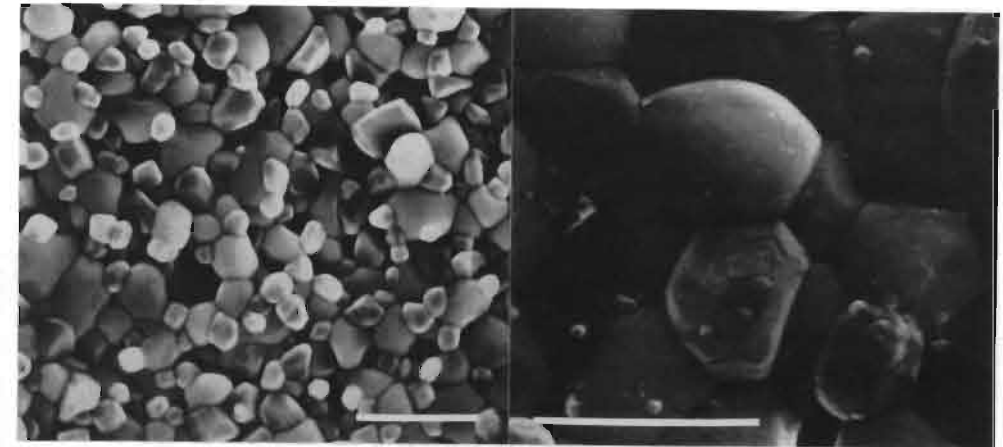


FIGURE 8

SEM photographs of partial translucent YAG pellets, sintered in air at 1600 $^{\circ}\text{C}$ during 16 h. Scale marker left image = 5 μm , right image = 2 μm .

ACKNOWLEDGEMENT

For performing analyses the authors wish to thank Mrs. A.M. Elemans (AA), G.J. Bezemer (TGA/DTA), H. de Jonge Baas (XRD), H.J.M. Heijligers (EDX - Jeol 840) and H.C.B. Ladan (SEM - Cambridge S200).

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