

Description

This invention relates to methods of producing yttrium-aluminium-garnet (YAG) fine particles and YAG base phosphor fine particles.

5 YAG is an oxide having the compositional formula of $Y_3Al_5O_{12}$ and is used as the starting material for a laser oscillator element or as an artificial jewel. The YAG solid solution system in which yttrium is partially replaced by terbium is a phosphor or luminophor material represented by the compositional formula $Tb_xY_{3-x}Al_5O_{12}$, where x is less than three and indicates the amount of substitution. The YAG material with
10 terbium is known to emit fluorescence efficiently when $x \geq 0.15$. This material has a high light emission saturation level and is suitable for a high luminosity phosphor screen such as that for a projection type television receiver, beam index tube or a display for an aircraft instrumentation system.

Among the factors influencing the properties of the YAG base phosphor materials are the particle size, uniformity, dispersibility and purity. Since it is thought that by optimizing these factors a cathode ray tube having a fine phosphor pattern, such as that for the recently developed high definition television system,
15 may be produced with high resolution and high image quality, studies are being conducted of the YAG base material as a promising phosphor material.

The YAG material and the YAG base phosphor material may be synthesized by substantially identical procedures.

One of the representative methods for synthesizing the YAG materials is a method comprising the steps
20 of crushing and mixing yttrium oxide and aluminium oxide in a ball mill, together with a sintering assisting agent to form a mixture; subjecting the mixture to a solid-phase reaction for a predetermined time at 1500°C to form a reaction product; and then crushing the reaction product to a fine particle size by a ball mill and classifying by a sieve. An improved method is similar, except that a flux is added during the solid phase reaction to reduce the physical strain applied to the YAG fine particles.

25 For producing the YAG base phosphor material, a method similar to that described above is used, but with the addition of terbium oxide to the yttrium oxide and aluminium oxide during the crushing and mixing step.

However, in these methods, when the reaction product from the the produced YAG fine particles or YAG base phosphor fine particles have a wide particle size distribution of 2 to $30\mu\text{m}$, so that coarse size
30 particles are unavoidably included in the produced particulate material. Moreover, as a prolonged time is involved in the ball-milling operation, impurities, such as metal oxides, tend to be mixed into the particulate material. There is a certain limitation in particle size reduction even with the use of the flux, such that it is usually difficult to produce particles having a particle size of less than $10\mu\text{m}$.

On account of these problems, deteriorated energy conversion efficiency, unnecessary coloration and/or
35 the lowered resolution may occur when the YAG base phosphor fine particles are used, for example, in a high definition television system.

There have also been proposed various liquid-phase reactions for producing such particles, for example in US patent specification US-A-4 180 477 (which discloses features corresponding to those of the pre-characterizing parts of claims 1 and 8 below), French patent specification FR-A1-0 030 170 (US-A-4 350
40 559), German patent specification DE-A-27 39 437 (GB-A-1 589 964), and German patent specification DE-A-29 37 428 (GB-A-2 032 450).

According to the present invention there is provided a method of manufacturing yttrium-aluminium-garnet fine particles, the method comprising:
45 preparing a solution comprising a first material selected from yttrium salts and hydrolyzates of yttrium compounds and a second material selected from aluminium salts and hydrolyzates of aluminium compounds; and
mixing said solution with an aqueous alkaline solution;
characterized by:
charging the mixed solution having a pH of not less than 10.0 into an autoclave, and heating said mixed
50 solution therein at a temperature of not less than 270°C to produce a precipitate; and
washing and drying said precipitate so as to obtain the yttrium-aluminium-garnet fine particles.

According to the present invention there is also provided a method of manufacturing yttrium-aluminium-garnet base phosphor fine particles, the method comprising:
preparing a solution comprising a first material selected from yttrium salts and hydrolyzates of yttrium
55 compounds, a second material selected from aluminium salts and hydrolyzates of aluminium compounds, and a third material selected from terbium salts and hydrolyzates of terbium compounds; and
mixing said solution with an aqueous alkaline solution;
characterized by:

charging the mixed solution having a pH of not less than 10.0 into an autoclave, and heating said mixed solution therein at a temperature of not less than 270°C to produce a precipitate; and washing and drying said precipitate so as to obtain the yttrium-aluminium-garnet base phosphor fine particles.

5 Thus, we have found that by subjecting yttrium and aluminium solubilized in an aqueous alkaline solution to a heating reaction in an autoclave at higher than a predetermined temperature, it is possible to produce fine YAG particles of a uniform particle size distribution as a single phase.

We have also found that, by adding terbium solubilized in an aqueous alkaline solution as an activator element to yttrium and aluminium, it is possible to produce fine YAG base phosphor particles of a uniform
10 particle size distribution as a single phase.

The invention will now be described by way of example with reference to the accompanying drawings, in which:

Figure 1 is a diagram showing an X-ray diffraction pattern of YAG fine particles produced in accordance with the present invention;

15 Figure 2 is a photomicrograph taken with a scanning type electron microscope of YAG fine particles produced in accordance with the present invention;

Figure 3 is a diagram showing the yield of YAG fine particles in relation to the pH of the solution;

Figure 4 is a diagram showing the yield of YAG fine particles in relation to the reaction temperature;

Figure 5 is a diagram showing the yield of YAG fine particles in relation to the reaction time interval;

20 Figure 6 is a diagram showing the X-ray diffraction pattern of the YAG base phosphor fine particles produced in accordance with the present invention;

Figure 7 is a photomicrograph taken with a scanning electron microscope of YAG base phosphor fine particles produced in accordance with the present invention;

25 Figure 8 is a diagram showing the yield of YAG base phosphor fine particles in relation to the pH of the solution;

Figure 9 is a diagram showing the yield of YAG base phosphor fine particles in relation to the reaction temperature;

Figure 10 is a diagram showing the yield of YAG base phosphor fine particles in relation to the reaction time interval; and

30 Figure 11 is a diagram showing the lattice constant of the YAG base phosphor fine particles in relation to the amount of terbium substitution.

Since the YAG fine particles and YAG base phosphor fine particles are to be produced by liquid phase reaction in an aqueous solution system, it is necessary for yttrium, aluminium and terbium as the starting materials to be solubilized. For this reason, hydrolyzates of the compounds containing these elements or
35 salts of these elements are employed.

For producing these hydrolyzates, it suffices to dissolve halogenides or various salts as later described of yttrium, aluminium or terbium in water, or to hydrolyze aqueous solutions thereof in an aqueous alkaline solution such as LiOH, NaOH, KOH or NH_4OH .

40 The above salts may include salts of oxoacids, such as nitrates or sulphates, or of organic acids, such as acetates.

As the alkaline solution for dissolving the above starting materials, aqueous solutions of hydroxides of alkali metals, such as Li, Na or K are employed.

The pH is selected to be not lower than 10.0. With the pH less than 10.0, the single phase cannot be achieved sufficiently and the purity becomes insufficient. This purity may be ascertained by X-ray
45 diffraction. In the case of the YAG fine particles, the preferred pH range is 10.0 to 13.3 and, with a more preferred pH range of 11.0 to 12.6, a single phase product may be obtained at a high yield rate. In the case of the YAG base phosphor fine particles, the preferred pH range is 10.2 to 14.1 and, with a more preferred pH range of 11.0 to 13.5, a single phase product may be obtained at a high yield rate. Since the pH influences the particle size of the produced YAG fine particles and YAG base phosphor fine particles, it
50 needs to be set suitably depending on the desired properties.

A temperature not lower than 270°C is employed. With the temperature lower than 270°C, the intensity of the X-ray diffraction ascribable to products other than the desired product becomes higher while the purity is lowered. For reducing the reaction time and realizing more efficient synthesis, a temperature of not lower than 300°C is more preferred. Although there is no limitation to the upper temperature limit, it is set to
55 about 380°C in consideration of the critical vapour pressure of the reaction system.

It will be noted that the reaction time interval is preferably not shorter than five minutes, and preferably not less than ten minutes.

After termination of the reaction, the YAG fine particles or YAG base phosphor fine particles, obtained as precipitates, are washed with cold or lukewarm water by decantation, centrifugation or filtration. The metal ions in the alkaline solution, such as Li, Na, K ions, adsorbed to the precipitates, are removed in this manner, and the remaining product is then dried.

It will be noted that the YAG base phosphor fine particles may be admixed further with Ga for improving the brightness or luminance.

It will be seen from the foregoing that the YAG fine particles and YAG base phosphor fine particles obtained are extremely small in particles size and uniform in particle size distribution, while having such advantages that the particle size may be controlled by the pH of the reaction solution and that there is no risk of mixing in metal oxides in the course of the production process. The YAG base phosphor fine particles having these advantages are highly effective when used as the phosphor for a CRT for which high resolution is a requirement.

The invention will now be explained with reference to illustrative examples and by reference to the drawings.

Example 1

This example is concerned with preparation of YAG fine particles from yttrium nitrate, $Y(NO_3)_3 \cdot 3.5H_2O$, and aluminium chloride, $AlCl_3 \cdot 6H_2O$.

Firstly, 6.34 g of yttrium nitrate, $Y(NO_3)_3 \cdot 3.5H_2O$, and 11.3 g of aluminium chloride, $AlCl_3 \cdot 6H_2O$, were dissolved in 40 ml of pure water to produce a solution A. A predetermined amount of sodium hydroxide was then dissolved in 40 ml of pure water to produce a solution B into which the solution A was added slowly drop-wise with agitation so as to avoid gelation. The resulting system was further admixed with pure water to produce 100 ml of a reaction solution C. The pH value of the reaction solution C was adjusted by controlling the addition of an amount of sodium hydroxide.

The reaction solution C was charged into an autoclave fitted with a platinum inner container and reacted with agitation at $360^\circ C$ for one hour. After termination of the reaction, decantation was repeatedly performed with pure water to remove alkali metal ions from the white-coloured precipitates produced during the above reaction. The resulting mass was subjected to filtration and washing with water and dried overnight at $100^\circ C$ in a dryer to produce a white-coloured solid product.

The white-coloured solid product obtained with the pH value of the reaction solution C of 12.3 was subjected to an X-ray diffraction using $CuK\alpha$ -rays. The results are shown in Figure 1, in which the ordinate and the abscissa denote the intensity of diffraction by arbitrary units and the diffraction angle $2\theta(^{\circ})$, respectively, since the X-ray diffraction pattern coincides with the cards 33-40 of JCPDS (Joint Committee on Powder Diffraction Standards), the product could be identified to be the cubic crystal YAG ($Y_3Al_5O_{12}$).

Figure 2 shows the photomicrograph of the white-coloured solid product, which was taken with a scanning type electron microscope. It is seen from this Figure that there have been produced YAG fine particles that are 2 to 3 μm in particle size and extremely uniform in particle size.

Then, for optimizing the conditions for preparation of the YAG fine particles, an investigation was made of the changes in the results due to changes in the pH value of the reaction solution C, changes in the reaction temperature and changes in the reaction time interval.

First, the pH dependency was examined in the following manner. The pH values of the reaction solution C were changed widely by changing the amount of sodium hydroxide employed and the reaction was performed for each product. The X-ray diffraction was then performed of each white-coloured solid product to find the relative yield of YAG as the area of a peak corresponding to the diffraction from the (420) plane, which was then plotted against pH. The results are shown in Figure 3, in which the ordinate and the abscissa indicate the relative yield of YAG in percentage (%) and the pH value of the reaction solution, respectively. It is seen from this figure that YAG is produced in the pH range of 10.0 to 13.3 and at a higher yield rate in the pH range of 11.0 to 12.6.

The temperature dependency was examined in the following manner. With the pH value of the reaction solution set to 12.3, the reaction was carried out for one hour with various reaction temperatures. Each produced white-coloured solid product was subjected to X-ray diffraction to find similarly the relative yield of YAG which was then plotted against the reaction temperature. The results are shown in Figure 4, in which the ordinate and the abscissa denote the relative yield of YAG in percentage (%) and the reaction temperature ($^{\circ}C$), respectively. It is seen from this figure that YAG is produced at a temperature of not lower than $270^\circ C$ and that the reaction proceeds most efficiently at about $360^\circ C$.

Finally, the reaction time was examined in the following manner. With the pH value of the reaction solution C of 12.3 and with the reaction temperature of $360^\circ C$, the reaction was carried out for various

reaction time intervals. Each white-coloured solid product was subjected to X-ray diffraction to find similarly the relative yield amount of YAG which was then plotted against the reaction time. The results are shown in Figure 5 in which the ordinate and the abscissa denote the relative yield amount of YAG in percentage and the reaction time interval in minutes, respectively. It is seen from this figure that YAG starts to be yielded in several minutes from the start of the reaction and the yield amount reaches saturation in about ten minutes.

Example 2

This example is concerned with the preparation of YAG fine particles from yttrium chloride, YCl_3 , and aluminium chloride, AlCl_3 .

First, 36.6 g of yttrium chloride and 62.5 g of aluminium chloride were dissolved in 400 ml of pure water to produce a solution A. This solution was then added slowly drop-wise into 400 ml of an aqueous solution of sodium hydroxide with agitation to avoid gelation. Then, pure water was added to the reaction system to produce a reaction solution C. The pH value of the reaction solution C was 12.6.

This reaction solution C was charged into an autoclave having a platinum inner container and reacted for six hours with agitation at 360°C . After termination of the reaction, the white-coloured precipitates produced in the above reaction were washed by decantation, filtration and washing with water and dried in a dryer at 100°C for 12 hours to a white-coloured solid product.

As a result of the X-ray diffraction and observation with an electron microscope, the white-coloured product was identified to be YAG fine particles of high purity and fine uniform particle size.

Example 3

This example is concerned with the investigation of the change in results caused by the addition of aluminium to the reaction solution in the preparation of YAG fine particles from yttrium nitrate, $\text{Y}(\text{NO}_3)_3 \cdot 3.5\text{H}_2\text{O}$, and aluminium chloride, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$.

First, 63.4 g of yttrium nitrate, $\text{Y}(\text{NO}_3)_3 \cdot 3.5\text{H}_2\text{O}$, and 75.4 g of aluminium chloride $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, were dissolved in 400 ml of pure water to produce a solution A. This solution A was added slowly drop-wise into 400 ml of an aqueous solution of sodium hydroxide with agitation to avoid gelation. The resulting solution was then divided into ten equal volume parts, into each of which aluminium chloride AlCl_3 , was added in amounts of 0 g, 7.54 g, 15.1 g, ..., 67.9 g, that is, in amounts sequentially increasing by 10% of the initial amount of AlCl_3 , and pure water was further added to produce reaction solutions C_0 to C_9 , each being 100 ml in capacity. Thus, the reaction solution C_0 contains a stoichiometrically required amount of aluminium and the solutions C_1 to C_9 contain aluminium in amounts of 10% to 90% in excess to the stoichiometrically required amount of aluminium. The pH value of each of these solutions was adjusted to 12.6 using aqueous solutions of sodium hydroxide.

The above reaction solutions C_0 to C_9 were charged each into an autoclave fitted with a platinum inner container, and reacted at 360°C for one hour. After termination of the reaction, the white-coloured precipitates produced in the course of the above reaction were washed by decantation, filtration and washing with water and dried in a dryer at 100° overnight to produce a white-coloured product.

On analysis of the white-coloured solid product by X-ray diffraction, the white-coloured solid product obtained from the reaction solutions C_3 to C_9 showed approximately the same pattern as the X-ray diffraction shown in Figure 1 and, thus, could be identified to be the high-purity YAG. However, the X-ray diffraction pattern of the white-coloured solid product synthesized from the solutions C_0 to C_2 showed peaks indicating the co-existence of yttrium hydroxide, $\text{Y}(\text{OH})_3$. It is seen from this that an excess amount of aluminium by about 30% over the stoichiometrically necessary amount on the theoretical numbers of moles is required in the reaction with respect to yttrium.

Example 4

In this example, an investigation has been made of changes in the particle size of the YAG fine particles by the change in pH of the reaction solution C in preparation of YAG fine particles from yttrium nitrate, $\text{Y}(\text{NO}_3)_3 \cdot 3.5\text{H}_2\text{O}$, and aluminium chloride, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$.

First, 25.3 g of yttrium nitrate, $\text{Y}(\text{NO}_3)_3 \cdot 3.35\text{H}_2\text{O}$, and 45.2 g of aluminium chloride, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, were dissolved in 160 ml of pure water to produce a solution A. This solution A was added gradually drop-wise into 100 ml of an aqueous solution of sodium hydroxide with agitation to avoid gelation. Then, pure water was added to the system to produce 320 ml of a solution, which was then divided into four equal parts. Each of these partial solutions was raised to 100 ml by adding a solution of pure water and different

amounts of sodium hydroxide. In this manner, the solutions C_I to C_{IV} having pH values of 11.6, 12.3, 12.6 and 13.0 were produced.

Each of these solutions C_I to C_{IV} was charged into an autoclave having a platinum inner container and reacted with agitation at 360°C for one hour. After termination of the reaction, the white-coloured precipitates produced by the above reaction were washed by decantation, filtration and washing with water and dried overnight in a dryer at 100°C to produce a white-coloured solid product.

On analysis of the white-coloured solid product by X-ray diffraction, the white-coloured solid products obtained from the reaction solutions C_I to C_{IV} were found to be the high purity YAG, although they exhibited slightly different values of the diffraction strength.

An observation of these solid products with an electron microscope has revealed that the product obtained from the reaction solution C_I having the pH value of 11.6 has a particle size of approximately 0.1 μm, and the product obtained from the reaction solution C_{IV} having the pH value of 13.0 has the particle size of approximately 10 μm, and that the particle size can be controlled within the range of approximately 0.1 to 10 μm through adjustment of the pH value.

Example 5

This example is concerned with the preparation of the YAG base phosphor fine particles from yttrium nitrate, Y(NO₃)₃·3.5H₂O, and terbium chloride, TbCl₃.

First, 19.7 g of sodium hydroxide was dissolved in pure water to produce 60 ml of an aqueous alkaline solution into which 12.04 g of yttrium nitrate, Y(NO₃)₃·3.5H₂O; 22.61 g of aluminium chloride, AlCl₃·6H₂O; and 0.497 g of terbium chloride TbCl₃, were added gradually under agitation and pure water was further added to produce 100 ml of a reaction solution D.

This reaction solution was charged into an autoclave fitted with a platinum inner container and reacted with agitation at 370°C for one hour. After termination of the reaction, decantation was repeatedly performed using pure water to remove alkali metal ions from the white-coloured precipitates produced in the above reaction. The resulting product was subjected to further filtration and washing with water and then dried overnight in a dryer at 100°C to produce a white-coloured solid product.

This solid product was subjected to an X-ray analysis using CuK α- rays. The results are shown in Figure 6, in which the ordinate indicates the intensity of diffraction in arbitrary units and the abscissa the diffraction angle 2θ(°). This X-ray diffraction pattern roughly coincided with the pattern of the cubic crystal YAG (Y₃Al₅O₁₂) indicated in the aforementioned JCPDS card 33-40.

When irradiated with UV light having a wavelength of 254 to 366 nm, the white-coloured product emitted green fluorescence. Also, on fluorescence X-ray analysis using a standard sample having the aforementioned composition of Tb_xY_{3-x}Al₅O₁₂ has revealed that the pattern coincided with that of the standard sample of x = 0.15 and hence the aforementioned white-coloured solid product had a composition of Tb_{0.15}Y_{2.85}Al₅O₁₂. The lattice constant calculated at this time on the basis of the X-ray diffraction peak was 12.025 × 10⁻¹⁰ m.

Figure 7 shows a photo of the white-coloured solid product, taken with a scanning type electron microscope. It is seen that there have been produced YAG base phosphor fine particles having an extremely uniform particle size.

Then, for optimizing the conditions for producing the YAG base phosphor fine particles, investigations were made into changes of the pH value of the reaction solution, changes of the reaction temperature and changes of the reaction time interval, as in Example 1 above.

The results of investigations into pH dependency are shown in Figure 8, wherein the ordinate indicates the relative yield amount of the YAG base phosphor in percentage and the abscissa indicates the pH value of the reaction solution D. The reaction conditions are 374°C and one hour. It is seen from this figure that the YAG base phosphor is produced in the pH range of 10.2 to 14.1 and is produced at a high yield rate in the pH range of 11.0 to 13.5.

The results of the investigations into the temperature dependency are shown in Figure 9, wherein the ordinate shows the relative yield amount of the YAG base phosphor in percentage and the abscissa the reaction temperature in (°C). The pH value of the reaction solution D is 12.5 and the reaction time interval is one hour. It is seen from this figure that the YAG base phosphor is produced at a temperature of not lower than 275°C and the reaction proceeds most efficiently at about 360°C. It is also seen that the temperature not higher than 250°C results in the increased peak of diffraction due to some other phase and, hence, is not suitable for synthesis.

Finally, the results of investigations into the different reaction time intervals are shown in Figure 10, wherein the ordinate shows the relative yield amount of the YAG base phosphor in percentage and the

abscissa the reaction time interval in hours. The pH value of the reaction solution is 12.5 and the reaction temperature is 374°C. It is seen from this figure that the YAG base phosphor starts to be yielded in several minutes after the start of the reaction and reaches saturation in about ten minutes.

5 Example 6

In this example, investigations have been made into the changes in the composition of the YAG base phosphor and in the lattice constant when the amounts of addition of yttrium nitrate, $Y(NO_3)_3 \cdot 3.5H_2O$, and terbium chloride, $TbCl_3$, in the reaction solution of Example 5 changes.

10 First, 12.04 g of aluminium chloride, $AlCl_3 \cdot 6H_2O$, and the amounts shown in Table 1 below of yttrium nitrate, $Y(NO_3)_3 \cdot 3.5H_2O$, and terbium chloride were added gradually into pure water containing a suitable amount of sodium hydroxide with agitation and pure water was finally added to the reaction system to give seven different 100 ml reaction solutions D.

15 Each reaction solution D was reacted in an autoclave with agitation at 374°C for two hours. The white-coloured solid products were obtained from the produced white-coloured precipitates by the above described procedure of washing and then drying. An X-ray fluorescent analysis was performed of these white-coloured solid products to determine the composition of each white-coloured solid product. The results are shown in Table 1.

20 TABLE 1

25	terbium chloride (g)	yttrium nitrate (g)	composition of solid products
	0	12.67	$Y_3 Al_5O_{12}$
	0.166	12.46	$Tb_{0.05}Y_{2.95}Al_5O_{12}$
30	0.497	12.04	$Tb_{0.15}Y_{2.85}Al_5O_{12}$
	0.995	11.41	$Tb_{0.3}Y_{2.7}Al_5O_{12}$
	3.316	8.449	$Tb_1Y_2Al_5O_{12}$
35	6.632	4.225	$Tb_2Y_1Al_5O_{12}$
	9.948	0	$Tb_3Al_5O_{12}$

40 An X-ray diffraction analysis was performed of these YAG base phosphor fine particles $Tb_xY_{3-x}Al_5O_{12}$. It was found that each diffraction pattern was of the same phase as that shown in Figure 6 but demonstrated a slight shift in the diffraction peak angle. The lattice constant was calculated on the basis of these diffraction peak angles and plotted against the amount of substitution of terbium x. The results are shown in Figure 11, from which it is seen that a linear relationship exists between the amount of substitution
45 of terbium x.

Example 7

50 In this example, investigations were made into the changes in the composition of the YAG base phosphor fine particles due to changes in the amount of addition of aluminium in the above reaction solution D.

First, 2.485 g of terbium chloride, $TbCl_3$; 60.2 g of yttrium nitrate, $Y(NO_3)_3 \cdot 3.5H_2O$; and 75.3 of aluminium chloride, $AlCl_3 \cdot 6H_2O$, were dissolved in 200 ml of pure water and the resulting solution was admixed with sodium hydroxide and thereby neutralized.

55 The resulting solution was divided into five equal parts into which aluminium chloride was added sequentially in amounts of 7.53 g, 15.1 g, ..., 37.7 g, thus, in amounts of 10%, 20%, ... 50% in excess to the initial amount of aluminium chloride. Finally, pure water was added to produce different 100 ml reaction solutions D_1 to D_5 . The pH value of each of these reaction solutions D_1 to D_5 was adjusted to 13.3 with

sodium hydroxide.

The above reaction solutions D₁ to D₅ were reacted at 360°C for one hour with agitation in an autoclave. The white-coloured solid products were obtained from the precipitates by the processes described above. These white-coloured solid products were analyzed by an X-ray diffraction, from which it was seen that the diffraction pattern of each of the white-coloured solid products obtained from the reaction solutions D₃ to D₅ was about the same as that shown in Figure 6 but each of the white-coloured solid products obtained from the reaction solutions D₁ and D₂ also contained small amounts of yttrium hydroxide, Y(OH)₃. From this it is seen that the amount of aluminium corresponding to at least 2.3 times of mols of yttrium is required to suppress the formation of yttrium hydroxide, Y(OH)₃, in the reaction of the aqueous alkaline solution.

Example 8

In this example, investigations were made into changes in the particle size of the YAG base phosphor by changes in the pH of the reaction solution D.

First, 3.48 g of terbium chloride, 84.3 g of yttrium nitrate, Y(NO₃)₃·3.5H₂O, and 153.3 g of aluminium chloride, AlCl₃·6H₂O, were dissolved in 350 ml of pure water and the resulting solution was neutralized with sodium hydroxide.

This solution was divided into seven equal parts and each of the parts had a predetermined amount of sodium hydroxide and pure water added to give seven 100 ml solutions with different pH values. Thus, reaction solutions D₆ to D₁₂ having the pH values shown in Table 2 below were prepared.

Each of these reaction solutions D₆ to D₁₂ was reacted in an autoclave at 374°C for one hour with agitation. White-coloured solid products were produced from the precipitates by the above-described procedure. These white-coloured solid products were analyzed by X-ray diffraction and found to be the YAG base phosphor of different peak strengths but the same phase.

These white-coloured solid products were observed with a scanning type electron microscope. It was, thus, found that the YAG base phosphor having the particle size of 0.2 to 5 µm was produced by change in the pH value. The results are shown in Table 2.

TABLE 2

reaction solutions	pH	particle size (µm)	reaction solutions	pH	particle size (µm)
D ₆	12.6	0.2	D ₁₀	13.7	3 - 5
D ₇	12.9	0.5 - 1	D ₁₁	13.9	2 - 3
D ₈	13.3	2 - 3	D ₁₂	14.1	1 - 2
D ₉	13.5	3 - 5			

Thus, it is seen that the particle size of the produced YAG base phosphor fine particles can be controlled by the pH of the reaction solution D.

Claims

1. A method of manufacturing yttrium-aluminium-garnet fine particles, the method comprising: preparing a solution comprising a first material selected from yttrium salts and hydrolyzates of yttrium compounds and a second material selected from aluminium salts and hydrolyzates of aluminium compounds; and mixing said solution with an aqueous alkaline solution; characterized by: charging the mixed solution having a pH of not less than 10.0 into an autoclave, and heating said mixed solution therein at a temperature of not less than 270 °C to produce a precipitate; and washing and drying said precipitate so as to obtain the yttrium-aluminium-garnet fine particles.
2. A method according to claim 1 wherein the pH of said mixed solution is in the range 10.6 to 13.3.
3. A method according to claim 1 wherein the pH of said mixed solution is in the range 11.0 to 12.6.
4. A method according to claim 1, claim 2 or claim 3 wherein said temperature is in the range 300 °C to 390 °C.



sodium hydroxide.

The above reaction solutions D₁ to D₅ were reacted at 360°C for one hour with agitation in an autoclave. The white-coloured solid products were obtained from the precipitates by the processes described above. These white-coloured solid products were analyzed by an X-ray diffraction, from which it was seen that the diffraction pattern of each of the white-coloured solid products obtained from the reaction solutions D₃ to D₅ was about the same as that shown in Figure 6 but each of the white-coloured solid products obtained from the reaction solutions D₁ and D₂ also contained small amounts of yttrium hydroxide, Y(OH)₃. From this it is seen that the amount of aluminium corresponding to at least 2.3 times of mols of yttrium is required to suppress the formation of yttrium hydroxide, Y(OH)₃, in the reaction of the aqueous alkaline solution.

Example 8

In this example, investigations were made into changes in the particle size of the YAG base phosphor by changes in the pH of the reaction solution D.

First, 3.48 g of terbium chloride, 84.3 g of yttrium nitrate, Y(NO₃)₃·3.5H₂O, and 153.3 g of aluminium chloride, AlCl₃·6H₂O, were dissolved in 350 ml of pure water and the resulting solution was neutralized with sodium hydroxide.

This solution was divided into seven equal parts and each of the parts had a predetermined amount of sodium hydroxide and pure water added to give seven 100 ml solutions with different pH values. Thus, reaction solutions D₆ to D₁₂ having the pH values shown in Table 2 below were prepared.

Each of these reaction solutions D₆ to D₁₂ was reacted in an autoclave at 374°C for one hour with agitation. White-coloured solid products were produced from the precipitates by the above-described procedure. These white-coloured solid products were analyzed by X-ray diffraction and found to be the YAG base phosphor of different peak strengths but the same phase.

These white-coloured solid products were observed with a scanning type electron microscope. It was, thus, found that the YAG base phosphor having the particle size of 0.2 to 5 µm was produced by change in the pH value. The results are shown in Table 2.

TABLE 2

reaction solutions	pH	particle size (µm)	reaction solutions	pH	particle size (µm)
D ₆	12.6	0.2	D ₁₀	13.7	3 - 5
D ₇	12.9	0.5 - 1	D ₁₁	13.9	2 - 3
D ₈	13.3	2 - 3	D ₁₂	14.1	1 - 2
D ₉	13.5	3 - 5			

Thus, it is seen that the particle size of the produced YAG base phosphor fine particles can be controlled by the pH of the reaction solution D.

Claims

1. A method of manufacturing yttrium-aluminium-garnet fine particles, the method comprising:
preparing a solution comprising a first material selected from yttrium salts and hydrolyzates of yttrium compounds and a second material selected from aluminium salts and hydrolyzates of aluminium compounds; and
mixing said solution with an aqueous alkaline solution;
characterized by:
charging the mixed solution having a pH of not less than 10.0 into an autoclave, and heating said mixed solution therein at a temperature of not less than 270 °C to produce a precipitate; and
washing and drying said precipitate so as to obtain the yttrium-aluminium-garnet fine particles.
2. A method according to claim 1 wherein the pH of said mixed solution is in the range 10.6 to 13.3.
3. A method according to claim 1 wherein the pH of said mixed solution is in the range 11.0 to 12.6.
4. A method according to claim 1, claim 2 or claim 3 wherein said temperature is in the range 300 °C to 390 °C.



5. A method according to any one of the preceding claims wherein the amount of aluminium in said mixed solution is not less than 30% over the stoichiometrically necessary amount.
6. A method according to claim 5 wherein the pH of said mixed solution is in the range 10.6 to 13.3, and said temperature is in the range 300 °C to 390 °C.
7. A method according to claim 1 which includes replacing a portion of the first material with a third material selected from terbium salts and hydrolyzates of terbium compounds.
8. A method of manufacturing yttrium-aluminium-garnet base phosphor fine particles, the method comprising:
 - preparing a solution comprising a first material selected from yttrium salts and hydrolyzates of yttrium compounds, a second material selected from aluminium salts and hydrolyzates of aluminium compounds, and a third material selected from terbium salts and hydrolyzates of terbium compounds; and
 - mixing said solution with an aqueous alkaline solution;
 - characterized by:
 - charging the mixed solution having a pH of not less than 10.0 into an autoclave, and heating said mixed solution therein at a temperature of not less than 270 °C to produce a precipitate; and
 - washing and drying said precipitate so as to obtain the yttrium-aluminium-garnet base phosphor fine particles.
9. A method according to claim 8 wherein the pH of said mixed solution is in the range 10.2 to 14.1.
10. A method according to claim 8 wherein the pH of said mixed solution is in a range 11.0 to 13.5.
11. A method according to claim 8, claim 9 or claim 10 wherein said temperature is in the range 300 °C to 390 °C.
12. A method according to any one of claims 8 to 11 wherein the amount of aluminium in said mixed solution is not less than 30% over the stoichiometrically necessary amount.

Patentansprüche

1. Verfahren zur Herstellung von feinen Teilchen aus Yttrium-Aluminium-Granaten, umfassend
 - das Ansetzen einer Lösung aus einem ersten, aus Yttriumsalzen und Hydrolysaten von Yttriumverbindungen ausgewählten Material und einem zweiten, aus Aluminiumsalzen und Hydrolysaten von Aluminiumverbindungen ausgewählten Material und
 - das Vermischen dieser Lösung mit einer wässrigen alkalischen Lösung,
 - gekennzeichnet** durch die Einbringung der vermischten Lösung mit einem pH von nicht weniger als 10,0 in einen Autoklaven und das Erhitzen der Lösung darin auf eine Temperatur von nicht weniger als 270 °C zwecks Gewinnung einer Ausfällung und
 - Waschen und Trocknen der Ausfällung unter Erhalt der feinen Yttrium-Aluminium-Granat-Teilchen.
2. Verfahren gemäß Anspruch 1, wobei der pH-Wert der vermischten Lösung zwischen 10,6 und 13,3 liegt.
3. Verfahren gemäß Anspruch 1, wobei der pH-Wert der vermischten Lösung zwischen 11,0 und 12,6 liegt.
4. Verfahren gemäß Anspruch 1, 2 oder 3, wobei die Temperatur im Bereich von 300 bis 390 °C liegt.
5. Verfahren gemäß einem der vorangehenden Ansprüche, wobei der Anteil an Aluminium in der vermischten Lösung um nicht weniger als 30 % über dem stöchiometrisch notwendigen Wert liegt.
6. Verfahren gemäß Anspruch 5, wobei der pH-Wert der vermischten Lösung im Bereich von 10,6 und 13,3 liegt und die Temperatur im Bereich von 300 bis 390 °C gehalten wird.



7. Verfahren gemäß Anspruch 1,
dadurch **gekennzeichnet**,
daß ein Teil vom ersten Material durch ein drittes, aus Terbiumsalzen und Hydrolysaten von Terbium-
verbindungen ausgewähltes Material ersetzt wird.
8. Verfahren zur Herstellung von feinen, als Basis für Leuchtstoffe geeigneten Teilchen aus Yttrium-
Aluminium-Granaten, umfassend:
das Ansetzen einer Lösung aus einem ersten, aus Yttriumsalzen und Hydrolysaten von Yttriumverbindungen
ausgewähltem Material,
einem zweiten, aus Aluminiumsalzen und Hydrolysaten von Aluminiumverbindungen ausgewähltem
Material und einem dritten, aus Terbiumsalzen und Hydrolysaten von Terbiumverbindungen ausgewähltem
Material und
das Vermischen dieser Lösung mit einer wässrigen alkalischen Lösung,
gekennzeichnet durch die Einbringung der vermischten Lösung mit einem pH von nicht weniger als
10,0 in einen Autoklaven und das Erhitzen der Lösung darin auf eine Temperatur von nicht weniger als
270 °C zwecks Gewinnung einer Ausfällung und
Waschen und Trocknen der Ausfällung unter Erhalt von feinen Teilchen aus Yttrium-Aluminium-
Granaten als Basis für Leuchtstoffe.
9. Verfahren gemäß Anspruch 8, wobei der pH-Wert der vermischten Lösung zwischen 10,2 und 14,1
liegt.
10. Verfahren gemäß Anspruch 8, wobei der pH-Wert der vermischten Lösung zwischen 11,0 und 13,5
liegt.
11. Verfahren gemäß Anspruch 8, 9 oder 10, wobei die Temperatur im Bereich von 300 bis 390 °C liegt.
12. Verfahren gemäß einem der Ansprüche 8 bis 11, wobei der Anteil an Aluminium in der vermischten
Lösung um nicht weniger als 30 % über dem stöchiometrisch notwendigen Wert liegt.

Revendications

1. Procédé de fabrication de fines particules d'yttrium-aluminium-grenat, le procédé comprenant les
étapes :
de préparation d'une solution comprenant un premier matériau choisi parmi des sels d'yttrium et
des hydrolysats de composés d'yttrium et un second matériau choisi parmi des sels d'aluminium et
des hydrolysats de composés d'aluminium ; et
de mélange de ladite solution avec une solution alcaline aqueuse ; caractérisé en ce que :
on charge la solution mélangée ayant un pH supérieur ou égal à 10,0 dans un autoclave, et on
chauffe ladite solution mélangée à l'intérieur de celui-ci à une température supérieure ou égale à
270 °C pour produire un précipité ; et
on lave et on sèche ledit précipité afin d'obtenir les fines particules d'yttrium-aluminium-grenat.
2. Procédé selon la revendication 1, dans lequel le pH de ladite solution mélangée se trouve dans
l'intervalle de 10,6 à 13,3.
3. Procédé selon la revendication 1, dans lequel le pH de ladite solution mélangée se trouve dans
l'intervalle de 11,0 à 12,6.
4. Procédé selon la revendication 1, la revendication 2 ou la revendication 3, dans lequel ladite
température se trouve dans l'intervalle de 300 °C à 390 °C.
5. Procédé selon l'une quelconque des revendications précédentes, dans lequel la quantité d'aluminium
dans ladite solution mélangée est supérieure ou égale de 30 % par rapport à la quantité stoechiométrique
nécessaire.
6. Procédé selon la revendication 5, dans lequel le pH de ladite solution mélangée se trouve dans
l'intervalle de 10,6 à 13,3 et ladite température se trouve dans l'intervalle de 300 °C à 390 °C.



7. Procédé selon la revendication 1 qui comprend le remplacement d'une partie du premier matériau par un troisième matériau choisi parmi des sels de terbium et des hydrolysats de composés de terbium.
8. Procédé de fabrication de fines particules de phosphore à base d'yttrium-aluminium-grenat, le procédé comprenant les étapes :
- 5 de préparation d'une solution comprenant un premier matériau choisi parmi des sels d'yttrium et des hydrolysats de composés d'yttrium, un second matériau choisi parmi des sels d'aluminium et des hydrolysats de composés d'aluminium et un troisième matériau choisi parmi des sels de terbium et des hydrolysats de composés de terbium ; et
- 10 de mélange de ladite solution avec une solution alcaline aqueuse ; caractérisé en ce que :
- on charge la solution mélangée ayant un pH supérieur ou égal à 10,0 dans un autoclave, et on chauffe ladite solution mélangée à l'intérieur de celui-ci à une température supérieure ou égale à 270 ° C pour produire un précipité ; et
- 15 on lave et on sèche ledit précipité afin d'obtenir les fines particules de phosphore à base d'yttrium-aluminium-grenat.
9. Procédé selon la revendication 8, dans lequel le pH de ladite solution mélangée se trouve dans l'intervalle de 10,2 à 14,1.
- 20 10. Procédé selon la revendication 8, dans lequel le pH de ladite solution mélangée se trouve dans l'intervalle de 11,0 à 13,5.
11. Procédé selon la revendication 8, la revendication 9 ou la revendication 10, dans lequel ladite température se trouve dans l'intervalle de 300 ° C à 390 ° C.
- 25 12. Procédé selon l'une quelconque des revendications 8 à 11, dans lequel la quantité d'aluminium dans ladite solution mélangée est supérieure ou égale de 30 % par rapport à la quantité stoechiométrique nécessaire.