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Nanopowders synthesized by solution combustion method and their applications

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Introduction

An innovative technique for the synthesis of nanocrystalline oxide powders with high crystalline quality is "solution combustion method" which was invented by S.Park et al.[1] This technique offers added advantages over other methods as the simplicity of experimental setup, the surprisingly short time between the preparation of the reactants and the availability of the final product, and savings in external energy consumption. The idea was arisen from the reaction between the oxidant and fuel of liquid rocket propellants. The explosion energy of the reaction is utilized to synthesize nano crystalline oxide powders.

TABLE 9.1

Comparison between liquid propellant and solution combustion method

	Liquid propellant	SCM
Oxidant	O ₂ etc. (liquid)	Metal nitrate (solid)
Fuel	H₂ etc. (liquid)	Glycine etc. (solid)
Remarks	1) explosion upon contact	 1) dissolved in water 2) explosion after evaporation of water

The difference between the liquid propellant and solution combustion method is summarized in table 9.1. Liquid oxidant and fuel are used for liquid propellant. However, solid oxidant and fuel are used for the solution combustion method. The liquid materials such as liquid oxygen and liquid hydrogen are very expensive and tough to control because extremely low temperatures are required to keep the oxygen (below -183°C) and hydrogen (below-253°C) liquid. Contrarily, the solid materials such as metal nitrates and glycine are very cheap and easy to control because they are just dissolved in water at room temperature.

The basis of the solution combustion method comes from the thermochemical concepts used in the field of propellants. Self-propagating combustion reaction takes place when propellants are ignited. In the solution combustion method, as shown in table 9.1, metal nitrates and fuels are used as starting materials. Stoichiometry of the metal nitrate and fuel mixture can be calculated based on the total oxidizing and reducing valency of the oxidant (metal nitrate) and the fuel, which serves as a numerical coefficient for stoichiometric balance so that equivalence ratio (φ_e) is equal to unity and the energy released is maximum. As an example, the oxidizing valence of zinc nitrate is -10 while the reducing valence of carbohydrazide is +8 and that of glycine is +9. Hence, 1 mole of zinc nitrate requires 1.25 moles of carbohydrazide or 1.11 moles of glycine to keep the equivalence ratio (φ_e) unity.

The solution combustion method begins with the mixture of oxidants that oxidize easily, eg., nitrates and a suitable organic fuel (like glycine, urea, carbohydrazide) that acts as a reducing agent. The mixture is brought to boil until it ignites and a self-sustaining and rather fast combustion reaction takes place, resulting in a dry, crystalline and unagglomerated, nanocrystalline oxide powder. The large amount of gases formed can result in the appearance of flames, which can reach temperatures in excess of 1500° C.

In solution combustion method, the energy released from the exothermic reaction between the nitrates and the fuel, which is usually ignited at a temperature much lower than the actual phase transformation temperature, can rapidly heat up the system to a high temperature and sustain it long enough, even in the absence of an external heat source, for the synthesis to occur.

In a typical solution combustion method, a beaker containing an aqueous redox mixture of stoichiometric amounts of nitrate and glycine is heated on a hot plate inside a chamber. The solution boils and froths, followed by the appearance of flame yielding a voluminous product. The explosive power is controlled by dissolving the oxidant and fuel in water. As a matter of fact, there are two purposes for the water solution. First of all, it is necessary to prevent the direct contact of the oxidant and fuel. The reaction only occurs when all of the water is evaporated. Secondly, it makes the oxidant and fuel uniformly mixed. As the water is evaporated, the solution becomes viscous generating large number of air bubbles. At this point, the oxidant reacts with the fuel generating intense heat (high temperature) and nontoxic gases such as N_2 , CO_2 and H_2O . Following is an example of the reaction.

$$Zn(NO_3)_2 6H_2 O(s) + 1.11H_2 NCH_2 COOH(s) \rightarrow ZnO(s) + 1.56N_2(g) + 2.22CO_2(g) + 8.78H_2 O(g)$$

Here, the nitrate group (NO₃⁻) actually reacts with the fuel for combustion. The generated heat and gases result in instantaneous high pressure, which leads to explosion. The large number of explosion occurs simultaneously but each explosion occurs in very small space. The explosive power, thus, is not so high. It is as high as cornpopping. The experiment is performed inside a stainless steel (fig. 9.1). The synthesized powder is collected mostly by the screen and partially by the filter.



FIGURE 9.1



The solution combustion method provides a high temperature, high pressure and short time reaction (explosion) environment. These three synthesis conditions are very difficult to obtain at once and are crucial to get high quality nanocrystalline oxide powders. In this chapter, ZnO, ZnGa₂O₄, BaTiO₃ and La_{0.7}Ca_{0.3}MnO₃nanopowderswere synthesized by the solution combustion method and their photocatalytic, optoelectric, dielectric and magnetic properties were investigated.

Synthesis of nanopowders and their applications

ZnO nanopowder: photocatalytic application

1. Background

When ZnO is irradiated with UV light of appropriate energy greater than its bandgap, highly mobile electron-hole pairs can be generated. These carriers then migrate to the surface and in turn are trapped by reactants adsorbed on the surface, giving rise to powerful redox chemistry.[2] Therefore, ZnO is of interest as a photocatalyst, especially, in the degradation of environmental pollutants.[3] It has almost the same bandgap energy as titanium dioxide (TiO₂) and hence its photocatalytic activity is anticipated to be similar to that of TiO₂. But only a limited research has been carried out to realize its full potential as a semiconductor photocatalyst.[4-5]

Synthesis of fine zinc oxide powders were tried by several chemical methods such as spray pyrolysis, sol-gel technique, vapor method, thermal decomposition and precipitation from organic solutions.[6-10] However, the characteristics of zinc oxide synthesized by these methods were not good enough to use for a photocatalyst compared to other materials such as TiO_2 . That is the reason why is TiO_2 generally used for a photocatalyst.[11-14]

It was reported that metal ions such as lead, chromium, copper, silver and mercury could be removed/recovered from dilute aqueous solutions using TiO_2 .[15] However, few studies were conducted to recover metal ions using ZnO since it is well known that TiO_2 is the best photocatalyst.[16] Our research group is investigating on the substitute of TiO_2 and working on ZnO as another potential semiconductor photocatalyst.

As mentioned above, our research group developed a novel process (SCM) to synthesize ZnO nanopowders. Here, the SCM ZnO nanopowders were used to recover gold metal ions from real plating wastewater using photocatalytic reaction.

2. Experiment

Zinc hydroxide powder [Zn(OH)₂, Junsei (Japan)] or zinc nitrate powder [Zn(NO₃)₂ 6H₂O, 3N, High purity chemicals lab.(Japan)] was used for the starting material. Glycine [H₂NCH₂COOH, Yakuri pure chemicals co. Ltd (Japan)] or carbohydrazide [H₂NNHCONHNH₂, Aldrich (USA)] was used for the fuel. Here the zinc hydroxide powder was dissolved in nitric acid before using, to form zinc nitrate. The starting material (zinc nitrate or zinc hydroxide dissolved in nitric acid) was dissolved in distilled water in a beaker and fuel (glycine or carbohydrazide) was added to the starting material solution. The solution mixture was then heated on a hot plate with stirring. As the distilled water was evaporated, the solution became viscous and generated small bubbles. The viscous solution was then transferred in another stainless steel beaker and heated inside a chamber for ignition. The nitrate group (NO₃⁻) reacted with the fuel. At this point, temperature shot up to 1500-1800°C instantaneously with flame and combustion. This intense heat resulted in instantaneous high pressure, which led to explosion. The ZnO powder was formed in this high temperature and pressure environment. At this point the powder was gathered up by the collector, which was placed above the beaker. The powder was annealed at 400°C for one hour.

For the purpose of comparison of photocatalytic recovery rate, P25 TiO_2 powder (Degussa, Germany) and commercial ZnO powder (Junsei Chemicals Ltd (Japan)) were purchased. The powders were then used as photocatalysts for the removal of gold ions from the aqueous solution.

For photocatalytic reaction, 3.0 g/L of the photocatalyst powder was mixed in plating wastewater containing 60 ppm of gold ions.

X-ray diffractometer (XRD) was used to confirm the crystalline phase of the synthesized ZnO powder. Scanning electron microscope (SEM) was also used to investigate the average particle size and shape. Specific surface area of the powder was measured by brunaueremett teller (BET) method. Fluoro-spectrometer (SIM-AMINCO) was used to measure photoluminescence (PL) emission values as a function of wavelength. Different ZnO powders were synthesized with changing the amount of carbohydrazide.

3. Results and discussion

In this section, metal nitrate was used for the starting material (oxidant), and glycine was used as a fuel, in order to synthesize ZnO powders. The fuel reacted with nitric acid group ($NO_{x=1, 2, 3}$) and formed highly volumetric gases such as N_2 , CO_2 and H_2O . At this point, temperature shot up to 1500-1800°Cinstantaneously with flame and combustion. The ZnO powders were synthesized with the aid of this heat. The ZnO powders were synthesized with changing the amount of fuel.

Figure 9.2 shows XRD peaks of the synthesized ZnO powders. Especially the ZnO powder with fuel/oxidant ratio of 0.8 showed highest XRD peaks that indicate best crystalline quality. As shown in fig. 9.3, it also showed best powder characteristics, such as average grain size of 30nm and the specific surface area of $120m^2/g$.



FIGURE 9.2

XRD patterns of ZnO powders synthesized using glycine and zinc hydroxide (F: fuel, O: oxidant)

Figure 9.4 shows photoluminescence (PL) spectra of commercial state of the art ZnO (Junsei, Japan), commercial state of the art TiO₂ (P-25 Degussa, Germany) and ZnO powders synthesized by SCM with different glycine/Zn(OH)₂ ratios. As shown in fig. 9.4, commercial state of the art ZnO powder showed two peaks: one is in the vicinity of 500 nm, and the other one is near 400 nm. The peak near 500 nm probably came from the energy transition between O vacancy level and valence band edge. The UV peak near 400 nm might be from band to band transition. However, ZnO powder synthesized by the SCM showed only one sharp peak near 390 nm that was a little bit shifted to UV side. This peak is equivalent to the energy gap of ZnO (\sim 3.2 eV). These results indicate that the ZnO powder synthesized by the SCM did not show defect energy levels inside the energy

gap. The defects were probably annealed out due to the high temperature during the synthesis process. The SCM ZnO powder showed higher PL intensity at near UV wavelength than other commercial ZnO and TiO₂ powders. Especially ZnO powder with fuel/oxidant ratio of 0.8 showed highest PL intensity at UV. This means that the ZnO powder absorbs 3 fold more UV light than the commercial state of the art TiO₂ powder.



FIGURE 9.3 SEM photograph of the synthesized ZnO powders



FIGURE 9.4

PL spectra of commercial ZnO (Junsei, Japan), commercial TiO₂ (P-25 Degussa, Germany) and the SCM ZnO powders synthesized with different glycine/Zn(OH)₂ ratios

Figure 9.5 shows the concentration of metal ions in plating wastewater before photocatalytic reaction. It contains K, P, Au, Na, Ni, Cu and Zn ions. Figure 9.6 is a schematic band diagram showing materials that could be reduced by photoinduced electrons in ZnO. As shown in fig. 9.6, Au, Ni and Cu could be reduced by ZnO. Ionization tendency is high in order of Ni, Cu and Au. This

means that Au has highest possibility of reduction. The Au ions are therefore selectively recovered. This is the reason why high purity gold was obtained by photocatalytic ZnO nanopowder.



FIGURE 9.5 Concentration of metal ions in plating wastewater before photocatalytic reaction







Au recovery rate by photocatalytic reaction of commercial ZnO (Junsei, Japan), commercial TiO₂ (P-25 Degussa, Germany) and the SCM ZnO powders synthesized with glycine/Zn(OH)₂ ratio of 0.8

As mentioned above, results from XRD and PL measurements led us to select the ZnO powder with glycine/Zn(OH)₂ ratio of 0.8 for Au recovery experiment. As shown in fig. 9.7, the photocatalytic reaction using SCM ZnO nanopowder completely recovered the gold ions after irradiating UV for 45 min, even though the photocatalytic reaction using the state of the art commercial TiO₂ (P-25 Degussa, Germany) recovered only 17 % of the gold ions after 45 min. The photocatalytic gold recovery efficiency by SCM ZnO nanopowder is about 6 fold higher compared to the case by the state of the art commercial TiO₂ nanopowder. This is a remarkable result considering that, as well known, the TiO₂ is the best photocatalyst out of all kinds of photocatalytic materials.

Photocatalytic reactivity seems to depend on the preparation method of photocatalytic powders rather than the crystalline phase, specific surface area or even kinds of material. Preparation methods have effects on surface properties such as surface defect levels. Generally it is known that the smaller particle size results in the more surface defects. In present SCM ZnO case, however the level of surface defects seemed to be minimized even though the powder was synthesized in nano size. The surface defects might be annealed out during synthesizing process that reaches to about 1500-1800 °C.

4. Summary

Nanosized singlephase ZnO powders with average grain size of 30nm and the specific surface area of $120m^2/g$ were obtained by the SCM. Surprisingly, the Au ions in the plating wastewater were completely removed within just 45min when the SCM ZnO powder was used for photocatalytic reaction. Au recovery rate with the SCM ZnO powder was 6 fold higher than that of commercial state of the art photocatalytic powders including ZnO and TiO₂. This result was strongly supported by the PL measurement data showing that the PL intensity of the SCM ZnO powder was about 3 fold higher than that of the commercial state of the art TiO₂ powder.

The purity of recovered gold was about 99.6% in weight% and 98.8% in atomic%. This purity reaches to the level of commercial 24K gold (99.9%). Furthermore, the ZnO nanopowder synthesizing method and gold recovery process are very cost effective. Finally double effects,

purification of wastewater and recovery of expensive gold metal, could be obtained simultaneously using SCM ZnO nanopowder.

ZnGa₂O₄ nanopowder: optoelectric application

1. Background

FEDs (field emission displays) have recently gained much attention as they are considered next generation flat panel displays. Especially of great interest are SEDs (surfaceconduction electronemitter displays) which are a type of FEDs, because of their relative easiness of fabrication (no emitter tips) and low energy consumption. The energy consumption of SEDs is even lower than that of CRTs. Their energy consumption depends very much on the emission efficiency of phosphors. The high efficiency phosphors are therefore one of key technologies for the SEDs. Sulfide type phosphors are presently commercially available. However, they were developed for CRT. These phosphors could generate sulfide gas and result in corrosion of emission tips (FEDs) or electron emitting electrodes (SEDs) since they are operated under high vacuum condition. Furthermore, low power consumption is essential for portable displays. These requirements make many researchers work on oxide type phosphors such as ZnGa₂O₄ phosphors.[17-24]

Recently, this research group proposed the solution combustion method to synthesize highly pure nanosized metal oxide powders. Using this method, the heating and evaporation of metal nitrate solution with glycine results in selffiring and generates intense heat by exothermic reaction. Due to its high temperature and pressure reaction condition, highly pure nanosized metal oxide powders could be synthesized.[25] In this section, undoped and Mndoped ZnGa₂O₄ phosphors were prepared by both SCM and SSRM (solid state reaction method). The properties of these ZnGa₂O₄ phosphors will be discussed with comparison.

2. Experiment

 $Zn(NO_3)_2 \cdot 6H_2O(Junsei Co.)$ and $Ga(NO_3)_3 \cdot 6H_2O(Aldrich Co.)$ powders were used for starting materials to prepare SCM $ZnGa_2O_4$ powders. The starting materials were dissolved in distilled water in beaker. Glycine (Yakuri pure chemicals co. Ltd) was then added to the starting solution as a fuel. Here both Zn and Ga nitrates act as oxidants during reaction. The mixture solution in the beaker was heated on hot plate with stirring. As the distilled water was evaporated, the mixture solution was heated to be exploded and eventually combusted. Here the heating temperature was only $100^{\circ}C$ to evaporate water. The $ZnGa_2O_4$ powder was formed in the high temperature and pressure combustion environment. The SCM $ZnGa_2O_4$ powder was calcined at $400^{\circ}C$ for 1hr to remove organic remains. To dope the SCM $ZnGa_2O_4$ powder with Mn, $Mn(NO_3)_2 \cdot xH_2O(Aldrich Co.)$ powder was mixed with starting materials. Then it was followed same procedure mentioned above.

On the other hand, ZnO(Junsei Co.) and Ga_2O_3 (Aldrich Co.) powders were used for starting materials to prepare SSRM $ZnGa_2O_4$ powder. They were mixed with ethanol and ball-milled for 24hrs. Then they were dried at 400°C for 30min. To obtain SSRM $ZnGa_2O_4$ powder, the mixed powders were calcined at 1200°C for 10hr. The properties of the both $ZnGa_2O_4$ phosphors were investigated by TGA (Thermogravimetric analysis), SEM, BET, PL and XRD.

3. Results and discussion

As shown in fig. 9.8(a), the weight of reacting powders decreased when it was calcined up to 600° C.

At lower temperature region, it decreased rapidly because the ethanol used during ball-milling was removed. At higher temperature region, the reaction between ZnO and Ga_2O_3 powders would be started. At higher than 600° C, $ZnGa_2O_4$ powders would be formed. Uheda and coworkers reported that the solid state reaction is completed above 1000° C.[26] The SCM $ZnGa_2O_4$ powders were also tried to calcine up to 1200° C to see if there is any weight change. Figure 9.8(b) shows that the organic remains were removed at near 200° C. There was almost no weight change after 200° C.



FIGURE 9.8 TGA graphs of $ZnGa_2O_4$ powder (a) prepared by SSRM and (b) prepared by SCM



FIGURE 9.9

XRD patterns of $ZnGa_2O_4$ powder (a) calculated, (b) prepared by SSRM(1200°C, 10hrs), (c) prepared by SCM(as synthesized) and (d) prepared by SCM(400°C, 1hr)

Theoretical XRD pattern of $ZnGa_2O_4$ powders with spinel structure was shown in fig. 9.9(a). The XRD pattern of fig. 9.9(b) was obtained from SSRM $ZnGa_2O_4$ powders which were calcined at $1200^{\circ}C$ for 10hrs. This pattern shows that the crystalline quality of SSRM $ZnGa_2O_4$ powders reached to the theoretical level. Figure 9.9(c) shows small extra peaks which probably came from carbon remains formed during combustion. These were completely removed after calcined at $400^{\circ}C$ for 1hr as shown in fig. 9.9(d). Figure 9.9(d) shows that the crystalline quality of SCM $ZnGa_2O_4$ powders also

reached to the theoretical level even though they were calcined at 400° C for 1hr rather than at 1200° C for 10hrs.

As shown in fig. 9.10, the average particle size of SSRM $ZnGa_2O_4$ powders was about 5µm. However, that of SCM $ZnGa_2O_4$ powders was about 50nm. This small particle size was probably due to the instantaneous high pressure explosion during reaction. Based on BET measurement, the specific surface area of both SSRM $ZnGa_2O_4$ and SCM $ZnGa_2O_4$ powders is $1.79m^2/g$ and $86.54m^2/g$ respectively.



FIGURE 9.10

SEM photographs of $ZnGa_2O_4$ powder (a) prepared by SSRM(1200°C, 10hrs) and (b) prepared by SCM (400°C, 1hr)

PL emission spectra of both SSRM ZnGa₂O₄ and SCM ZnGa₂O₄ powders are shown in fig. 9.11. Here a Xe lamp was irradiated on the powders. Both spectra are relatively broad ranging from 350nm to 650nm. They show peaks at near 470nm. The emission intensity (peaks at near 470nm) of SCM ZnGa₂O₄ powders was about 1.5 fold higher compared to that of SSRM ZnGa₂O₄ powders. This might be mainly due to the large specific surface area that is 48 fold larger than that of SSRM ZnGa₂O₄powders. Because the operation voltage in displays such as field emission displays is low, the penetration of electrons into the phosphor particle is very shallow. The low penetration of electrons into the particle means that emission from the phosphor must involve energy transfer within the shallow surface layer such as several 10Å below the surface. It is clear that, at low voltages, the nature and perfection of the surface of the phosphors play an important role in the performance of phosphors. The large surface area, thus, could contribute to the high intensity. Furthermore, the surface perfection of SCM ZnGa₂O₄ powders might be very good because of its high instantaneous phosphors. The large surface area, thus, could contribute to the high intensity. Furthermore, the surface perfection of SCM ZnGa₂O₄ powders might be very good because of its high instantaneous phosphors. The large surface area, thus, could contribute to the high intensity.



FIGURE 9.11 Emission spectra of ZnGa₂O₄ powder



XRD patterns of Zn_{1-x}Mn_xGa₂O₄ powder prepared by SCM

Figure 9.12 represents XRD patterns of $Zn_{1-x}Mn_xGa_2O_4$ powder prepared by SCM. The added amount of Mn^{2+} ions was ranging from 0.001 mole% to 0.012 mole%. The $Zn_{1-x}Mn_xGa_2O_4$ powders were heat treated at 650°C for 5hrs. All of the XRD patterns of $Zn_{1-x}Mn_xGa_2O_4$ powders were corresponding to that of pure $ZnGa_2O_4$ powders shown in fig. 9.9(a). This means that the addition of Mn^{2+} ions did not change any crystalline structure. The added Mn^{2+} ions replaced the Zn lattice sites.

As shown in fig 9.13, the emission peak shifted from blue to green color when the Mn²⁺ ions were

added to SCM ZnGa₂O₄ powders. The peaks were at near 513nm for all cases. The green emission spectra probably came from the fact that Mn^{2+} ions replace tetrahedral Zn^{2+} sites rather than Mn^{4+} ions replace octahedral Ga³⁺ sites. The highest peak was obtained when the added amount of Mn^{2+} ions was 0.003 mole%. The peak was lowest when the added amount of Mn^{2+} ions was 0.001 mole%. This means that the added amount of Mn^{2+} ions was not enough. It shows almost same peak height when Mn^{2+} ions of 0.006 mole% and 0.009 mole% were added. The peak became lower with Mn^{2+} ions of 0.012 mole%. This indicates that the concentration quenching occurs if the Mn^{2+} ions are added more than 0.003 mole%. In this case, extra Mn^{2+} ions might act as defects.



FIGURE 9.13

Emission spectra of $Zn_{1-x}Mn_xGa_2O_4$ powders prepared by SCM with changing the added amount of Mn^{2+} ions

4. Summary

The emission intensity (peaks at near 470nm) of SCM $ZnGa_2O_4$ powders was about 1.5 fold higher compared to that of SSRM $ZnGa_2O_4$ powders. This might be due to the large specific surface area that is 48 fold larger than that of SSRM $ZnGa_2O_4$ powders.

The emission peak shifted from blue to green color when the Mn^{2+} ions were added to SCM $ZnGa_2O_4$ powders. The peaks were at near 513nm. The highest peak was observed with Mn^{2+} ions of 0.003 mole%. Furthermore the spectra became sharper than those of pure $ZnGa_2O_4$ powders. This is more desirable for displays which use three pure color phosphors with red, green and blue colors.

In the design of phosphors for low voltage operations, there are three key factors to be considered, the morphology and size, the stoichiometry and composition, and the surface quality. It seems that the solution combustion method mostly satisfies these factors. This might be very useful for high efficiency and low voltage phosphors for displays such as field emission displays and plasma display panels.

BaTiO₃ nanopowder: dielectric application

1. Background

Inorganic AC powder EL (electroluminescence) devices provide wide viewing angle, ruggedness to

shock and vibration, and wide usage temperature range. These features meet the requirements for demanding applications such as emergency guide lights in airplanes, backlight for LCDs (liquid crystal displays) and variety of niche applications, for example, displays which are used for industrial process control and instrumentation, medical equipment, civil and military avionics, and transportation.[27-31]

However, their low brightness and low energy efficiency are practical obstacles to be used for LCD backlights of mobile applications such as cellular phones and other wireless devices. It is very difficult to achieve both high brightness and high energy efficiency (low current density) simultaneously because they are tradeoff characteristics. There are two key factors which determine the brightness and current density of AC powder EL devices. Those are phosphor powders and dielectric powders. In general, the phosphor powders affect the brightness. The dielectric powders have effects on both brightness and current density. BaTiO₃ powders are usually used for the dielectric layer of the AC powder EL device.

In this section, $BaTiO_3$ powders were synthesized by the solution combustion method. AC powder EL devices with the SCM $BaTiO_3$ powders and commercial $BaTiO_3$ powders were fabricated, and their dielectric, electrical and optical characteristics were compared.

2. Experiment

 $Ba(NO_3)_2$ powders and TiO(NO_3)_2 powders were used for source materials (oxidants) to synthesize $BaTiO_3$ powders. $Ba(NO_3)_2$ powders are commercially available but $TiO(NO_3)_2$ powders are commercially not available because it is very difficult to obtain stable intermediate sources. Synthesis process for $TiO(NO_3)_2$ powders was thus developed in this work. First of all, $TiCl_4$ solution was hydrolyzed by ammonia solution to obtain Ti-hydroxide. The Ti-hydroxide was then dissolved in nitric acid and continuously mixed to get $TiO(NO_3)_2$ powders. On the other hand, glycine powders were used for fuel.

The source materials, $Ba(NO_3)_2$ powder and $TiO(NO_3)_2$ powder, were dissolved in distilled water in a beaker and the fuel was added to the source material solution. The solution mixture was then heated with stirring. After the distilled water was evaporated, the nitrate group (NO_3) reacted with the fuel. At this point, temperature shot up to $1500-1800^{\circ}$ Cinstantaneously with flame and combustion. This intense heat resulted in instantaneous high pressure, which led to explosion. Therefore, the BaTiO₃ powders were formed on high temperature, high pressure and short time reaction conditions. The SCM BaTiO₃ powders were measured by XRD and SEM.

In this section, AC powder EL devices were prepared. A schematic device structure is displayed in fig. 9.14. The following is a brief description of the device fabrication. First of all, a piece of a commercial ITO (indium tin oxide) film was used for the substrate of the device. The ITO film was fabricated by depositing ITO thin film on a PET (polyethyleneterephthalate) substrate. The ITO film is transparent so that the emitted light can pass through. A light emitting layer was then screen printed on the ITO film. The light emitting layer was a mixture of ZnS:Cu powders and polymer binder (polyester). After drying the light emitting layer, a dielectric layer was screen printed on top of the light emitting layer. The dielectric layer was a mixture of BaTiO₃ powders and polymer binder. Here two kinds of BaTiO₃ powders, SCM BaTiO₃ powders and commercial BaTiO₃ powders (HPC: High purity chemicals lab., Japan), were tried to compare their effects on the AC powder EL device characteristics. After drying the dielectric layer, carbon paste was used for another electrode layer. Eventually, two sets of AC powder EL devices were prepared and their electro-optical characteristics were investigated.



Schematic structure of AC powder EL device

3. Results and discussion



FIGURE 9.15



As shown in fig. 9.15, the XRD result confirms that the synthesized SCM BaTiO₃ powders are high quality crystalline powders showing sharp peaks which are indexed to those of BaTiO₃ crystals. Figure 9.16 shows particle shapes and sizes of SCM BaTiO₃ powders and commercial BaTiO₃ powders. The SCM BaTiO₃ powders had smooth spherical shape but the commercial BaTiO₃ powders had rough irregular shape. Average particle size of the commercial BaTiO₃ powders was about 1µm. However, average particle size of the SCM BaTiO₃ powders was about 22 times smaller than that of the commercial BaTiO₃ powders.



SEM photographs of (a) SCM BaTiO₃ powders and (b) commercial BaTiO₃ powders (HPC)

The smaller particle size and larger specific surface area could lead to increase in contact area at interface between phosphor layer and dielectric layer. This could effectively block the electrons which pass through the dielectric layer. Therefore, more electrons could be involved in electroluminescence. This might be the reason why the AC powder EL device with SCM BaTiO₃nanopowders showed higher brightness than that with commercial BaTiO₃ powders as shown in fig. 9.17. Especially, the brightness of the EL device with SCM BaTiO₃nanopowders was about 31% higher than that with the commercial BaTiO₃ powders at 200V.

Figure 9.18 shows the leakage current as a function of applied voltage for the AC powder EL devices. Surprisingly, both kinds of the EL devices showed almost same level of leakage current even though the brightness of the EL device with SCM $BaTiO_3$ nanopowders was higher up to 31 %. This is probably attributed to two facts.



Brightness as function of applied voltage at 400Hz for each AC powder EL device with a dielectric layer using (a) SCM BaTiO₃ powders and (b) commercial BaTiO₃ powders (HPC)

Firstly, as mentioned above, the dielectric layer with SCM $BaTiO_3$ nano powders has larger interface contact area with phosphor layer. Secondly, it has higher particle packing density than that with the commercial $BaTiO_3$ powders.



FIGURE 9.18

Current density as a function of applied voltage at 400Hz for each AC powder EL device with a dielectric layer using (a) SCM $BaTiO_3$ powders and (b) commercial $BaTiO_3$ powders (HPC)

As shown in fig. 9.19, the dielectric layer with SCM BaTiO₃nanopowders shows higher dielectric constant than that with the commercial BaTiO₃ powders. This seems due to higher particle packing density (smaller particle size) and higher crystalline quality of SCM BaTiO₃ nanopowders. This higher dielectric constant also supports the higher brightness of EL device with SCM BaTiO₃ nanopowders. Especially, the dielectric constant of the dielectric layer with SCM

BaTiO₃nanopowders was about 12 which approaches to that of sputter deposited thin films (~14) at 400Hz even though it was a screen printed thick film.[27]



FIGURE 9.19

Dielectric constant as a function of frequency for each dielectric layer with (a) SCM $BaTiO_3$ powders and (b) commercial $BaTiO_3$ powders (HPC)

4. Summary

BaTiO₃ nanopowders were synthesized by the solution combustion method. The particle size of the SCM BaTiO₃ powders was about 45nm and their specific surface area was $115m^2/g$. The particle size of the SCM BaTiO₃ nanopowders was about 22 times smaller than that of the commercial BaTiO₃ powders. The synthesized SCM BaTiO₃ nanopowders were used for the dielectric layer of AC powder EL device. The smaller particle size and higher crystalline quality of the SCM BaTiO₃ nanopowders probably resulted in lower leakage current and higher dielectric constant of the dielectric layer. Those characteristics might lead to the result that the brightness of the EL device with SCM BaTiO₃ nanopowders was about 31% higher than that with the commercial BaTiO₃ powders at 200V even though the leakage current was almost same.

La_{0.7}Ca_{0.3}MnO₃ nanopowder: magnetic application

1. Background

In general, the resistance of conductors increases with magnetic field because the field slows the flow of electrons down. However, in some materials, the resistance decreases with the magnetic field. Among such materials, some show more than 1000% decrease in the resistance under the magnetic field. Such materials are called colossal magnetoresistance (CMR).[32] Even though studies on these materials were started in the 1950s, they did not attract much attention since there were not enough applications. Recently, however, more sensitive and applicable CMR materials are required as the highspeed information technologies are developed. At present, several tens % of increased sensitivity could be obtained by multilayered metals, which are used for MR head applications. This could be an obstacle to achieve highly sensitive heads that can process

data at high speed. Recently, CMR materials, based on oxides, have attracted much attention to overcome this limit.

Many researchers have worked on $R_{1-x}A_xMnO_3$ (R: La or rearearth metal, A: Ca, Sr, Ba, Pb; x = 0.2-0.5) for CMR applications.[33-36] Among these, structural phase diagram and CMR effect with the variation of x in La_{1-x}Ca_xMnO₃ have been reported since the perovskite structure is stable in a wide range of x values using Ca as 2 valence positive ion.[37,38] K. Dorr reported that La_{1-x}Ca_xMnO₃ showed best CMR properties when the x value was 0.3.[39]

The solution combustion method could be easily utilized to produce multicomponent ceramic materials by mixing nitrate group and glycine, which is a nonequilibrium synthesis method.[40] It might be very interesting to synthesize $La_{1-x}Ca_xMnO_3$ powders using SCM. Therefore, in this section, the syntheses of $La_{1-x}Ca_xMnO_3$ powders were tried using both conventional solid state reaction method and solution combustion method. Powders prepared by both the methods were characterized and their properties were compared.

2. Experiment

 $La_{0.7}Ca_{0.3}MnO_3$ powders were prepared by two different methods. Out of those two methods, one was the conventional SSRM while the other was SCM that was a new trial by this research group.

In SSRM, La_2O_3 (3 N, High purity chemicals Lab. (Japan)), CaO (3 N, Duksan chemical engineering (Korea)) and MnCO₃ (3 N, Junsei (Japan)) were used as starting materials. After weighing the starting materials for designed composition, they were mixed and the mixture was pulverized using ethanol for 24 hrs. Then the pulverized powder was passed through 270 mesh sieve. Calcination temperature was roughly estimated by thermogravimetric analyzer at the temperature increase rate of 2°C /min. The calcination was performed at temperature ranging from 900°C to 1000°C for 24 hrs in air, to obtain single phase.

In SCM, La, Ca, Mn-nitrates (Aldrich, USA) and glycine (H_2NCH_2COOH , Yakuri pure chemicals Co. Ltd (Japan)) were used as starting materials and a fuel, respectively to synthesize $La_{0.7}Ca_{0.3}MnO_3$ powder. After completely dissolving the starting materials in distilled water, the fuel was added to the distilled water to be dissolved based on stoichiometry. Then the solution was heated on hot plate and stirred with magnetic bar at around 100°C. The magnetic bar was removed after most of the solvent was evaporated. The mixture was heated further until the explosive combustion of glycine was occurred. $La_{0.7}Ca_{0.3}MnO_3$ powder was synthesized by the intense heat, which was generated during the exothermic reaction (combustion of glycine). The synthesized powder was flown away by the violent reaction during powder synthesis. Fine wire meshes were used to collect the flying powder. The collected powder was calcined at650°C for 1h to remove unreacted carbon compounds and other organic matters.

Different analytical tools were used to investigate the characteristics of powders prepared by both the methods, SSRM and SCM. Powder crystallinity, the shape and size, and the specific surface area were measured using X-ray diffractometer (XRD), Scanning Electron Microscope (SEM) and Brunauer-Emmett-Teller (BET) methods, respectively. The powders were molded to form 25 mm diameter bars to measure thermal expansion coefficients using dilatometer. Poly vinyl alcohol (PVA) was added as a binder to avoid cracks on the bars. Thermal expansion coefficients were measured by heating up to 1400°C at the temperature increase rate of1min in air after pressing the bars with 30 N/cm² of pressure.

3. Results and discussion

In this section, La_{0.7}Ca_{0.3}MnO₃ powders were prepared using both SSRM and SCM. In SSRM, metal oxides and metal carbonates were used as source materials while in SCM, metalnitrates and glycine were used as oxidants and a fuel, respectively. Figure 9.20 shows the thermogravimetricanalysis (TGA) graphs that could be used to estimate the calcination temperatures. Figure 9.20(a) and 9.20(b) represent TGA graphs of powders for SSRM and as prepared powder by SCM, respectively.



FIGURE 9.20

TGA graphs of La_{0.7}Ca_{0.3}MnO₃ powders prepared by (a) solid state reaction method and (b) solution method

SSRM powder showed gradual weight loss up to 25% at 700°C. This weight loss is probably attributed to the evaporation of carbonate out of $MnCO_3$ and organic materials used during powder fabrication process. However, in SCM, the weight of the powder was sharply decreased above 500°Cand was saturated at around 650°C. Below 500 °C, the weight loss seems to be due to the evaporation of remained organic materials during the decomposition of incompletely combusted glycine. Above 500°C, the abrupt weight loss might be due to the evaporation of NO_x

adsorbed on as prepared powder surface that was originated from nitrates.[41] Therefore, the reasonable calcination temperature would be about 700°C and 650°C for SSRM and SCM powders, respectively.

Figure 9.21 shows XRD peaks of SSRM powder calcined for 24hrs at 100° C, 900° C, and 700° C, respectively. The XRD peaks indicate that La_{0.7}Ca_{0.3}MnO₃ single phase and unreacted materials were coexisted up to 900° C. Complete La_{0.7}Ca_{0.3}MnO₃ single phase was obtained at 1000° C. Such a high calcination temperature of SSRM powder would probably be attributed to two reasons. Firstly, it is very difficult to achieve uniform mixing of La, Ca and Mn using ball milling. On the other hand, each metal ion should diffuse uniformly during calcination to form single phase perovskite structure. However, it is difficult for these metal ions to uniformly diffuse throughout the total volume because of their different diffusivity.



FIGURE 9.21

XRD patterns of $La_{0.7}Ca_{0.3}MnO_3$ powders prepared by solid state reaction method and calcined at (a) $1000^{\circ}C$ for 24hrs, (b) $900^{\circ}C$ for 24hrs, and (c) $700^{\circ}C$ for 24 hrs

In the SCM, however, as shown in fig. 9.22., uniform La_{0.7}Ca_{0.3}MnO₃ single phase powder could be obtained easily even though the powder was calcined at 650°Cfor 1hrin air. The XRD peaks showed much higher intensity than those of the SSRM powder. Since the higher relative intensity signifies higher crystallinity, SCM powder had higher crystallinity even though it required less energy than the SSRM powder. The temperature instantaneously shoots up above 1500°C with flame and combustion of the fuel during the solution combustion synthesis process. Since the powder was synthesized using this heat, high temperature was not necessary for calcination. Here, unreacted

intermediates would, probably, not form as the powder was synthesized at high temperature. This might be the reason why the higher peak intensity was observed for the SCM powders. Furthermore, during reaction, the instant explosion at high temperature seemed to result in nanosized powder. Figure 9.23(a) and 9.23(b) show SEM photographs of SSRM powder(x 5,500) and SCM powder(x 120,000) indicating the particle sizes of 2-3 μ m and 30-50nm, respectively. Comparison of fig. 9.23(a) and 9.23(b) shows the particle size of SSRM powder was about 60 fold larger than that of SCM powder even though the SSRM powder was ball-milled for 24 hrs.



FIGURE 9.22

XRD patterns of $La_{0.7}Ca_{0.3}Ca_{0.3}MnO_3$ powder prepared by solution combustion method and calcined at 650 ^oC for 1hr

This seems to be due to the grain growth during high temperature calcination in SSRM. In SCM, all the starting materials were dissolved in water forming transparent solutions; that is to say, the starting materials were ionic solutions. The solution became gel-like as the distilled water was evaporated. Then the solution was combusted with explosion by the fuel. This exothermic reaction was occurred instantaneously by the combustion of the fuel. The instant heat from the explosive combustion would not allow the formation of amorphous phases. Here, the heating time would be long enough to form nucleus but too short for grain growth. This combustion synthesis might be the critical reason for the nanosized powder and the large specific surface area.

Table 9.2 shows the specific surface areas of powders prepared by SCM and SSRM. The specific surface area of SCM powder was about 26 fold larger than that of SSRM powder. Higher sinterability was expected from the spherical SCM powder that had no grain growth and pulverization as shown in fig. 9.23. Generally the large specific surface area enhances the reactivity, which, in turn, decreased the sintering temperature of the powder.



SEM photographs of $La_{0.7}Ca_{0.3}Ca_{0.3}MnO_3$ powders prepared by (a) solid state reaction method (x5,500) and (b) solution combustion method (x120,000)

TABLE 9.2

Results of BET Analysis for $La_{0.7}Ca_{0.3}Ca_{0.3}MnO_3$ Powders by Solid State Reaction Method and Solution Combustion Method

Preparation Method	SSRM	SCM
Specific Surface Area(m ² /g)	3.48	92

Figure 9.24 shows the change in thermal expansion coefficients with temperature. Shrinkage was started at around 650°C and 850°C for SCM powder and SSRM powder, respectively. This fact indicates that the SCM powder shrinks at lower temperature. Shrinkage of the powder at lower temperature indicates its low temperature sinterability, which comes from the higher reactivity due to its large specific surface area as mentioned above. From the curves, we may see that the SCM powder can be sintered at about 200°C lower than that of the SSRM powder.

4. Summary

In this section, synthesis of $La_{0.7}Ca_{0.3}MnO_3$ powders was tried using conventional method, SSRM as well as a new method, SCM. Both the powders were then characterized and their properties were compared. In SSRM, $La_{0.7}Ca_{0.3}MnO_3$ single phase was obtained after the heat treatment of the powder at 1000°Cfor 24hrs while in the case of SCM, single phase nanosized $La_{0.7}Ca_{0.3}MnO_3$ powder was obtained easily after heat treating the powder at a low temperature of 650°C for 1hr only. Specific surface area of the polycrystalline $La_{0.7}Ca_{0.3}MnO_3$ powder, obtained from SCM, was measured to be 92 m²/g, which was about 26 fold larger than the specific surface area of the powder obtained from SSRM. On the other hand, the particle size of the SCM powder was about 60 fold smaller than that of SSRM powder even though the succeeding powder was abal-milled for 24 hrs. Due to its fine particle size, the sintering temperature of the SCM powder was about 200°C lower than that of SSRM powder.

This method, SCM, is anticipated to be very attractive for the low cost synthesis because of its low calcination temperature, short calcination time and simple process.



Dilatometric measurement of thermally activated volume expansion of $La_{0.7}Ca_{0.3}MnO_3$ powders prepared by (a) solid state reaction method and (b) solution combustion method

Conclusion

ZnO, ZnGa₂O₄, BaTiO₃ and La_{0.7}Ca_{0.3}MnO₃ nanopowders were synthesized by a unique and innovative method which is called solution combustion method. These nanopowders were utilized as photocatalytic, optoelectric, dielectric and magnetic materials. Following conclusions have been reached.

Photocatalytic ZnO nanopowders were synthesized using various oxidants and fuels. Single phase ZnO powders were obtained. The ZnO powder synthesized using $Zn(OH)_2$ and glycine as an oxidant and a fuel at fuel/oxidant ratio of 0.8, showed best powder characteristics such as average grain size of 30 nm and the specific surface area of $120m^2/g$. The photocatalytic gold recovery efficiency by this SCM ZnO nanopowders was about 6 fold higher compared to the case by the state of the art commercial TiO₂nanopowders. The purity of recovered gold was about 99.6% in weight% and 98.8% in atomic%. Especially, in this study it was tried to recover gold metal ions from not-simulated wastewater but real plating wastewater. This technology is therefore very viable and cost-effective to obtain high purity gold from plating wastewater.

 $ZnGa_2O_4$ phosphors were prepared by both SCM and SSRM. The particle size of SCM phosphor was about one hundredth of SSRM phosphor. The PL intensity of SCM phosphor was about 1.5 fold higher than that of SSRM phosphor. The SCM phosphor was also tried to be doped with Mn^{2+} ions. The highest PL peak was observed with Mn^{2+} ions of 0.003 mole%. The peak was shifted from blue (470nm) to green (513nm) color. These results might be very useful for high efficiency phosphors for displays such as field emission displays and plasma display panels.

BaTiO₃nanopowderswere synthesized by SCM. Especially, the source material for Ti was developed in this study because it is not commercially available. The SCM BaTiO₃ powders and commercial BaTiO₃ powders were used for the dielectric layer of AC powder electroluminescence (EL) device. Their effects on AC powder EL device characteristics were studied. The small size (~45nm) and high crystalline quality of SCM BaTiO₃nanopowders resulted in high brightness and low current density of the EL device. The EL device with the SCM BaTiO₃nanopowders showed about 31% higher brightness than that with the commercial $BaTiO_3$ powders even though the current density was same. This technology could be used for low power consumption AC powder EL devices.

 $La_{0.7}Ca_{0.3}MnO_3$ powders were prepared by both SCM and SSRM. They were calcined at various calcination temperatures and time intervals in the air. In the SSRM, single phase $La_{0.7}Ca_{0.3}MnO_3$ was obtained after heat treatment of the powder at 1000° Cfor 24hrs. However, in the SCM, single phase nanosized $La_{0.7}Ca_{0.3}MnO_3$ powder could be obtained easily when the powder was heat-treated at 650° C for 1hr only. Specific surface area of the polycrystalline $La_{0.7}Ca_{0.3}MnO_3$ powder, using this method (SCM), was measured to be $92m^2/g$. The specific surface area was about 26 fold larger than that of the SSRM powder. This SCM $La_{0.7}Ca_{0.3}MnO_3$ nanopowder would be a good candidate for colossal magnetoresistance materials.

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