Mechanochemical Synthesis of $ZnWO_4$ Nanoparticle Scintillator via Anodized Nanoparticle

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1. Introduction

The photoluminescence characteristics of AWO_4 (A = Cd, Zn, Ca, Pb) have been widely investigated because of the potential application of scintillator. [1,2,3] In this structure, WO6 molecular is formed instead of octahedral coordination because W is surrounded by six oxygen. [4] WO6 group has an important role in scintillation properties. [5]

ZnWO4 has broad blue-green emission band. This emission band is caused by WO_6 complex structures. [6] ZnWO4 is widely used because of its stronger scintillation property than other tungstate scintillator. [6,7]. Lead and cadmium are harmful to the environment and the human body, so there is a limit to the use of CdWO4 and PbWO4. [8,9] Zinc tungstate is manufactured in various ways. [5] However, the solid state reaction method is cheap and can be mass produced. [10,11] The solid state reaction methods have typically high temperature (traditional) solid state methods and mechanochemical reaction methods. The traditional solid state method make compound bulk materials at high temperatures, so the size of generated particles are uniform and more than 1000 nm. [12] Mechanochemical reaction is the method of mechanical collision that causes a reaction. . The typical way of this method is a high energy ball milling. This ball milling method has the advantage of not only making particles smaller than 1000 nm, but also making compound nanoparticle at low temperatures. [13]

Our research team synthesized $ZnWO_4$ by high energy ball milling to use anodized nanoparticle. Using anodizing oxide method, nanoparticles are produced in the form of hydroxide and oxide. [14] Hydroxide structure can do mechanical reaction well. [15] Small time of ball milling reduce impurities generated from ball and bowl.

2. Methods and Results

Anodized zinc and tungsten nanoparticles in the form of hydroxide and oxide were synthesized to use anodization oxidation method. Anodized zinc nanoparticles and tungsten nanoparticles were subjected into mechanochemical reaction using planetary high energy ball milling. Material properties of synthesized ZnWO4 by mechanical reaction were evaluated using Scanning Electron Microscope (SEM) and X-Ray Diffraction (XRD). PL measurement was performed in 325 nm UV irradiation condition.

2.1 Synthesis of Anodized Nanoparticle

The synthesizing method of anodized nanoparticles using anodizing oxidation method is as shown in Fig. 1. Ammonium floride or potassium chloride is dissolve in water as electrolyte. Pt electrode and tungsten or zinc wire are put in 1M solution. Applied voltage is from 10 to 100 V.

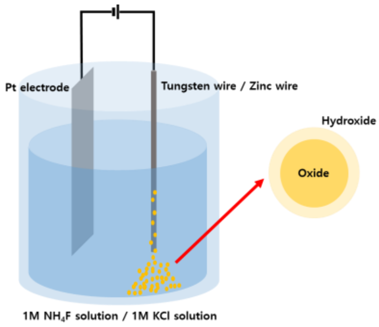

Fig. 1. Anodizing oxidation method for synthesizing nanoparticle

Material properties of anodized nanoparticle were evaluated through SEM and XRD. The size of synthesized nanoparticles are between 50 and 300 nm. According to XRD pattern of Fig. 3, anodized nanoparticles are composed of oxide and hydroxide.

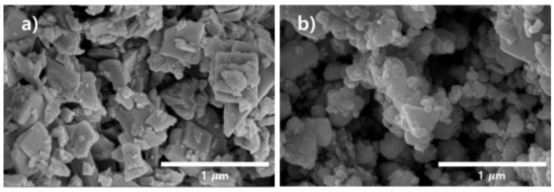

Fig. 2. SEM image of anodized tungsten nanoparticle (a) and anodized zinc nanoparticle (b)

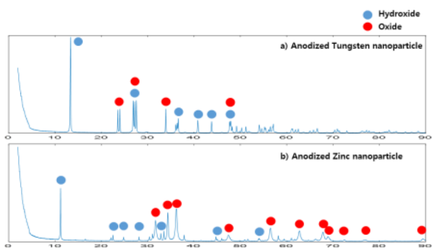

Fig. 3. XRD pattern of anodized tungsten nanoparticle (a) and anodized zinc nanoparticle (b)

2.2 High Energy Ball Milling

High energy ball milling is a ball-milling process in which powder mixture placed in ball-milling is exposed to high energy collisions in the bowl. This method can produce compound nanoparticles by using mechanical reaction and cracking, as shown in Fig 4.

Using planetary ball milling method anodized tungsten nanoparticles and anodized zinc nanoparticles were synthesized into ZnWO4 nanoparticle. A stoichiometric mixture of anodized nanoparticles in a 1:1 molar ratio was subjected to 1h, 3h, 5h of 650 rpm planetary ball milling to use 5 mm SUS304 ball and SUS304 bowl.

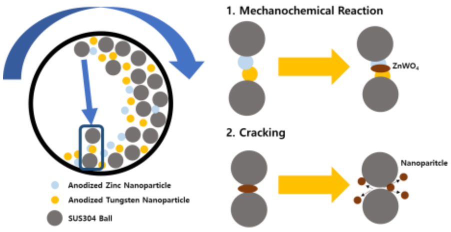

Fig. 4. Mechanism of mechanochemical reaction and cracking via high energy ball milling

2.3 Result

The photoluminescence intensity of $ZnWO_4$, created under the conditions of 1h, 3h, and 5h of 650 rpm planetary ball milling, was measured in the 325 nm UV irradiation. As can be seen in Fig. 5, $ZnWO_4$, made under conditions of 1 h, 650 rpm, did little luminescence property. $ZnWO_4$, made in 5 h, 650 rpm conditions, had a photoluminescence intensity of 10 times better than ball milling for 3 h.

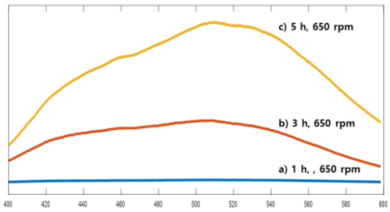

Fig. 5. Photoluminescence intensity of $ZnWO_4$ synthesized in conditions of 650 rpm planetary ball milling for 1h (a), 3h (b), 5h (c)

As shown in Fig.6, WO3 has been detected because anodized nanoparticles do not fully respond if the time of ball milling is smalled than 5 hours. As SEM image of Fig. 7, $ZnWO_4$ is formed from 50 to 200 nm.

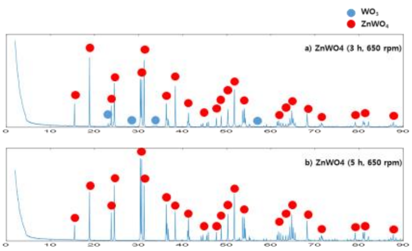

Fig. 6. XRD pattern of $ZnWO_4$ synthesized in conditions of 650 rpm planetary ball milling for 3h (a), 5h (b)

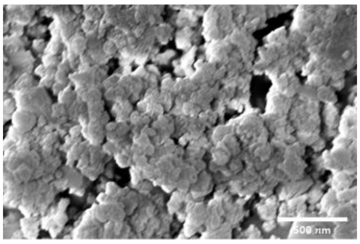

Fig. 7. SEM image of $ZnWO_4$ synthesized in condition of 650 rpm planetary ball milling for 5h

3. Conclusions

High energy ball milling with anodized nanoparticle are cheap and mass producing technologies. As shown in Fig. 8, photoluminescence of zinc tungstate is good under 50 kV_p X-ray irradiation conditions. These results should be compared with other commercialized scintillating materials for evaluating the quality of synthesized zinc tungstate.

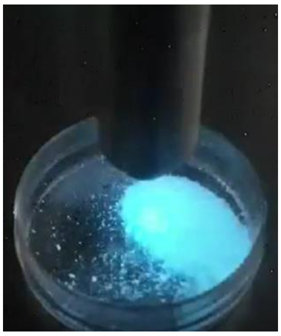

Fig. 8. Image of $ZnWO_4$ (650 rpm planetary ball milling for 5h) under 50 kV_p X-ray tube

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