Synthesis of Lu_2O_3 - Bi_2O_3 Nanoparticles

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This paper deals with a synthesis of a new ionising radiation attenuation composite material from Lu_2O_3 - Bi_2O_3 nanoparticles structure, that has never been described yet. The paper describes the preparation of Lu_2O_3 - Bi_2O_3 nano- and microparticles by three methods: a self-combustion synthesis (types of fuel used were urea, citric acid, glycine, and tartaric acid), a solid-state method (processing by annealing under the melting point of Bi_2O_3) and a coprecipitation method (precipitation of ammonia of various concentrations). Polymer solution was prepared from Lu_2O_3 - Bi_2O_3 nanoparticles, that were dissolved in ethanol and mixed with Polyvinyl Butyral. PVB - Lu_2O_3 - Bi_2O_3 solution was homogenised by ultrasound. Afterwards, nanofibers were processed by an electrospinning method from PVB - Lu_2O_3 - Bi_2O_3 polymer solution. All the products were examined and characterised by Scanning electron microscopy and X-Ray diffraction. PVB - Lu_2O_3 - Bi_2O_3 nanofibers were characterised and their X-Ray attenuation effect was tested. This paper proceeds from one of the author's bachelor thesis ¹.

Keywords: Metal oxides nanoparticles, nanofibers, X-Ray, lead-free materials, PVB.

1 Introduction

In recent years, there is a trend in searching new possibilities of applications of composite materials in the field of radiation protection. People use ionising radiation in many ways, for example in medicine, power engineering, security, etc. Ionising radiation attenuation materials which are used nowadays have many negative effects on user's health and better alternatives of this kind of protection should be explored. Following up on a previous research, the aim of the work is to develop a lead-free X-Ray protection material using Lu_2O_3 - Bi_2O_3 nanoparticles at the instigation of SÚJCHBO (Czech National Institute for Nuclear, Chemical and Biological Protection). This material should be breathable, flexible, lightweight, non-toxic, effective and is meant to be a part of the new 'smart uniform', that will be used by Czech soldiers in dangerous environments. It is possible that this material could serve in many different fields of human activities. Synthesis of Lu_2O_3 - Bi_2O_3 nanoparticles has never been described yet, so, for the research, synthesis methods of similar compounds (Fe-BiO_3 , ferrites, perovskites) were found [2, 3]. After thorough research, three methods were chosen for the preparation of Lu_2O_3 - Bi_2O_3 nano- and microparticles.

Solid-state top-down method:

This method uses an easy top-down principle. Preparation of oxidic microparticles and their subsequent

mechanical modification was used [4]. In the mentioned paper, a preparation of $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Lu}_2\text{O}_3)_x$ ($x = 0.1, 0.2, 0.3, 0.4, 0.5$) compounds is described. $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Lu}_2\text{O}_3)_x$ microparticles were produced as a non-toxic yellow pigment and characterised by TGA and DTA analysis (Graph 1). DTA analysis showed, that 735 °C is the minimal temperature of an endothermic effect and Lu_2O_3 dissolves in Bi_2O_3 structure. 735 °C is the temperature at which Bi_2O_3 crystallises in delta modification ⁵. Delta- Bi_2O_3 has the lowest density of all its modifications, so there is probably the greatest chance, that Lu^{3+} ions would enter the crystal structure of Bi_2O_3 . This process is the basis of the solid-state method of oxidic nanoparticles synthesis.

Self-combustion synthesis:

Self-combustion synthesis, a.k.a. self-propagating high temperature synthesis is a fast and easy way to prepare oxidic nanoparticles. The right choice of homogenous oxidation reagent and organic fuel is crucial for this method. Glycine, citric acid, tartaric acid and urea are some examples of organic fuels that can be used. Each of those has its own properties that can influence the course of the self-combustion reaction (speed, activation energy, etc.) [6].

Coprecipitation:

Coprecipitation is an easy and reproducible method intended for preparation of metal nanoparticles and metal oxides nanoparticles. This method consists of few basic steps: chemical reaction, nucleation,

growing and agglomeration. Supersaturated solution is essential to start the precipitation mechanism [7].

Graph 1 TGA and DTA analysis of $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Lu}_2\text{O}_3)_x$ ($x = 0.1, 0.2, 0.3, 0.4, 0.5$) [3]

2 Experimental

Solid-state top-down method:

For this method, Lu_2O_3 and Bi_2O_3 oxides were mixed in stoichiometric amount and then were homogenized in an agate mortar. Afterwards, the homogenized mixture was gradually calcinated in an electric furnace up to the maximum temperature 770 °C within 2 hours. The product was homogenized in agate mortar and placed into the electric furnace up to the maximum temperature 770 °C within 2 hours again. The final product was homogenized again and had a form of fine yellow powder (Fig. 1).

Fig. 1 Final product of solid-state method

Self-combustion synthesis:

Self-combustion synthesis methodology proceeds from previous research [8]. This methodology was not exactly suitable for these metal oxides reactions, so it had to be modified – the temperature of the final heating process was increased to 800 °C. For the self-combustion synthesis experiments, metal oxides were transferred to precursors in form of nitrates, $\text{Bi}(\text{NO}_3)_3$ and $\text{Lu}(\text{NO}_3)_3$ by mixing starting oxides with nitric acid and heating the mixture up. For this kind of reactions, different fuels were chosen – glycine, citric acid, urea and tartaric acid. Nitrate precursors were mixed with fuel in stoichiometric amounts and then heated up to obtain gel consistent solution. Final solution reacted by self-combustion mechanism that was initiated in several ways – by heating it in a microwave oven, heating it on an electric plate and heating it by a

focused sun beam. In this phase, two kinds of product appeared – black and yellow powder. To homogenise the final product, the mixture was processed in agate mortar and heated up to 800 °C in an electric furnace. Again, the product in form of fine yellow powder appeared. It was observed at this point, that there are little differences in colour and structure depending on the fuel that was used.

Coprecipitation:

For this method, it was necessary to prepare nitrate precursors first. Nitrate mixture solution was added by drops from burette to a beaker placed on a magnetic agitator containing aqueous solution of ammonium hydroxide NH_4OH . This process led to a white precipitate, that needed to be dried, then it was placed into an electric furnace and heated up to 800 °C. The final product was a fine yellow powder.

PVB - Lu_2O_3 - Bi_2O_3 nanofibers preparation:

Micro- and nanoparticles prepared in previous steps were dissolved in ethanol. To homogenise the particles, the solution was processed by ultrasound (20 kHz / 10 min.). Homogenised solution was then mixed with a certain amount of PVB (depending on required concentration ratio of PVB to nanoparticles), which produced a polymer solution ready for DC electrospinning. Concentration of particles to PVB was 3:1 and 8:1. Polymer solution has been processed by the string DC electrospinning method on the Nanospider machine under following conditions: electrode distance: 16 cm, supply voltage: 30 kV and temperature: 22.8 °C.

3 Results and discussion

All of the synthesised products were analysed by SEM, EDX (Scanning electron microscope Zeiss Ultra Plus with full microanalytic set EDS + WDS + EBSD), Technical university of Liberec) and XRD (X-Ray diffractometer X'Pert PRO, VŠCHT Prague). **Solid-state method** is very simple and effective, so it would be desirable for this method to provide a pure and homogenous product. SEM and XRD analysis (VŠCHT Prague) showed, that the solid-state method leads to a polydistributed and non-homogenous product. Due to XRD analysis, stoichiometric structure of this product is $\text{Lu}_{0.67}\text{Bi}_{1.33}\text{O}_3$, so we know that part of Lu_2O_3 oxide stays out of reaction. It is probably impossible to get Lu_2O_3 - Bi_2O_3 compound with any other stoichiometry by this method.

As it is possible to see on Fig. 2, nanoparticles prepared by the solid-state method form microparticles. These bigger units are very hard to shatter, so this product cannot be homogenised.

Most of the fuels used for **self-combustion synthesis** react too quickly. The most effective fuel

for the self-combustion synthesis of Lu_2O_3 - Bi_2O_3 nanoparticles is tartaric acid. Nanoparticles prepared with tartaric acid are homogenous (see Fig. 3) and according to an XRD analysis, these nanoparticles are very pure. Product crystallises in cubic system with lattice parameter $A = 5.41 \text{ \AA}$. Most of the particles have a size of 50 – 200 nm. Nanoparticles prepared by this method form bigger units, but it is obvious that it would be easy to shatter them, for example with ultrasound.

Coprecipitation reaction provided the most unified product – spherical nanoparticles in range of 50 – 100 nm (Fig. 4). XRD analysis was not able to specify lattice structure of this product, the closest crystal structure is cubic compound $\text{Ce}_{0.6}\text{Lu}_{0.4}\text{O}_{1.8}$ with the same lattice parameter $A \approx 5.4 \text{ \AA}$. To obtain as homogenous product as possible, coprecipitation aperture was enhanced with ultrasound, so that the particles could be shattered shortly after their formation. Quantitative analysis showed, that as the only one of the three methods, coprecipitation provided demanded product with stoichiometric amount of Lu_2O_3 : Bi_2O_3 in a ratio of 1:1.

Fig. 2 SEM of solid-state Lu_2O_3 - Bi_2O_3 nanoparticles at 25 kx

Fig. 3 SEM of self-combustion synthesis Lu_2O_3 - Bi_2O_3 nanoparticles at 25 kx

Fig. 4 SEM of coprecipitation Lu_2O_3 - Bi_2O_3 nanoparticles at 25 kx

All the products were processed to make up nanofibrillar textile. Results show that this textile is non-toxic, breathable and very flexible. Depending on the concentration of particles it has its specific colour (Fig. 5).

Fig. 5 Processed nanofibre textile with concentration of particles to PVB 8:1

Fig. 6 SEM images of prepared Lu_2O_3 - Bi_2O_3 textile (self-combustion synthesis method nanoparticles), 5 $\times$

Figure 6 shows the way of implementation of oxidic nano- and microparticles prepared by the solid-state method. The image was taken by scanning electron microscopy. The left image is provided by secondary electrons and the right image is provided by back scattered electrons. SEM images of the structure were taken in topographical contrast using secondary

electron detector.[8]

The prepared textile is very lightweight and could be comfortable to wear. The most important property of this textile is the radiation attenuation effect. This was tested on one of the potential workplaces – X-Ray examination in a hospital (Fig. 7).

Fig. 7 X-Ray image of radiation attenuation effect of prepared Lu_2O_3 - Bi_2O_3 textile

On Fig. 7, a radiation attenuation effect of Lu_2O_3 - Bi_2O_3 is shown. Two polymer solutions of different concentrations of the coprecipitation particles were prepared. After processing these solutions by the

electrospinning method, two types of nanofibrillar textile were made. The textile was cut into pieces and put together in various numbers of layers to see how the attenuation effect would intensify. To find out

which concentration ratio of particles to PVB could be adequate for maximum attenuation effect, nanofibillar textile of concentration 19:1 ratio of Bi_2O_3 nanoparticles to PVB was prepared. As seen on Fig. 8, five

layers of this textile are able to attenuate around 75 % of radiation.

Fig. 8 X-Ray image of radiation attenuation effect of prepared Bi_2O_3 textile

4 Conclusion

All the examined methods of producing Lu_2O_3 - Bi_2O_3 nanoparticles are suitable for a synthesis of oxidic nanoparticles. Solid state method provides heterogeneous particles of the size in range 100 nm – 3 μm and this method seems to be the most effective. On the other hand, solid-state method leads to a polydistributed and non-homogenous product with stoichiometry $\text{Lu}_{0.67}\text{Bi}_{1.33}\text{O}_3$, so we know that part of Lu_2O_3 oxide stays out of reaction. The most effective fuel for the self-combustion synthesis of Lu_2O_3 - Bi_2O_3 nanoparticles is tartaric acid. This method leads to nanoparticles with stoichiometric amount of Lu_2O_3 : Bi_2O_3 in a ratio of 1:1. Nanoparticles prepared with tartaric acid are homogenous and easy to shatter by ultrasound. Coprecipitation reaction provided the most homogenous product – spherical nanoparticles in range of 50 – 100 nm with stoichiometric amount of Lu_2O_3 : Bi_2O_3 in a ratio of 1:1. The particles of size 50 – 200 nm in PVB solution are very suitable for electrospinning processing. When incorporated into the nanofibers, these nanoparticles are able to effectively attenuate X-Ray.

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