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To cite this article: V Jokanovic *et al* 2008 *J. Phys.: Conf. Ser.* **100** 012010

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Design of Li phosphorous doped bronzes obtained by using spray pyrolysis

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Abstract:

The ultrasonic spray pyrolysis technique has been, during last three decades, one of the major techniques of synthesis a wide variety of materials. One of the most important among the ionic conductors is lithium phosphorous doped tungsten bronze.

The main goal of this investigation is producing full or hollow spheres of these bronzes of very narrow distribution. The mean size and size distribution specter of all materials were determined by the SEM analysis. The results were compared with the values obtained from the theoretical model. The assembled results indicate the possibility of a rigorous particle structure designing of all obtained powders.

Key words: lithium phosphorous doped tungsten bronzes, spray pyrolysis, structure design and sub-design

1. Introduction:

Ultrasonic spray pyrolysis - USP method provides the ability to control and maintain uniform chemical and phase composition of the final powder products and simultaneously to produce submicron and micron size nanostructured dense or hollow particles. The numerous attempts to modeling process of atomization and conversion of droplets in particle form have been made. They show very different approaches not only to the processes of generation droplets during atomization process as one of the most important steps of the USP, but also to the process of precipitation and final consolidation of droplets in particle form.

Among them one of the most promising is our approach, founded to the theory of the break-up capillary wave, forming at the surface of a liquid column of precursor as a consequence of applied ultrasonic field. As it is shown in numerous previous investigations which include various ceramic systems, like alumina, silica, mullite, cordierite, anatase, calciumhydroxyapatite, yttriumsilicate, gadoliniumsilicate, pseudowollastonite, yttriumaluminate, phosphorous doped bronzes, it is clear that this approach in difference to the all others show better opportunities to the understanding at the first place of the atomization process, as the process which essentially influences to the further nanostructure designing of the powders. The obtained data from the experimental investigations of these materials obtained by USP and by the theoretical model estimations have been in full agreement, frequently.

This paper elaborates the application of the USP to production of Li phosphorous doped tungsten bronzes-LPTB. From the previous explanation it is clear that this method is applied for production of LPTB, from two main reasons. Firstly, the reaction method gives a product with well-controlled mean particle size, and consistency in particle design. Secondly, the attainable consistency in the characteristics of the reaction product obtained permits the testing of a selected above theoretical model [1-3] developed for determination of the particle size at particle level.

Therefore by designing of the periodical physical field we show how it is able to access to the genesis of a particle as well as to the structural and substructural characteristics of the synthesized powders.

2. Experimental

The LPTB is prepared from two steps: synthesis of $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 29\text{H}_2\text{O}$ and ionic exchange H^+ in hetero poly acid with Li^+ ions. NaWO_4 is used as a precursor of W and H_3PO_4 as a precursor for P. Previously, H_3PO_4 is mixed by HCl. Ether and distilled water is added additionally. In a heavier phase, which was contained form the water saturated by ether, the hetero polyacid of $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 29\text{H}_2\text{O}$ was extracted. $\text{LiHPW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ (LHPW) is obtained by reaction of ionic exchange at 80°C between H^+ ions in hetero polyacid and Li^+ ions in LiCl . Hence, the LHPW diluted in distilled water is used, as a precursor of LPTB for ultrasonic spray pyrolysis. Finally, the solution was pyrolysed under following conditions: the frequency of ultrasonic atomizer was 1.7 MHz, working temperature in the tabular furnace was 1000°C and the carrier gas –air- flow rate was 0.011 m/s. Obtained particles were then very collected in a glass vessel.

The morphology, size distribution, the mean size of MPTB particles and their substructure were determined by using scanning electron microscopy-SEM (JOEL:JKSM-5300).

3. Theoretical model of secondary particle structure design

Force frequency of the ultrasound oscillator induces equivalent waves in the given liquid column, in direction perpendicular to direction of disturbance (transversal waves) and in direction parallel to direction disturbance (longitudinal waves). In general, formed standing waves are ellipsoidal, basically determined by the relationship between the damping factors for transversal and longitudinal waves, depending very much on thickness of the sprayed solution liquid column.

Beside that, size distribution of the aerosol droplets is influenced by physical characteristics of that solution (surface tension and viscosity), and geometry of the vessel containing the solution. For sufficiently thin liquid columns, damping factors of transversal and longitudinal waves differ only negligibly, which is why so obtained standing waves are spherical. In the general case of the ellipsoidal form, standing waves can be represented in the form of Laplace equation, which solution gives the set of radius dimensions equivalent to given wave-damping factor [1-3]:

$$d = \frac{1}{\pi} \left(\frac{2\sigma\pi}{\rho f^2} \right)^{\frac{1}{3}} [l(l-1)(l+2)]^{\frac{1}{3}}, \quad (1)$$

where d is droplet radius, σ surface tension of the liquid, ρ density of the precursor solution, f frequency of ultrasonic atomizer and l is integer, which can only take the values $l \geq 2$.

Based on the values of mean size droplets diameter, the mean powder particle diameter can be calculated from the following equation [1-3]:

$$d_p = d_n \left(\frac{c_{pr} M_p}{\rho_p M_{pr}} \right)^{\frac{1}{3}} \quad (2)$$

The particle size distribution can be estimated by equation [1-3]:

$$I_1 : I_2 : \dots : I_N = \frac{1}{\Delta f_1} : \frac{1}{\Delta f_2} : \dots : \frac{1}{\Delta f_n} \quad (3)$$

where I_1, I_2, I_N are the intensities (the participation) of the appearance of corresponding discrete values of the particle diameters in a given spectra, or the corresponding numerical values defining the appearance frequencies of a given discrete values, while $\Delta f_1, \Delta f_2, \dots, \Delta f_n$ are displacements of the real frequencies from the forced frequency of the ultrasonic oscillator caused by damping factor of the precursor liquid column. The relative ratios of intensities (the frequency of a particular diameter) when normalized gives the basic relationship for calculation of the absolute value of the intensity [1-3]:

$$I_1 + I_2 + \dots + I_N = 1 \quad (4)$$

4. Results and discussion

The obtained LPTB particles by ultrasonic spray pyrolysis method at a level of its distribution (by statistical treatment measured experimental data obtained over electron microscopy) has been investigated (Fig.1).

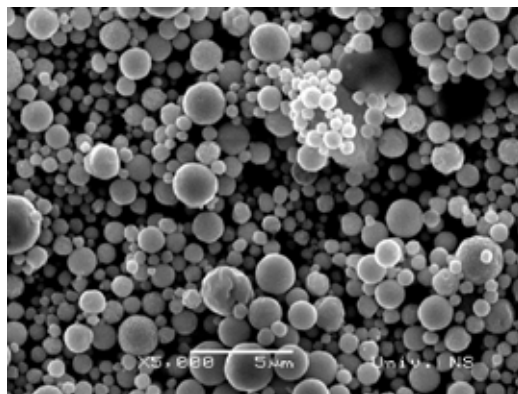


Figure1: Typical distribution of particle size diameters of MPTB particles

By measurements of diameters of around 200 LPTB particles, the mean diameter of particles, its participation and discrete values of each fraction contained inside of the whole specter of distribution were determined. From these data, it has been found that the mean diameter of the particles was $0.97 \mu\text{m}$, range of distribution was $0.38 \mu\text{m} - 2.4 \mu\text{m}$. Most of them belong to the range $0.38 \mu\text{m} - 1.73 \mu\text{m}$ (about 93 % particles).

In order to determine interrelation and coincidence between the theoretical model, defining discrete values in the distribution spectra with its population balance (balance for each value contained in that spectrum, by using eq.2-4) for the lithium phosphorous doped tungsten bronzes-LPTB particles and experimentally determined values for the same particles were analyzed, as it is presented in Tab 1.

Table 1: Experimentally and theoretically determined diameter values of LPTB (d_e i d_t) and their population balances (I_e and I_t):

$d_e, \mu\text{m}$	0.38	0.48	0.58	0.67	0.96	1.06	1.25	1.35	1.73	2.02	2.4
I_e	0.05	0.07	0.13	0.16	0.21	0.1	0.06	0.09	0.06	0.04	0.03
$d_t, \mu\text{m}$	0.4	0.62	0.79	1.15	1.34	1.53	1.78				
I_t	0.19	0.26	0.14	0.12	0.1	0.1	0.09				

The values of the mean diameter (0.93 μm , obtained by using eq.1), and the range of diameter distribution of LPTB particles (0.4-1.78) has been estimated also, by this theoretical model of break-up capillary waves [1-3].

It is evident from these values that the experimental and theoretical mean diameter size and distribution size data were in good agreement, showing that this model can be used for prediction of particle size distribution for this system.

All particles show very high sphericity. Prevailing mechanism of their precipitation is volume precipitation even for particles with average size diameter. Large particles were also dominantly precipitated by volume precipitation mechanism, while only some largest among them are precipitated partially by surface precipitation mechanism.

Conclusion

In this paper the synthesis of precisely tailored nanostructured LPTB particles by ultrasonic spray pyrolysis is described.

Experimental data obtained by statistical treatment of measured data of particle size and distribution by using electron microscopy method and data obtained over application model of break-up capillary waves has shown that they were in mutual satisfied agreement.

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Acknowledgements: This work is supported by Serbian Ministry of Science