SCS-assisted preparation of magnetically soft Li and LiZnMn ferrite nanopowders with enhanced bioavailability and bioactivity suitable for use in food technology

K D Martinson¹, A D Beliaeva², G G Nianikova² and I B Panteleev²

¹Ioffe Institute, 26 Politekhnicheskaya street, Saint Petersburg, 194021, Russia
²Saint-Petersburg State Institute of Technology, 26 Moskovsky prospect, Saint Petersburg, 190013, Russia

E-mail: martinsonkirill@mail.ru

Abstract. This article provides information about the bactericidal performances of lithium ferrites nanopowders obtained via heat-treatment of amorphous products of solution combustion approach. XRD, EDX, SEM, and VSM were used to investigate morphology features, structural and magnetic parameters. The inhibition zone test with Escherichia coli, Bacillus cereus, and Staphylococcus citreus as the bacterial source was used to investigate the antibacterial performances. It was found that pure single-phase Li and LiZnMn ferrites with an average size of particles − 35 and 44 nm, respectively, are formed under the SCS-assisted method. The investigation of magnetic behavior indicates the magnetically soft nature of the obtained powders with moderate coercivity force \( H_c \) values equal to 116.1 Oe for Li-ferrite and 54.3 Oe for LiZnMn-ferrite. When studying the antibacterial activity, the inhibition zones were measured as 16-17 mm for \( E. \text{ coli} \), 15-25 mm in the case of \( B. \text{ cereus} \), and 13-16 mm for \( S. \text{ citreus} \), and the findings is the synthesized compositions are suitable for use in the agricultural sector.

1. Introduction
Pathogens, which cause a wide number of diseases, especially, infectious diseases, are currently of great research interest because of the serious threat they pose to humanity and world economy [1]. Although many of the known diseases have disappeared for one reason or another, controlling infectious diseases is a laborious and difficult task largely due to their resistance to modern medicine, which can easily be associated with uncontrolled and inappropriate use of antibiotics [2-3]. The declining efficacy of existing generations of antibiotics mean that various pathogens continue to cause significant harm to humanity [4]. The prevailing method of suppressing the spread of infectious diseases is using chemical disinfectants, antibiotics, and other types of antibacterial materials that can effectively suppress microorganisms [5-6]. However, chemical disinfection is expensive, ineffective, and time-consuming, while antibiotics due to the resistance problem described above also have limitations in their repeated use, which ultimately reduces their antibacterial activity and ability to maintain their sterilizing effect [7-9]. Therefore, one of the most ongoing areas of research is the investigation for new types of functional materials with high antibacterial performances and possibility for further multiple use [10].

In recent decades, many different types of nanomaterials with antibacterial activity have appeared, among which there are nanostructures based on silver, gold, zinc, nickel, titanium, magnesium, and
many others [11-12]. Particular interest is shown in magnetic nanoparticles, which have many advantages, such as high specific surface area, good mass transfer rates, possibility of magnetic reduction, and surface modification [13]. Spinel ferrite (MFe2O4) and rare-earth orthoferrites (RFeO3), which have found wide application as catalysts [14] and photocatalysts [15], materials for producing sensors and detectors [16], magnetic fluids [17], radioelectronic devices [18], antibacterial materials [19], and in food technology [20] stand out among magnetic materials. Among the wide variety of spinel ferrites, lithium ferrites (Li-ferrites) doped with various metals are the most interesting compounds from a scientific and industrial point of view due to their unique functional properties [21].

In the current study, Li- and LiZnMn-ferrite composite nanoparticles were formed by SCS-method using the glycine’s dint. The bactericidal activity of the synthesized samples was determined against three test cultures: *Escherichia coli* (non-spore-forming gram-negative), *Bacillus cereus* (spore-forming gram-positive), and *Staphylococcus citreus* (non-spore-forming gram-positive). To conclude, the prospects of further practical use of this material type and possible ways of the development of the proposed technology for producing Li-ferrites, having a high degree of bactericidal activity, are shown.

### 2. Materials and methods

Method of the glycine-nitrate combustion at a stoichiometric ratio of glycine to nitrogen in nitrates was used to prepare two compositions: Li0.5Fe2.5O4 and Li0.45Zn0.05Mn0.06Fe2.43O4 – nanostructured Li-ferrites. The choice of the glycine-nitrate ratio was based on our previous work [21], where it was shown that at the given ratio the Li-ferrites with the highest degree of crystallinity are formed. The reagents, chosen as the initial components for the synthesis, are mentioned further: manganese nitrate 6-aqueous (chemically pure, Neva-Reaktiv), lithium nitrate 3-aqueous (chemically pure, Neva-Reaktiv), zinc nitrate 6-aqueous (chemically pure, Neva-Reaktiv), iron nitrate 9-aqueous (chemically pure, Neva-Reaktiv), aminoacetic acid (glycine) (chemically pure, Neva-Reaktiv), and distilled water. All the initial reagents were dissolved in 50 mL distilled water under a constant mechanical stirring and heating for 2 hours with an addition of small amount of 3M nitric acid. Then the solution thus obtained was heated until the evaporation of most of the water, after which the process of autoignition occurred with the obtaining of final product in a brown powder form, which formation proceeded according to the reactions 1 and 2 below:

\[
\text{LiNO}_3 + 5\text{Fe(NO}_3)_3 + 40/9\text{C}_2\text{H}_5\text{NO}_2 = 2\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4 + 80/9\text{CO}_2\uparrow + 56/9\text{N}_2\uparrow + 316/9\text{H}_2\text{O}\uparrow \quad (1)
\]

\[
0.45\text{LiNO}_3 + 0.05\text{Zn(NO}_3)_2 + 0.06\text{Mn(NO}_3)_2 + 2.43\text{Fe(NO}_3)_3 + 40/9\text{C}_2\text{H}_5\text{NO}_2 = \\
= \text{Li}_{0.45}\text{Zn}_{0.05}\text{Mn}_{0.06}\text{Fe}_{2.43}\text{O}_4 + 80/9\text{CO}_2\uparrow + 56/9\text{N}_2\uparrow + 316/9\text{H}_2\text{O}\uparrow \quad (2)
\]

The morphology as well as the chemical composition of the obtained samples were studied using scanning electron microscopy, energy dispersive X-ray and atomic absorption spectroscopy on a scanning electron microscope Vega 3 SBH (Tescan) equipped with an X-ray spectral microanalysis attachment (x-act, Oxford INCA), and an atomic absorption spectrometer – AA-7000 (Shimadzu). X-ray phase and X-ray structural analysis was performed using an X-ray diffractometer with CuKα emission (0.15405 nm) – Rigaku Smart Lab 3. The crystallite size’s distribution was determined using the fundamental parameters method in SmartLab Studio II software package. The construction of magnetic hysteresis loops was performed at a room temperature in fields ranging to 6000 Oe by a vibration magnetometer – Lake Shore 7410.

The bactericidal activity of the obtained samples was determined against three test cultures: *Escherichia coli* (non-spore-forming gram-negative), *Bacillus cereus* (spore-forming gram-positive),
and *Staphylococcus citreus* (non-spore-forming gram-positive). Agarized nutrient medium, Meat Enzyme Hydrolysate, was poured into Petri dishes. Inoculum was prepared from a daily bacterial culture in an isotonic solution (0.85% NaCl), according to a turbidity standard of 0.5 McFarland, brought to the surface of a nutrient medium in the amount of 100 μL per each cup and distributed using a spatula. Wells were then made in the thickness of the agarized medium using a sterile cork drill. The nanoparticles of the studied ferrites were pre-suspended in dimethyl sulfoxide (DMSO) at a concentration of 20 mg/mL, 50 μL per each well, were introduced into the wells. DMSO was used as a control sample. The cultures were incubated at 28 ℃ for 24 h. The obtained results were evaluated by the diameter of the inhibition zone of the growth of the studied cultures.

3. Results and discussion

The element analysis of synthesized as-burn products was examined by energy-dispersive X-ray and atomic absorption spectroscopy. Looking through the obtained results, the 1st sample corresponds by its chemical composition to a simple Li-ferrite \( \text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4 \), whereas the chemical composition of the 2nd sample corresponds to a multicomponent spinel ferrite \( \text{Li}_{0.45}\text{Zn}_{0.05}\text{Mn}_{0.06}\text{Fe}_{2.43}\text{O}_4 \). Although lithium is a light element and is capable of volatilizing during combustion, thus introducing an error between the calculated and obtained composition, there is a clear correlation between the combustion temperature of the flame and the amount of lithium lost [22]. Considering this peculiarity, Li-ferrite with a given composition is possible to synthesize using this method (the error of the determination method is vital to be taken into account).

The samples’ (ferrite powders, which were synthesized by the method of the glycine-nitrate combustion) morphology, was obtained using scanning electron microscopy (figure 1). Micrographs show that both of them exhibit a developed and porous structure, which is supposed to be typical for ferrites synthesized using the method of the combustion of the solution at a stoichiometric ratio of fuel to nitrogen in nitrates [23-24]. The porosity of the studied samples can easily be explained by the abundant outgassing process (\( \text{NO}_2 \), \( \text{CO}_2 \), etc.) occurring during the auto-ignition process. Slight differences in the morphology of the obtained compositions are explained by different temperatures of combustion of a flame during the final product formation and are described in detail in previous works [21; 25].

![Figure 1. SEM images of the Li\(_{0.5}\)Fe\(_{2.5}\)O\(_4\) (a-c) and Li\(_{0.45}\)Zn\(_{0.05}\)Mn\(_{0.06}\)Fe\(_{2.43}\)O\(_4\) (d-f) as-burnt nanopowders.](image)

The results of powder X-ray diffractometry of the obtained samples can be seen in figure 2. In concordance with the data presented further, the studied compositions tend to be single-phase Li-ferrites having a high crystallinity degree (96 % for sample 1 and 98 % for sample 2), which was
calculated using the Rietveld method. The average size of crystallites was determined with the help of the Scherrer formula and was 35 nm for the 1st ferrite sample, and 44 nm for the 2nd ferrite sample. Moreover, X-ray diffraction line broadening together with the fundamental parameters’ method were used in studying changes in the obtained samples’ disperse composition.

Figure 2. XRD patterns of the simple Li-ferrite (a) and LiZnMn-ferrite (b) synthesized via method of the solution combustion.

The obtained data display that the average crystallites’ size of calculated with the help of the method of fundamental parameters is in a good agreement with the data, which were found using the Scherrer formula within ± 5 nm. Small variability in the values of unit cell parameters (a = 8.324(4) for sample 1 and a = 8.357(9) for sample 2) is possible to be explained by the presence of zinc and manganese cations in the crystal lattice of the multicomponent Li-ferrite.

Magnetic hysteresis loops of the obtained compositions are shown in the figure 3. All synthesized samples exhibit a magnetically soft character of magnetic behavior, which is reflected in the tiny values of coercivity force, which is 116.1 Oe for the 1st ferrite sample and 54.3 Oe for the 2nd ferrite sample; the residual magnetization and saturation magnetization values are significantly different for the synthesized ferrites 1 and 2 are 56.3 and 123.1 emu/g for $M_s$, 15.4 and 8.4 for $M_r$, respectively. The difference in magnetic parameters is possible to be explained by the presence of additional zinc and manganese cations in the 2nd sample, which significantly changes the Li-ferrites’ functional properties [26, 27]. The presence of the mentioned magnetic characteristics in the studied samples makes it possible to conclude they are tending to be promising magnetically controlled antibacterial materials, which have become important industrial research targets in the past few years due to the possibility of significantly reducing the cost of their application [28].

The synthesized ferrites’ antibacterial activity was determined against three test cultures: *Escherichia coli* (non-spore-forming gram-negative), *Bacillus cereus* (spore-forming gram-positive), and *Staphylococcus citreus* (non-spore-forming gram-positive). Figure 4 presents the results of the study of the 1st and 2nd obtained samples, according to which both compositions exhibit the moderate bactericidal activity towards *Escherichia coli*, *Bacillus cereus*, and *Staphylococcus citreus*. In accordance with the obtained data towards *E. coli*, samples 1 and 2 show approximately the same inhibition zone, which was 16 mm and 17 nm, respectively. The most significant differences in the antibacterial activity of the obtained compositions were found when studying *B. cereus*, where the multicomponent ferrite (sample 2) demonstrated an inhibition zone of 25 mm, which is 1.8 times greater than that of the sample 1 (ordinary Li-ferrite), where the zone of inhibition was measured as 15 mm.
When mentioning *S. citreus*, the measured inhibition zone values are similar for both samples and slightly higher for the multicomponent composition (13 mm for the 1st sample and 16 mm for the 2nd).

**Figure 3.** Hysteresis loops of Li-ferrite powders prepared via solution combustion approach.

Furthermore, a comparative antibacterial activity analysis of similar systems (obtained by other chemical methods) towards some test cultures was implemented (table 1). The data indicate that the synthesized compositions exhibit antibacterial properties at the level of well-studied oxide ferrite systems, and in some cases even surpass them.

**Figure 4.** Inhibition zone images of Li-ferrites.

Although Zn-, Ni-, Co-, Mn-, and Cu-ferrites are mostly used as antibacterial materials, the table below demonstrates that Li-ferrites, including multicomponent ones, can successfully inhibit the growth of various cultures. Co- and Ni-ferrites have shown their low efficiency towards *E. coli* [30, 31], whereas both samples of Li-ferrites successfully inhibited the growth of this particular culture. The only sample that has shown a higher result than in the current study, was copper-doped Co-ferrite [29], which is primarily owing to the higher concentration of it, which was introduced into the culture medium. Thus, the SCS-method is considered to be promising for the obtaining of Li-ferrites’, which can further be used as antibacterial materials.
Table 1. Comparison of inhibition zone of ferrites in relation to different test cultures

| Test culture                  | Preparation’s concentration, mg/mL | Amount of preparation to be applied per well, μL | Diameter of the inhibition zone, mm | Link |
|-------------------------------|-----------------------------------|-------------------------------------------------|------------------------------------|------|
| Escherichia coli              |                                    |                                                 | 22-34                              |      |
| Staphylococcus aureus         | 5                                  | 100                                             | 16-29                              | [29] |
| Escherichia coli              |                                    |                                                 | N/A                                |      |
| Pseudomonas aeruginosa        | 20                                 | 50                                              | 12                                 | [30] |
| Klebsiella pneumoniae         |                                    |                                                 | 15                                 |      |
| Escherichia coli              |                                    |                                                 | N/A                                |      |
| Pseudomonas aeruginosa        | 60                                 | 50                                              | 17                                 | [31] |
| Staphylococcus aureus         |                                    |                                                 | 1.2                                |      |
| Escherichia coli              | 10-160                             | 50                                              | 14-31                              | [32] |
| Bacillus subtilis             |                                    |                                                 | 11-28                              |      |
| Escherichia coli              |                                    |                                                 | 16-17                              |      |
| Bacillus cereus               | 20                                 | 50                                              | 15-25                              |      |
| Staphylococcus citreus        |                                    |                                                 | 13-16                              | current study |

Note: N/A – not studied

4. Conclusion

In summary, nanostructured samples of simple Li-ferrite and multicomponent LiZnMn-ferrite were synthesized using the SCS-method using glycine (fuel) with a stoichiometric ratio of glycine to nitrogen in nitrates. Both morphological and structural parameters as well as magnetic and bactericidal properties were studied and determined for the obtained samples. It was stated that the studied compositions have magnetically soft magnetic properties with tiny coercive force values. Besides, the study of Li-ferrites in relation to three different test cultures: *Escherichia coli*, *Bacillus cereus*, and *Staphylococcus citreus* showed that they exhibit a moderate antibacterial activity in all three cases. The conducted research allows to assert that Li-ferrites obtained by the SCS-method are promising antibacterial materials, which can also be produced in large quantities at a low cost due to the prospects of their possible magnetic control.

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