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ELECTROMIGRATION IN LITHIUM-TITANIUM FERRITE CERAMICS SINTERED IN RADIATION-THERMAL MODE

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The study investigates electro-migration in Li–Ti ferrite ceramic samples sintered in radiation-thermal mode. To reveal radiation effects, similar measurements are performed for samples sintered in thermal mode. The effect of the state of grain boundaries and the presence of a low-melting additive on electrical properties of sintered ferrites is studied. It is found that structural rearrangement during radiation-thermal sintering occurs in early sintering stages, including the heating period. Study demonstrates that such behavior associated with radiation-induced intensification of the liquid phase spreading over the array of powder grains. In addition, it was shown that structural transformation may be caused by stimulation of intergranular slippage.

Keywords: electrical resistance, ferrites, sintering, electron beams, grain boundaries, low-melting additive.

Introduction

In terms of ceramic technology, the quality of sintering depends not only on the degree of sample compaction, but also on microstructure parameters, grain boundaries being most critical. Therefore, it is essential to determine the quality of grain boundaries formed in radiation-thermal (RT) sintering mode.In addition, it is supposed that the characteristics of radiation-induced intensification of compaction in the presence of a low-melting additive in early sintering stages (including the non-isothermal stage) differ from those observed in later stages. It can be assumed that these differences may be due to the effect of radiation on liquid-phase processes. To elaborate these ideas, the electrical transfer in Li–Ti ceramic ferrite samples sintered in RT mode was investigated. Similar measurements were performed for samples sintered in thermal (T) mode to reveal the radiation effects.

A universal requirement for the microstructure of ferrites is the maximum material density and equigranularity of its structure [1, 2]. To meet this requirement within economically reasonable annealing times, a number of methods have been developed to stimulate sintering processes: two-stage introduction of components, additional ferrite burdening by the ferrite powder of the same composition, liquid phase, accelerated sintering, the use of ultrasound [1, 3, 4–12].In recent years, the effect of ionizing radiation fluxes has been employed in the production and modification of materials. A fundamental phenomenon of multiple acceleration in the synthesis of multicomponent powder materials [13, 14] and sintering [15–19] in RT mode was discovered. Sintering processes of lithium-titanium ferrites have been most well studied under specific combined action of high temperatures and intense electron fluxes [20, 21]. The patterns of compaction of ferrite compacts were revealed and a multiple increase in the compaction rate of lithium-titanium ferrite samples under RT sintering in RT mode was shown [22, 23].Almost all the studies investigated structural, phase and mechanical properties of the materials produced in this mode, i.e. touched upon such branches of science as physics of sintering and powder metallurgy. The ultimate goal of any ferrite production technology is to achieve a desired level of performance properties. In this case, the main functional characteristics of ferrimagnets are electromagnetic properties. Therefore, controlled formation of the main electromagnetic properties can enhance the development of new technological processes. On the other hand, magnetic reversal processes and electromigration in ferrites relate to their microstructural features.

Therefore, the patterns of changes in electromagnetic properties can be used as a source of information on the nature of the processes occurring in sintering to provide an in-depth interpretation of the RT sintering mechanisms. In [24], the patterns of the formation of magnetic properties (parameters of the hysteresis loop) for ferrites sintered in thermal (T) and radiation-thermal (RT) modes are considered. However, the question about the electrical properties of ferrites sintered in T and PT modes remains open. Methods of studying the electrical conductivity are widely used to investigate the properties of oxide systems, including ferrites [25]. Similar to magnetic properties, electrical conductivity is a structure-sensitive parameter. However, in contrast to magnetic properties, the conductivity (resistance) is more sensitive to point defects and the type of the mixed-valence ion. No doubt, experimental data on electrical conductivity are also of applied interest since conductivity determines the level of eddy-current losses in microwave ferrites.

2. Experimental part

2.1 Materials

The study used powders of lithium-titanium ferrite synthesized from the mechanical mixture of oxides and carbonates containing (wt%): Li_2CO_3 – 11.2; TiO_2 – 18.65; ZnO – 7.6; $MnCO_3$ – 2.74; the rest was Fe_2O_3. Part of the sample was produced with the addition of 10% polyvinyl alcohol solution in the amount of 12 wt. % of the synthesized mixture. All samples were prepared by cold single-action compaction. The compacts were 13 mm in diameter and 2 mm thick.

2.2 Characterization techniques

The compaction mode used in the study was as follows: P = 130 MPa, 1 min holding time of the material under pressure; two sintering modes: RT and T. For RT sintering, the samples were exposed to a pulsed electron beam with energy of (1.5–2.0) MeV using an ILU-6 accelerator. The beam current in the pulse was (0.5–0.9) A, the irradiation pulse duration was 500 μs, the pulse repetition rate was (5–50) Hz, and the heating rate of the samples was 1000 °C/min. The samples were irradiated in a lightweight chamotte box with a wall bottom thickness of 15 mm. On the exposed side, the box was covered with a radiation-transparent protector with a mass thickness of 0.1 $g \cdot cm^{-1}$. The temperature was measured using a control sample placed in close proximity to the sintered samples.

T sintering was carried out in a preheated electric chamber furnace to provide the heating rate comparable to the radiation heating rate. The cell design and temperature control technique were similar to those used for RT sintering. Sintering in both modes was performed in the air. The electrical resistivity of ferrites was measured at a constant current based on a two-electrode scheme using pellet-shaped samples with a deposited near-electrode layer of soft graphite. The measurement temperature changed in the interval from (290–1300) K. The air pressure in the measuring cell did not exceed 19 Pa, and the heating rate was 10 degrees per minute. The electric field applied to the sample attained 10 V/cm.

3. Results and discussion

Figure 1 shows temperature dependences of the electrical resistivity (ρ_v) on the reciprocal temperature of ferrite samples after 30 min sintering at 1273 K (curves *1–3*). Curve *4* describes the resistance of the samples measured during their cooling in the measuring cell and during repeated measurements of ρ_v. Thus, curve *4* shows the resistance of vacuum heat treated samples ($\tau \geq$ 5 min) at 1273 K. The curve is plotted based on the results obtained in measuring ρ_v for all samples, including those unsintered but vacuum heat treated. Vacuum heat treated samples restore their initial resistance after short-term (~5 min) annealing in air at 1273 K. The exception is unsintered samples, which show resistance after heating in air comparable to that of heat sintered samples, that is, the temperature dependence corresponds to curve *2* in Fig. 1.The analysis of ρ_v temperature dependences shows that the resistance of ferrite samples in the low-temperature region (up to 650 K) decreases in the following order: sample sintered in heating mode → sintered in RT mode → heated in vacuum up to 1273 K. In the high-temperature region of (~700 K), the ρ_v approach significantly.

The monotonically decreasing dependencies indicate a complex spectrum of activation energy for charge carriers. In an explicit form, this spectrum can be obtained by differentiating the curves, Fig. 1:

$$E = k\,\frac{d(\lg \rho_V)}{d(1/T)} \tag{1}$$

The results of differentiation are shown in Fig.2. Fig.1 and Fig.2 show the sintering technique in the presence of a low-melting additive affects the specific electrical resistance, but the activation energy spectrum remains unchanged. In case no additive is used, ρ_v similar to the activation energy spectrum does not depend on the sintering technique.

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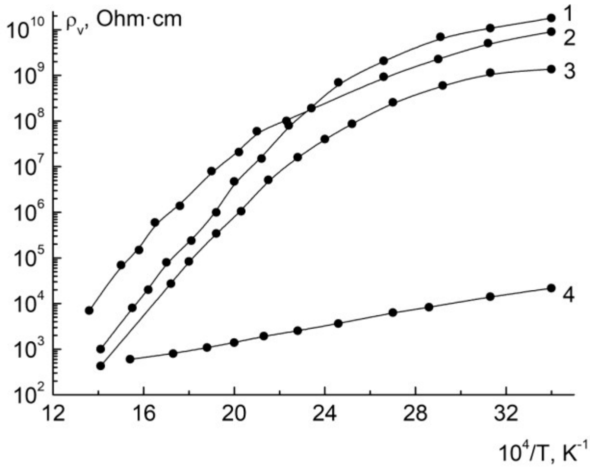
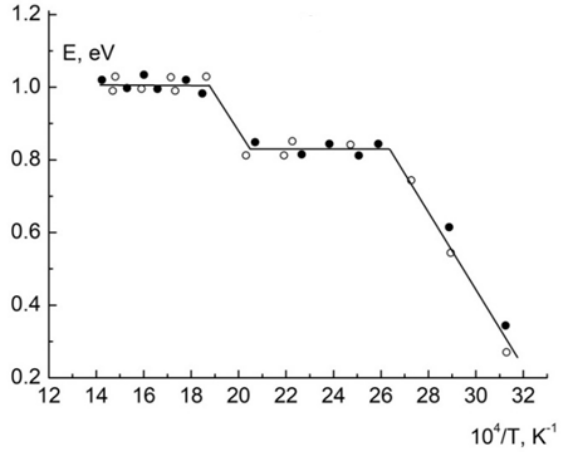


Fig.1. Temperature dependences ρ_v of Li–Ti ferrites. Solid-phase (*1*) and liquid-phase (*2, 3*) in T (*1, 2*) and RT (*3, 4*) sintering at 1237 K for 30 min and after vacuum heating at 1237 K for 10 min (*4*).



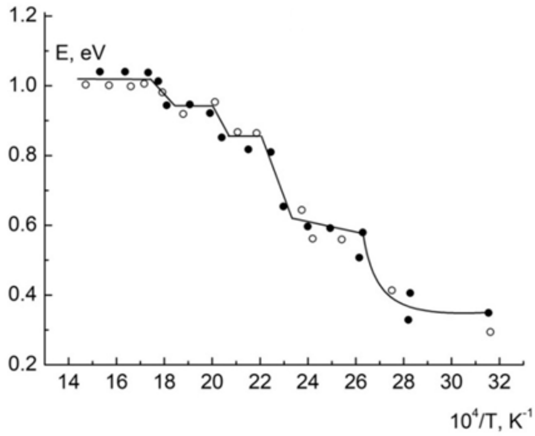


Fig.2. Activation energy spectra for electromigration in Li–Ti ferrites. Solid-phase (*a*) and liquid-phase (*b*) in T (•) and RT (o) sintering modes.

After vacuum heating, ρ_v and electromigration activation energy exhibit the lowest values, irrespective of the sintering technique (Fig.1, curve 4).A short heat treatment time sufficient for changes observed in $\rho_v$indicates that the structural rearrangement of the compacted sample significant for ferrite electrical properties occurs in early stages of sintering, including the heating period. This is confirmed by the volumetric shrinkage dependences of samples presented in Fig. 3.

Fig. 3 clearly shows that the samples are compacted by the start of isothermal sintering, and the degree of compaction in RT sintering mode is higher. A short heating period required for gas exchange with the atmosphere indicates redox reactions occurring in the surface layers of the sample structural elements. To interpret the results obtained, we consider the model of grains and inter layers and the hopping mechanism of electromigration with the participation of Fe^{2+} ions used for polycrystalline ferrites. In this model, the compacted sample is considered as a set of low-resistance ferrite particles separated by high-resistance interlayers. In the initial state, the compacted sample exhibits an undeveloped network of contacts and contains insignificant amount of Bi_2O_3 particles. The surfaces of powder ferrite grains are oxidized, therefore they show high resistance due to the minimum content of Fe^{2+} ions. Electromigration occurs through a hopping mechanism with the participation of mixed-valence ions (Fe^{2+}, Mn^{2+}, etc.).

Thus, the activation energy spectrum for electromigration is generated by barriers of intercrystalline interlayers formed during interparticle slippage at the initial stage of powder particle sintering. The number and cross-section of intergranular contacts (shunting effect) significantly affect ρ_v. Interparticle contacts are formed mainly when non-conductive oxidized surfaces of powder grains come into contact. Some of the boundaries become more conductive due to sintering. The conductivity of boundaries determines the sample resistance after sintering. Heating of the sample corresponds to reduction annealing in vacuum (due to oxygen volatility). Effective removal of oxygen from the developed network of oxidized grain boundaries leads to Fe^{2+} ion enrichment and sharply decreased resistance.

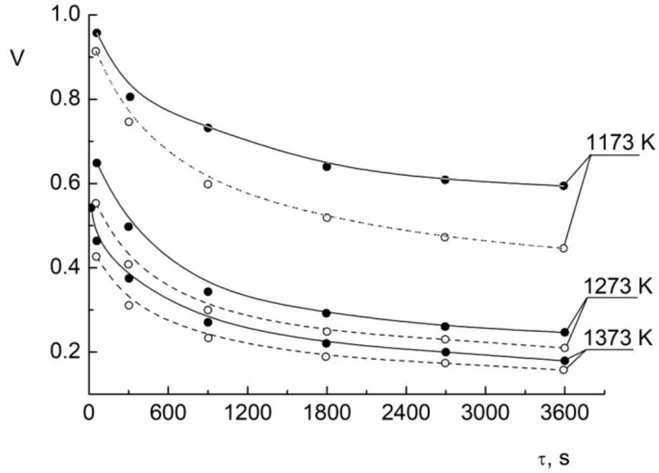


Fig.3. Dependences of the sample compaction on sintering time at different temperatures:
(•) T sintering; (○) RT sintering.

Curve *4* describes the conductivity of the sample in this state (Fig. 1). Shunting of the 'eutectic' boundaries of higher resistance makes the contribution of the latter to electromigration insignificant at this stage. However, additional annealing in air oxidizes looser 'non-eutectic' boundaries, and the sample resistance returns to its original values.

A decrease in the ρ_v of the samples sintered in RT mode in the presence of a low-melting additive shows a larger number of relatively low-resistance intergranular interlayers and indicates radiation-induced interparticle slippage. This effect can be observed only in the presence of a low-melting additive; therefore, the process can be identified with the radiation-induced intensification of liquid-phase processes, including liquid phase spreading over the array of powder grains.

The low-temperature (up to 373 K) region in $\rho_v = f(T)$ dependences mostly satisfies the above conditions. In this temperature range, the number and perfection of boundaries that limit electromigration increase during RT sintering mode in the presence of a fusible additive (Fig. 1). The absence of high-energy barriers in the activation energy spectrum indicates the highest perfection of the boundaries (Fig. 2). A decrease in the ρ_v indicates an increased effective area of the boundaries. In case of poor spreading of the liquid phase over the surface of powder particles, excessively thick films of this phase may form in some of its areas. In these conditions, the film impedes sintering of powder particles due to the repulsion effect [26]. It is probably due to this reason that the resistance of the compacted sample in the high-temperature region (T> 580 K) obtained in T sintering mode with the addition of Bi_2O_3 is higher compared to ρ_v of the sample obtained by solid-phase sintering.

Conclusion

In a comparative study, the influence of radiation-thermal sintering on the ferrite ceramic electromigration was determined. It was first shown that the structural rearrangement during radiation-thermal sintering occurs during early stages of sintering. Herewith the scientific significance of the results is determined by data on the reduction of electrical resistivity of samples obtained by radiation-thermalsintering compared to thermal sintering. This effect is caused by the formation of a large number of low-resistance intercrystalline layers, intensification of the liquid phase spreading process over the array of powder grainsand also by the radiation-induced stimulation of the intergranular slippage process.

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REFERENCES

1 Letyuk L.M., Nifontov V.A., Babich E.A., Gorelik S.S. Effect of low-melting additives on the formation of the microstructure and the properties of ferrites with a rectangular hysteresis loop. *Izv. Akad. NaukNeorg. Mater*. 1976, Vol. 12, pp. 2023 – 2026.[in Russian]

2 Zhuravlev G.I., Golubkov L.A., Strakhova T.A. Basic types of microstructure of ferrites and means of obtaining them. *Soviet Powder Metallurgy and Metal Ceramics*. 1990, Vol. 29, pp. 478 – 480.[in Russian]

3 Dmitriev M.V., Letyuk L.M., Shipko M.N. Study of oxygen diffusion in the surface layers of Mn-Zn ferrites. *Technical physics*. 1982, Vol. 27, pp. 338 – 339.

4 Letyuk L.M. Recrystallization of ferrites and its effect on the processes of microstructure formation in ferrospinels. *Soviet Powder Metallurgy and Metal Ceramics*. 1980, Vol.19, No. 5, pp. 359 – 364.

5 Zinovik M.A., Zinovik E.V. Ferrites with rectangular and square hysteresis loops. Powder Metallurgy and Metal Ceramics. 2005, Vol. 44, p. 66 – 74.

6 Letyuk L.M., et al. Special features of the formation of the microstructure of ferrites sintered in the presence of a liquid phase. *Izv.VysshikhUchebnykhZavedenij. ChernayaMetallurgiya*. 1979, Vol. 11, pp. 124 – 127. [in Russian]

7 Micheli A.L. Preparation of lithium ferrites by coprecipitation.*IEEE Transactions on Magnetics*. 1970, Vol.6, pp. 606 – 608.

8 Bronshteyn I.M., Dyubua B.Ch., Karasik B.S., Khinich I.I. Secondary electron emission of a platinum-barium alloy made by evaporation. *Radio Eng. Electron Phys*. 1974, Vol. 19, pp. 108 – 111.

9 Minin V.M. Effect of sintering conditions on the microstructure and electromagnetic properties of Li-Mg-Mn ferrite memory elements. *Soviet Powder Metallurgy and Metal Ceramics*. 1982, Vol. 21, pp. 698 – 701.

10 Zahir R., Chowdhury F.-U.-Z., Uddin M.M., et al. Structural, magnetic and electrical characterization of Cd substituted Mg ferrites synthesized by double sintering technique. *J. Magn. Magn. Mater*. 2016, Vol. 410, pp. 55 – 62.

11 ManjuraHoque S., Abdul Hakim M., Mamun Al, et al. Study of the bulk magnetic and electrical properties of $MgFe_2O_4$ synthesized by chemical method. *Materials Sciences and Applications*. 2011, Vol.2, pp. 1564 – 1569.

12 Hu J., Yan M., Luo W., Wu J.M. Effects of microstructure on the temperature dependence of relative initial permeability of NiCuZn ferrites. *Physica B*. 2007, Vol. 400, pp. 119 – 123.

13 Surzhikov A.P., Pritulov A.M., Lysenko E.N., et al. Calorimetric investigation of radiation-thermal synthesized lithium pentaferrite. *Journal of Thermal Analysis and Calorimetry*. 2010, Vol. 101, No. 1, pp. 11 – 13.

14 Yurov V.M., Baltabekov A.S., Laurinas V.C., Guchenko S.A. Dimensional effects and surface energy of ferroelectric crystals. *Eurasian phys. tech. j.* 2019, Vol.16, No.1, pp. 18 – 23.

15 El-Shobaky G.A., Ibrahim A.A. Solid-solid interactions between ferric oxide and lithium carbonate and the thermal stability of the lithium ferrites produced. *Thermochim. Acta*. 1987, Vol.118, pp. 151 – 158.

16 Salimov R.A., Cherepkov V.G., Golubenko J.I., et al. D.C. high power electron accelerators of ELV-series: status, development, applications. *J. Radiation Phys. Chem*. 2000, Vol.57, pp. 661 – 665.

17 Cleland M.R., Parks L.A. Medium and high-energy electron beam radiation processing equipment for commercial applications. *Nucl. Instr. Meth. B*. 2003, Vol.208, pp. 74 – 89.

18 Mehnert R. Review of industrial applications of electron accelerators. *Nucl. Instr. Meth.B*. 1996, Vol.113, pp.81 – 87.

19 Neronov V.A., Voronin A.P., Tatarintseva M.I., Melekhova T.E., Auslender V.L. Sintering under a high-power electron beam. *J. Less-Common Metals*. 1986, Vol.117, pp. 391 – 394.

20 .Surzhikov A.P., Lysenko E.N., Malyshev A.V., Pritulov, A.M. Kazakovskaya, O.G. Influence of mechanical activation of initial reagents on synthesis of lithium ferrite. *Russian Physics Journal*, 2012, Vol. 55, No. 6, pp. 672-677.

21 Boldyrev V.V., Voronin A.P., Gribkov O.S., Tkachenko E.V., Karagedov G.R., Yakobson B.I., Auslender V.L. Radiation-thermal synthesis. Current achievement and outlook. *J. Solid State Ion*. 1989, Vol.36, pp. 1 – 6.

22 Surzhikov A.P., Frangulyan T.S., Ghyngazov S.A., Koval N.N. Structural-phase transformations in near-surface layers of alumina-zirconium ceramics induced by low-energy high-current electron beams.*Nucl. Instr. Meth. B*. 2009, Vol. 267, No. 7, pp. 1072 – 1076.

23 Surzhikov A.P., Peshev V.V., Pritulov A.M., Gyngazov,S.A. Grain-boundary diffusion of oxygen in polycrystalline ferrites. *Russian Physics Journal*. 1999, Vol. 42, No. 5, pp. 490-495.

24 Stary O., Malyshev A.V., Lysenko E.N., Petrova A. Formation of magnetic properties of ferrites during radiation-thermal sintering. . *Eurasian phys. tech. j.* 2020, Vol.17, No.2, pp. 6 – 10.

25 Nikolaev E.V., Astafyev A.L., Nikolaeva S.A., Lysenko E.N., ZeinidenovA.K. Investigation of electrical properties homogeneity of Li-Ti-Zn ferrite ceramics. . *Eurasian phys. tech. j.*2020, Vol.17, No.1, pp. 5 – 12.

26 Geguzin J.E. *Physics of Sintering*. 1984, Moscow, Nauka, 360p.

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