

TG study of the $\text{Li}_{0.4}\text{Fe}_{2.4}\text{Zn}_{0.2}\text{O}_4$ ferrite synthesis

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Abstract. In this paper, the kinetic analysis of Li-Zn ferrite synthesis was studied using thermogravimetry (TG) method through the simultaneous application of non-linear regression to several measurements run at different heating rates (multivariate non-linear regression). Using TG-curves obtained for the four heating rates and Netzsch Thermokinetics software package, the kinetic models with minimal adjustable parameters were selected to quantitatively describe the reaction of Li-Zn ferrite synthesis. It was shown that the experimental TG-curves clearly suggest a two-step process for the ferrite synthesis and therefore a model-fitting kinetic analysis based on multivariate non-linear regressions was conducted. The complex reaction was described by a two-step reaction scheme consisting of sequential reaction steps. It is established that the best results were obtained using the Yander three-dimensional diffusion model at the first stage and Ginstling-Bronstein model at the second step. The kinetic parameters for lithium-zinc ferrite synthesis reaction were found and discussed.

1. Introduction

The solid-state synthesis is the main method of commercial production of microwave ferrites including zinc substituted lithium ferrites [1-3]. It involves two-stage high-temperature heating of reagent mixtures including synthesis of ferrites with the formation of single-phase ferrite compositions and further sintering at a higher temperature to produce high-density ferrite ceramics [4-10]. The dielectric and magnetic properties of lithium-substituted ferrites were intensively studied. However, the kinetic parameters for lithium ferrite synthesis reaction were not investigated, especially, for lithium-zinc ferrite with the chemical formula $\text{Li}_{0.4}\text{Fe}_{2.4}\text{Zn}_{0.2}\text{O}_4$, which is widely used in microwave technology.

The study of kinetic regularities of synthesis has two main objectives. The first is experimental determination of degree or rate of conversion depending on the conditions of the reactions and the mathematical description of the found dependence. The second is evaluation of kinetic parameters of the reaction and their interpretation in relation with the nature of ongoing processes.

Mathematical treatment of the kinetic data can be carried out in two ways:

- 1) Finding of equation that best describes experiment, and parameters which do not have a specific physical meaning;
- 2) Using of kinetic equations based on certain models of the interaction in solids. The parameters of these equations are related with the nature of ongoing processes.

For kinetic analysis of the synthesis reaction, equation is generally assumed:

$$de/dt = -k \cdot (T(t)) \cdot f(e, p) \quad (1)$$



where t – time; T – temperature; e - concentration of the initial material; p – concentration of the product, $f(e, p)$ – type of reaction. The reaction models $f(e, p)$, most commonly used in heterogeneous kinetics, are presented somewhere else [11]. It is assumed that the conversion function, $U(t, T, e, p)$, can be described by two different functions $k(T)$ and $f(e, p)$:

$$U(t, T, e, p) = k(T(t)) \cdot f(e, p) \quad (2)$$

For single-stage reactions $f(e, p)$ has a less complex form of $f(x)$, i.e. $e = 1 - \chi e$ and $x = p$ (x - degree of conversion). Thus, the complete separation of variables in the equation (2) and analytical solution of the differential equation (1) is only possible for the one-step reaction. For complex multistage of processes solution (1) leads to a system of differential equations for which it is impossible to separate the variables and there is no analytical solution.

From the technical aspect, the kinetic analysis will be examined as a tool for data reduction. The information will be extracted from a series of measurements with many data points in the form of one model with few parameters. This model will then serve in the preparation of predictions under another temperature program than used for the experiments and for process optimization.

The aim of this model-fitting kinetic approach is to find a kinetic model with minimal adjustable parameters which quantitatively describes the kinetics reaction [12]. This formal kinetic model can then be used for the kinetic analysis of thermal measurements, including the process of synthesis.

In this work, the kinetic model describing the process of lithium-zinc ferrite synthesis was obtained using the model-fitting kinetic analysis of ferrite formation employing thermogravimetric (TG) analysis. Also the kinetic parameters quantitatively describing the kinetics of synthesis process were obtained. The Netzsch Thermokinetics software (Version 2006.08, Netzsch-Geratebau GmbH) package was used for the non-linear regression model-fitting analysis.

2. Experimental

Commercial powders of zinc oxide – ZnO, iron oxide – Fe₂O₃ and lithium carbonate Li₂CO₃ were used as the initial reagents of reaction mixture for Li_{0.4}Fe_{2.4}Zn_{0.2}O₄ lithium-zinc ferrite synthesis. Li₂CO₃–ZnO–Fe₂O₃ mechanical mixture of initial reagents was thoroughly mixed in an agate mortar. Thermogravimetric (TG) and differential scanning calorimetric (DSC) measurements were performed using STA 449C Jupiter analyzer (Netzsch-Geratebau GmbH, Germany). Samples with a mass of ~ 10 mg were placed in the alumina crucibles. Both TG and DSC baselines were corrected by subtraction of predetermined baselines run under identical conditions except for the absence of sample. Samples were heated up to 800°C with programmed heating rate of 2.5, 5, 10, 20 °C/min. All experiments were performed under atmospheric pressure conditions. The Netzsch Proteus software packages were used for TG/DSC data analysis.

3. Results and Discussion

Figure 1 shows the TG/DSC curves for sample heated at 20 °C/min. The curves for samples heated at other heating rates were similar. The TG curve indicates a mass loss process at ca. 500-730 °C, which is connected to the reaction between the initial reagents according to the equation $\text{Li}_2\text{CO}_3 + 6\text{Fe}_2\text{O}_3 + \text{ZnO} \rightarrow 5\text{Li}_{0.4}\text{Fe}_{2.4}\text{Zn}_{0.2}\text{O}_4 + \text{CO}_2\uparrow$. A mass loss corresponds to the theoretical value of output CO₂.

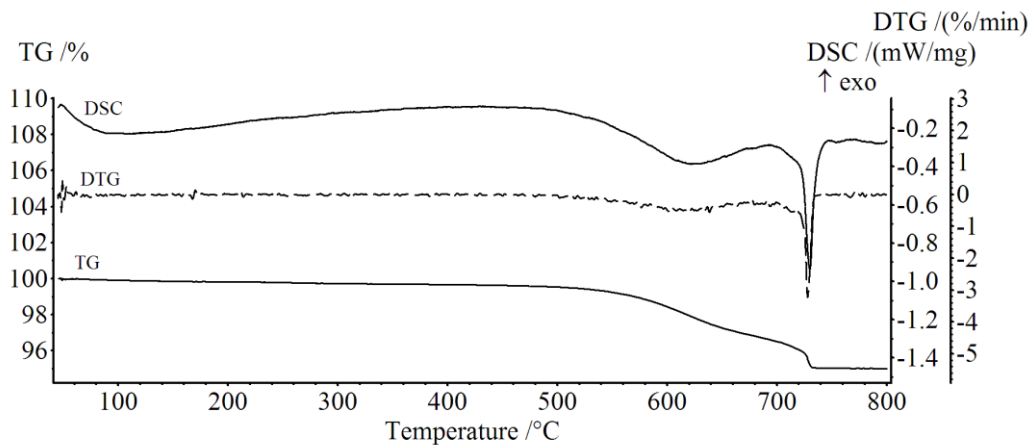


Figure 1. TG/DSC curves for lithium-zinc ferrite synthesis

The TG curves can be divided on two main stages, in which the temperature ranges depend on heating rate. From the derivate of TG (DTG) peak, the first stage is located at ca. 500-680°C. In the second stage, the maximum peak of DTG curve is at ca. 723 °C, and this stage corresponds to melting of the lithium carbonate [13, 14].

It is obvious that the reaction mechanism of Li-Zn ferrite synthesis is complex and changes during the reaction [15, 16]. Thus, it is unlikely that the total reaction can be described by a simple two-step reaction. Consequently, multistage model must be used to describe the kinetics of the reaction.

For the initial assessment of the kinetic parameters, the model-independent evaluation of the kinetic parameters was performed. For this, a model-independent method by Friedman analysis was used [17]. Figure 2 and figure 3 show the results of analysis by Friedman for all heating rates. From Friedman analysis, the pre-exponential factor and the activation energy of synthesis were used as input values for the model of non-linear regression.

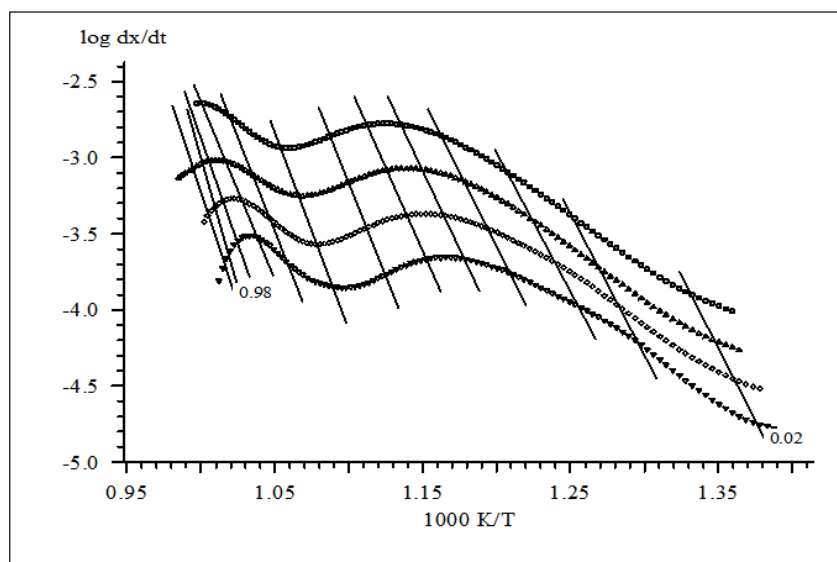


Figure 2. Friedman graphic for the reaction

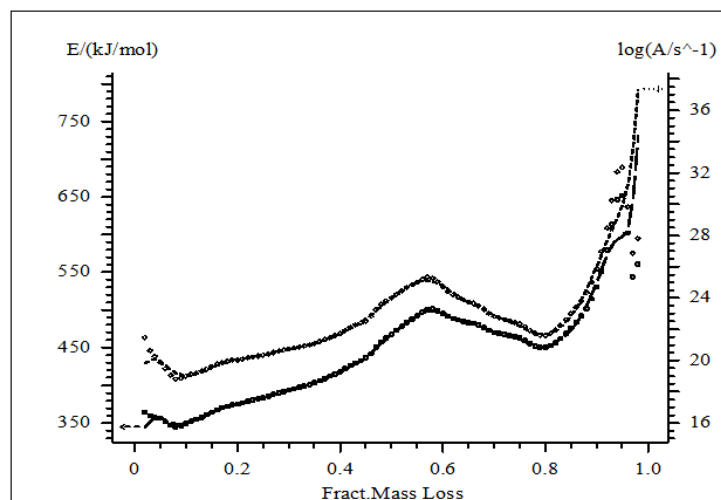


Figure 3. Arrhenius parameters derived from the Friedman analysis

The fitting of the TG curves by the model of non-linear regression was produced by the several kinetic models: model of Ginstling-Bronstein, Yander, model Abraham-Erofeev, etc. The best results were obtained using in the first stage the diffusion model of Yander and diffusion model of Ginstling-Bronstein in the second stage. Figure 4 shows the results from the non-linear regression analysis which summarized in Table 1.

According to the results, the activation energy at the first stage has a high value and is ~ 292 kJ/mol. Then, the activation energy increases and reaches values of ~ 397 kJ/mol. Such values is significantly higher than that of lithium ferrite (LiFeO_2) with a value of 111 kJ/mol [18] and ball milled zinc ferrite (ZnFe_2O_4) with a value of 138 kJ/mol [19]. This result may be due to the fact that the non-milled initial reagents. This result may be due to the fact that the non-milled reactants are characterized by low reactivity.

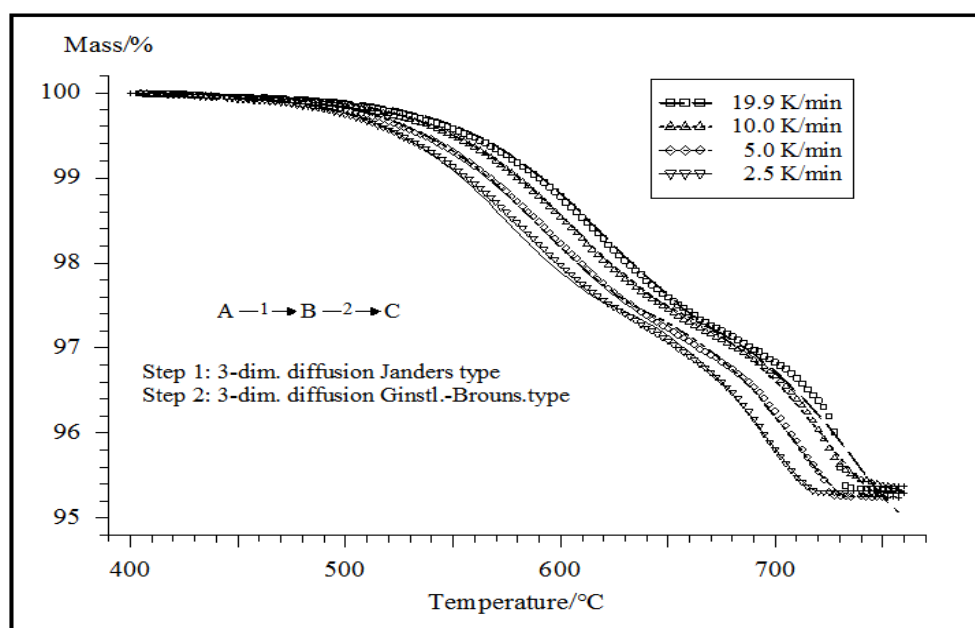


Figure 4. Fit for the non-linear regression of the TG kinetic data. Symbols - experimental points, lines - calculated curves

Table 1. Kinetic results derived from non-linear regression analysis

№	Parameter	Optimal value
0	$\log A1/s^{-1}$	14.27
1	E1 (kJ/mol)	291.98
2	$\log A2/s^{-1}$	17.75
3	E2 (kJ/mol)	397.34
4	FollReact. 1	0.48
5	Mass Loss1 (%)	-4.99
6	Mass Loss2 (%)	-4.69
7	Mass Loss3 (%)	-4.74
8	Mass Loss4 (%)	-4.67

Conclusions

The kinetic of Li-Zn ferrite synthesis up to temperatures 800°C was studied in air using non-isothermal thermogravimetric analysis. It was shown that the reaction mechanism of lithium-zinc ferrite synthesis is complex and changes during the reaction. A model-fitting kinetic analysis based on multivariate non-linear regressions was conducted for fitting of experimental TG curves.

It was established that the reaction can be described by a two-step reaction scheme consisting of sequential reaction steps. The best results were obtained using the diffusion models of Yander and Ginstling-Bronstein at the first and second stages, respectively. The fitting results the activation energy values for the ferrite synthesis of ~ 292 kJ/mol and ~ 397 kJ/mol, which correspond to the proceeding of the reaction in the first and second stages, respectively.

The values of the kinetic parameters can be advantageously used for further prediction of the ferrite synthesis in isothermal conditions.

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