

Investigation of heating rate effect on solid-phase interaction in $\text{Li}_2\text{CO}_3 - \text{Fe}_2\text{O}_3$ reaction mixture

E N Lysenko¹, E V Nikolaev¹, E A Vasendina¹

¹National Research Tomsk Polytechnic University, 30 Lenin Ave, 634050, Tomsk, Russia

E-mail: lysenkoen@tpu.ru

Abstract. The influence of heating rate on solid-phase interaction in $\text{Li}_2\text{CO}_3\text{-Fe}_2\text{O}_3$ reaction mixture was investigated by thermal analysis method. The powder mixture components were in the ratio corresponding to LiFe_5O_8 ferrite. The ferrite synthesis was performed by thermal heating of mixture reagents in thermal analyzer up to 800 °C in air at various heating rates in the ranges (5-50) °C/min. The results showed that the heating rate affects the solid-phase interaction in $\text{Li}_2\text{CO}_3 - \text{Fe}_2\text{O}_3$ reaction mixture. The reaction phase formation is accompanied by heat endothermic effect, which was observed in the DSC curve in the form of a complex broad peak. For all samples, this complex peaks were decomposed into simpler peaks, and thereby, the enthalpies of the individual phase transitions were determined. It was shown that the heating rate affects the values of enthalpy and temperatures of heat endothermic effects, so that the high heating rate shifts the proceeding of reaction to higher temperatures.

1. Introduction

Lithium ferrite (LiFe_5O_8) is very important magnetic material for practical application in microwave techniques [1, 2], as a cathode material for chemical current sources [3], and in chemical sensors [4]. Also, LiFe_5O_8 is a convenient model material for the study of new phenomena in complex-oxide systems, such as the phenomenon of radiation-thermal intensification of solid-phase processes in ferrites [5]. In the early works [6, 7], we reported that the isothermal annealing of lithium carbonate and iron oxide mixture in condition of electron beam heating leads to increase the synthesis rate of lithium ferrite in comparison with the synthesis by thermal annealing. This result indicates the presence of radiation effect in stimulation of lithium ferrite solid-phase synthesis. However, the main features in solid-phase interaction during lithium ferrite synthesis under different heating rate have not been studied. Such investigation will help to correctly interpret the results from radiation-thermal synthesis of lithium ferrites by high-energy electron beam, where mainly large heating and cooling rates are used. This problem can be solved by using TG/DSC methods widely used in lithium ferrite analysis [8-10].

Thus, in this paper, we present the investigation results of heating rate effect on solid-phase interaction in $\text{Li}_2\text{CO}_3 - \text{Fe}_2\text{O}_3$ reaction mixture.

2. Experimental

The commercial Fe_2O_3 and Li_2CO_3 powders were used as the initial reagents of reaction mixture for lithium ferrite synthesis. The powders were dried for 7 hours at the temperature of about 200 °C in a laboratory furnace. After that, powders were weighed in the proportions with according to the equation



$\text{Li}_2\text{CO}_3 + 5\text{Fe}_2\text{O}_3 \rightarrow 2\text{LiFe}_5\text{O}_8 + \text{CO}_2\uparrow$ and mixed by threefold rubbing through a sieve with a mesh of 110 microns. Samples were freely-placed in the crucibles, and the bulk density of powder was 0.95 g/cm^3 . Calorimetric investigations were carried out by STA 449C Jupiter thermal analyzer (Netzsch-Geratebau GmbH, Germany). The powders were heated up to $800 \text{ }^\circ\text{C}$ in air at various heating rates in the ranges $(5\text{-}50) \text{ }^\circ\text{C/min}$ and then were cooled with rate of $10 \text{ }^\circ\text{C/min}$. Rates range was limited by instrumental capabilities of the analyzer.

3. Results and discussion

Figure 1 shows the DSC curves for reaction mixture under heating at $5 \text{ }^\circ\text{C/min}$ and $50 \text{ }^\circ\text{C/min}$. Areas of the observed DSC peaks are enthalpy of reaction, normalized to the mass of the sample. The software package «Peak Separation» (Netzsch-Geratebau GmbH, Germany) was used for the separation of complex peaks into components. The DSC data (enthalpy S and temperatures T of peak position) are summarized in Table 1.

From calculation, the five endothermic peaks were observed on DSC curves for all samples under heating. The first three peaks S_1 ($\sim 545 \text{ }^\circ\text{C}$), S_2 ($\sim 612 \text{ }^\circ\text{C}$) and S_3 ($\sim 690 \text{ }^\circ\text{C}$) are included in broad peak on DSC curve under heating. The fourth peak S_4 ($\sim 730 \text{ }^\circ\text{C}$) is connected with lithium carbonate melting and decomposition; fifth $S_{\alpha-\beta}$ ($\sim 755 \text{ }^\circ\text{C}$) is phase transition "order-disorder" in LiFe_5O_8 lithium ferrite [10].

The values of enthalpy S_1 , S_2 , S_3 decrease with increasing heating rate, and the enthalpy value of sharp S_4 peak increases. At the same time, the low-intensity peak S_3 is not possible to determine when high heating rates. Probably, the first three peaks are caused by the ion exchange between the reagent particles in the solid state, and the fourth peak - exchanges between the solid ($\alpha\text{-Fe}_2\text{O}_3$) and liquid (Li_2CO_3) phases. Obviously, the increasing of heating rate reduces the time of interaction between the solid phase, and a large amount of unreacted lithium carbonate is present in mixture up to the temperature of Li_2CO_3 melting. The melting film instantly spreads over the surface of the Fe_2O_3 particles, increasing the area of interaction between lithium carbonate and iron oxide. Also, considering that this process is carried out at higher temperatures, it is easy to understand the reason a significantly higher efficiency of the second stage of lithium carbonate decomposition. Due to the increasing amounts of unreacted Li_2CO_3 (with increasing heating rate), the intensity of S_4 peak increases and overlaps adjacent S_3 and $S_{\alpha-\beta}$ peaks. It can be seen from Table 1, these peaks are confidently calculated at a heating rate of $20 \text{ }^\circ\text{C/min}$ inclusive, and so this rate can be taken as limiting in a detailed analysis of the DSC curves.

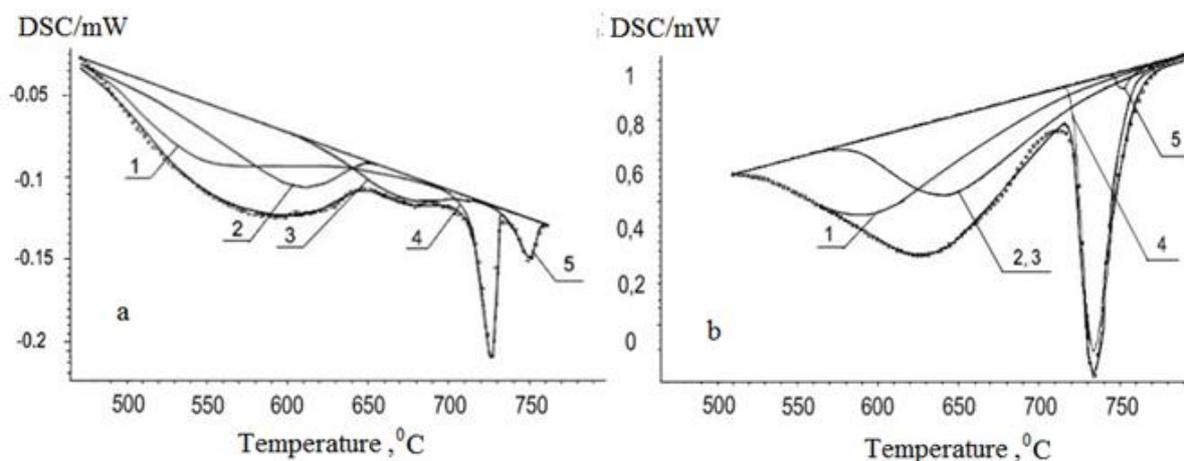


Figure 1. DSC curves for $\text{Li}_2\text{CO}_3 - \text{Fe}_2\text{O}_3$ mixture under heating at $5 \text{ }^\circ\text{C/min}$ (a) and $50 \text{ }^\circ\text{C/min}$ (b). 1 - S_1 , 2 - S_2 , 3 - S_3 , 4 - S_4 , 5 - $S_{\alpha-\beta}$.

Table 1. DSC data for $\text{Li}_2\text{CO}_3 - \text{Fe}_2\text{O}_3$ mixture under heating.

Heating rate	S_1	T_1	S_2	T_2	S_3	T_3	S_4	T_4	$S_{\alpha-\beta}$	$T_{\alpha-\beta}$
$^{\circ}\text{C}/\text{min}$	J/g	$^{\circ}\text{C}$	J/g	$^{\circ}\text{C}$	J/g	$^{\circ}\text{C}$	J/g	$^{\circ}\text{C}$	J/g	$^{\circ}\text{C}$
5	46.2	548	38.3	600	10.6	670	13.5	727	4.7	750
10	43.6	562	30.9	605	8.9	683	16.2	728	4.5	751
20	42.6	575	34.7	622	5.8	693	20.7	729.5	2.9	750
30	41.7	583	34.6	628	-	-	23.8	730.4	1.9	750
40	40.7	587	34.1	635	-	-	24.7	733	1.5	751
50	39.8	597	33.2	646	-	-	24.7	733.9	0.9	751

As above, the peak $S_{\alpha-\beta}$ is proportional to the enthalpy of $\alpha \rightarrow \beta$ transition, and therefore indicates the amount of $\alpha\text{-LiFe}_5\text{O}_8$ phase accumulated during the heating of the reaction mixture up to a temperature of 750-755 $^{\circ}\text{C}$. Since with the increasing of heating rate, the total time of reaction mixture annealing is reduced, and so the decrease in peak intensity is observed (see Table 1). From the fact that a tenfold increasing in the heating rate leads to only a five-fold decreasing in the intensity of the $S_{\alpha-\beta}$ peak, we can conclude about the nonlinear dependence between the duration of annealing time and quantity synthesized LiFe_5O_8 . According to result from DSC curves obtained in cooling regime, the content of lithium ferrite phase continues to increase. From this, the both a lithium ferrite and some intermediate phases are formed in the process of lithium carbonate decomposition. Most likely, lithium oxide and non-stoichiometric lithium ferrite phases (LiFe_5O_8 , LiFeO_2) are as the intermediate phases after the Li_2CO_3 decomposition.

4. Conclusion

Paper presented the investigation of heating rate effect on solid-phase interaction in $\text{Li}_2\text{CO}_3 - \text{Fe}_2\text{O}_3$ reaction mixture using thermal analysis. The powders for reaction mixture were used to obtain LiFe_5O_8 lithium ferrite.

The results show that the heating rate affects the solid-phase interaction in $\text{Li}_2\text{CO}_3 - \text{Fe}_2\text{O}_3$ reaction mixture. The complex peaks are observed on the DSC curves, which were decomposed into simpler peaks, and thereby, the enthalpies of the individual phase transitions were determined.

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