

# SYNTHESIS OF COMPLEX OXIDES WITH GARNET STRUCTURE BY SUPERCRITICAL ANTISOLVENT PRECIPITATION CO<sub>2</sub> TECHNIQUE

\*Sokolov I.E., Kolobanov A.I., Efremova E.I., Fomichev V.V.

MIREA- Russian Technological University

\*e-mail:sokolov\_iliya@yahoo.com

## INTRODUCTION

The most common magnetic oxides widely used as soft, hard, or moderate ferrites are spinels, garnets, and hexaferrites. Magnetic oxides, due to their structure, can contain various cations at the positions of the crystal lattice, which provides a wide variation of properties. Yttrium iron garnet (YIG) Y<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> is an example of ferrimagnetic ceramics. It belongs to the group of magnetic oxides characterized by specific magnetic and magneto-optical properties. Substituted garnets and ferrites find numerous applications as soft ferrites. A YIG crystal has many attractive characteristics, such as low dielectric loss, a narrow width of the resonance line in the microwave region, and also a good value of saturated magnetization. New-generation devices based on YIG have been developed, such as delay lines, tuning filters, generators, isolators, and memory blocks with bubble storage. It is also used in telecommunications and magneto-optical technology. The desired properties for specific applications can be obtained by controlling the synthesis conditions or by adding appropriate substituents to the YIG. The main advantage of soft magnetic ceramics as compared to their metal counterparts is that they are electrical insulators. This property is fundamental for maintaining low eddy current losses and is one of the main reasons for the use of magnetic ceramics in areas where such losses should be minimized. In this work, the authors first performed the synthesis and study of the phase formation of YIG using the supercritical fluid antisolvent method at the initial stage. Such an approach should ensure the production of yttrium iron garnet in the form of nanosized particles of a controlled size – precursors of magnetic materials.

## EXPERIMENTAL PART

In order to study the stages of the formation of a complex oxide Y<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> with the garnet structure, a precursor was obtained by co-micronizing salts from a common solution with a ratio of components corresponding to YIG composition. The precursor was synthesized in an experimental laboratory unit SAS-50 (WatersCorp.)(Figure 1). The initial solution was prepared in an ultrasonic bath by dissolving yttrium(III) acetate (99.9%, Sigma-Aldrich) and basic iron(III) acetate in dimethyl sulfoxide (for synthesis, MERCK) in a 3:5 molar ratio. The experiments were carried out at a pressure of 15 MPa and a temperature of 40°C. CO<sub>2</sub> feed rate was 50 ml/min. The initial solution feed rate was 1 ml/min. The nozzle diameter was 100 μm. In order to create an equilibrium fluid composition in the reactor, 10 ml of pure solvent was fed into the reactor after the system reached the specified pressure and temperature. When the initial solution supply was complete, 20 ml of pure solvent was fed into the reactor to flush the pump and nozzle lines. After completion of the experiment, the supply of CO<sub>2</sub> fluid was continued for 20 minutes to remove the organic solvent from the surface and bulk of the obtained product.

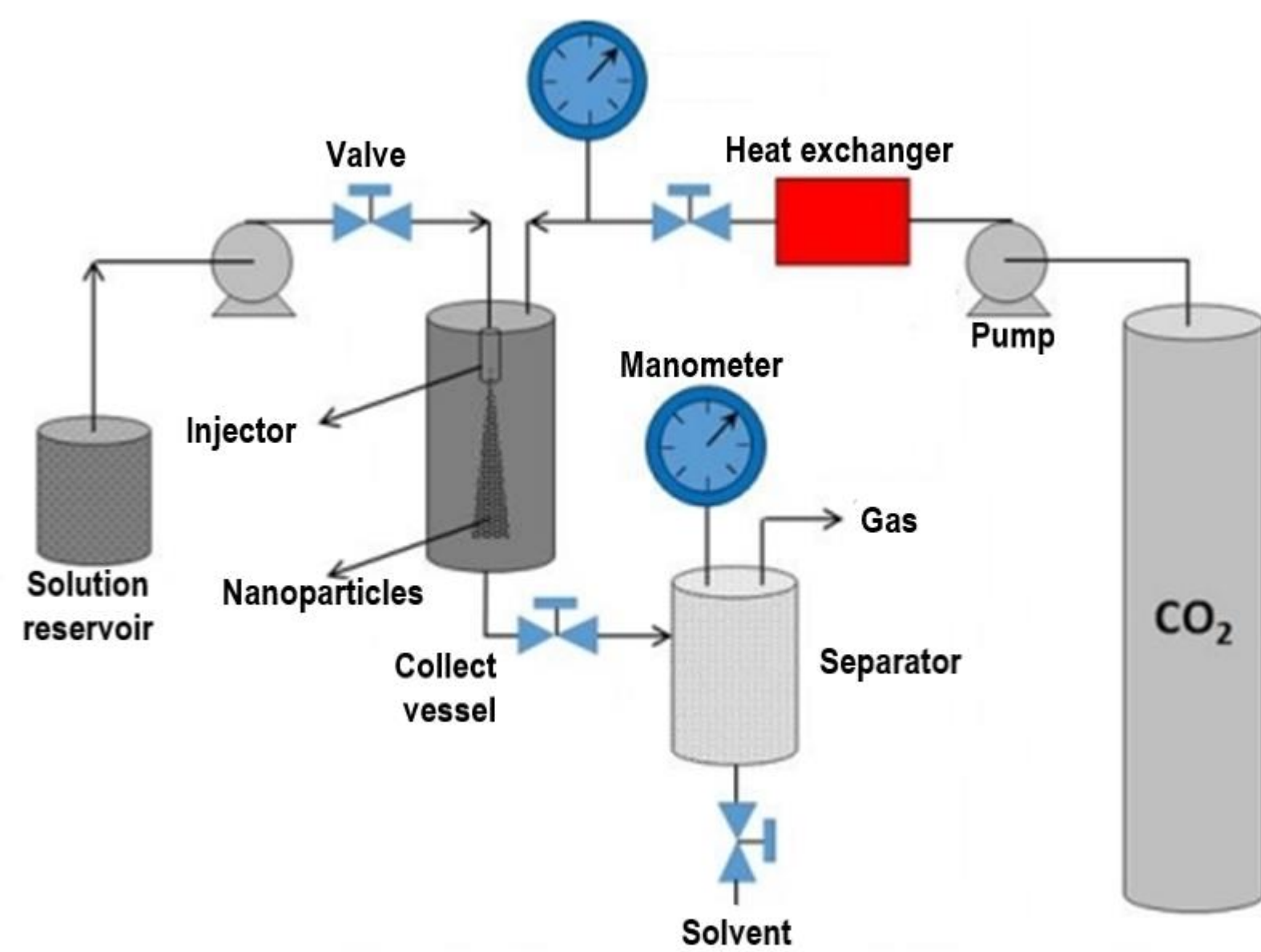


Figure 1 – Experimental apparatus for micronization with SAS process.

## RESULTS AND DISCUSSION

The freshly prepared sample is a mixture of the starting acetate salts, which is confirmed by the recorded IR absorption spectra of the YIG precursor (Figure 2). The absorption bands at 1560, 652, and 619 cm<sup>-1</sup> correspond to the stretching and deformation vibrations of the –COO fragment. The absorption bands at 1424 cm<sup>-1</sup> and 1047 cm<sup>-1</sup> correspond to the deformation vibrations of the CH<sub>3</sub> group. The band at 943 cm<sup>-1</sup> corresponds to the stretching vibration of the C–C bond. Above 2800 cm<sup>-1</sup>, a broad absorption band is observed. It includes components of the stretching vibrations of the methylene group of the acetate anion and the stretching vibrations of sorbed water molecules. The band corresponding to the deformation vibration of water molecules appears as a shoulder on the high-frequency slope of the intense band at 1560 cm<sup>-1</sup>. Below 1150 cm<sup>-1</sup>, absorption bands corresponding to the vibrations of the metal-oxygen ensembles were recorded. It should be born in mind that the sample was obtained at low temperatures in the nonequilibrium mode, and no crystal structure can be formed under these conditions. The data of X-ray phase analysis confirm the amorphous nature of the freshly prepared sample of precursors, as evidenced by the halo in the diffractogram (Figure 3). Figure 4 shows the thermogram of a freshly prepared sample of the YIG precursor. One can note on the curve four sections of mass loss up to a temperature of 850 °C.

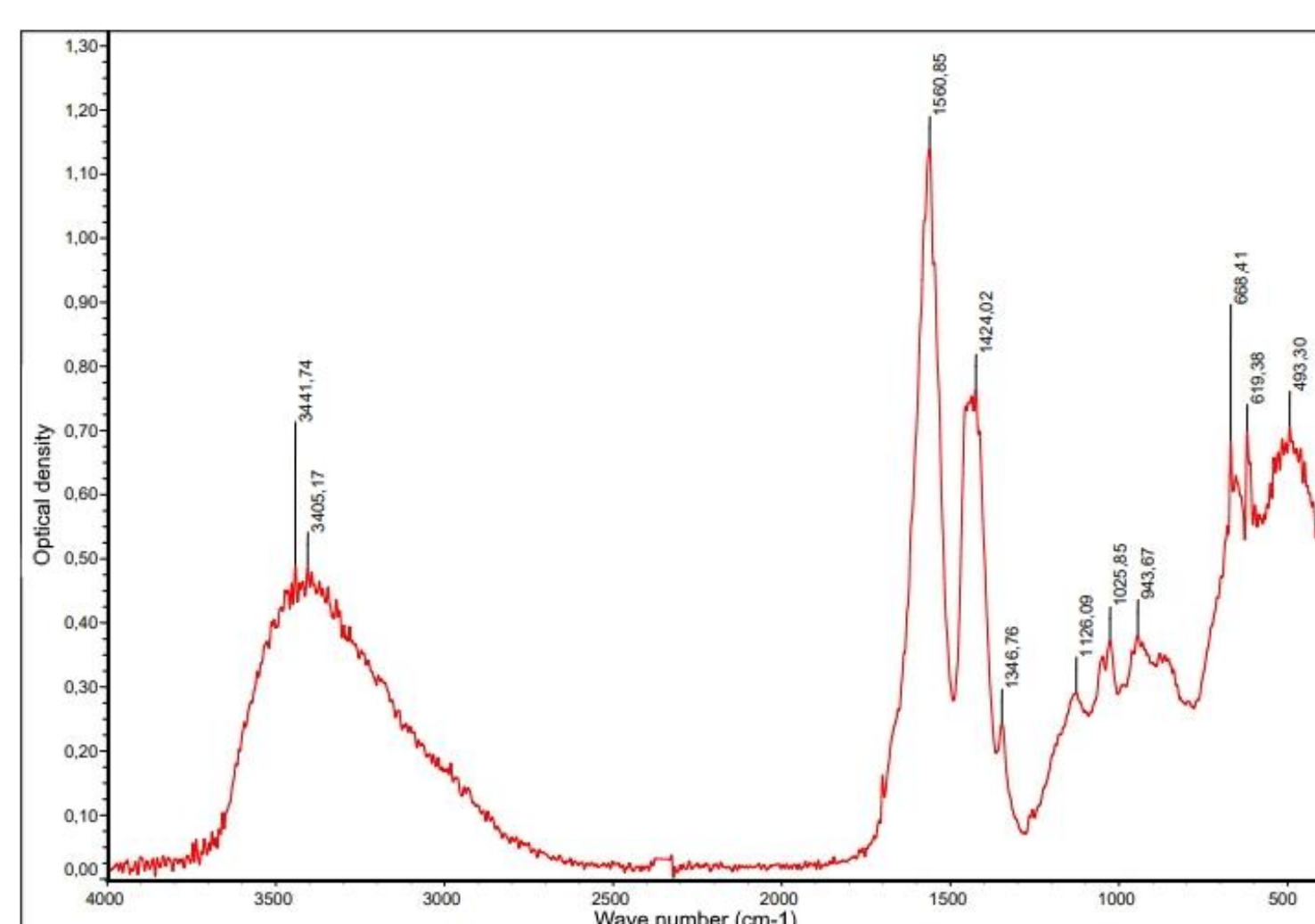


Figure 2 – The IR spectrum of a freshly prepared YIG precursor.

The first mass loss (I) in the temperature range of 50–275 °C amounts to 37% and is associated with the processes of removing residual organic solvent and water from the pores of the sample, as well as with the thermal destruction of the complex based on yttrium and iron acetates to a solid solution of yttrium oxycarbonate (Y<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>) and iron metahydroxide (FeO (OH)).

The existence of these processes is confirmed by the behavior of the absorption bands at 1494, 1398, 1121, 1067 and 841 cm<sup>-1</sup> on the IR spectrum of a freshly prepared sample calcined at 400 °C. These bands relate to the stretching and deformation vibrations of the carboxyl group of the oxocarbonate (Figure 5), and the absorption bands below 800 cm<sup>-1</sup> correspond to the vibrations of the yttrium-oxygen system. Figure 6 shows the IR spectra of a freshly prepared sample of a YIG precursor calcined at 600 and 800 °C.

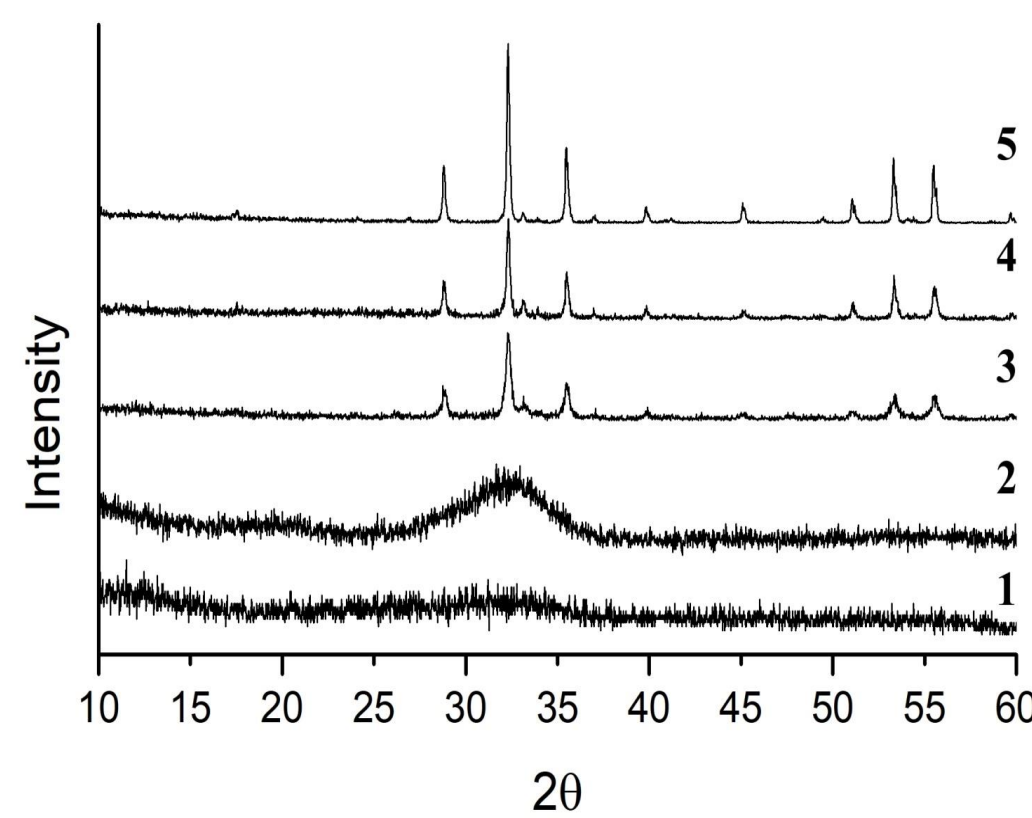


Figure 3 – Diffractograms of a freshly prepared YIG precursor and a precursor calcined at various temperatures: freshly prepared (1), calcined at a temperature of 520 °C (2), 600 °C (3), 800 °C (4) and 1000 °C (5).

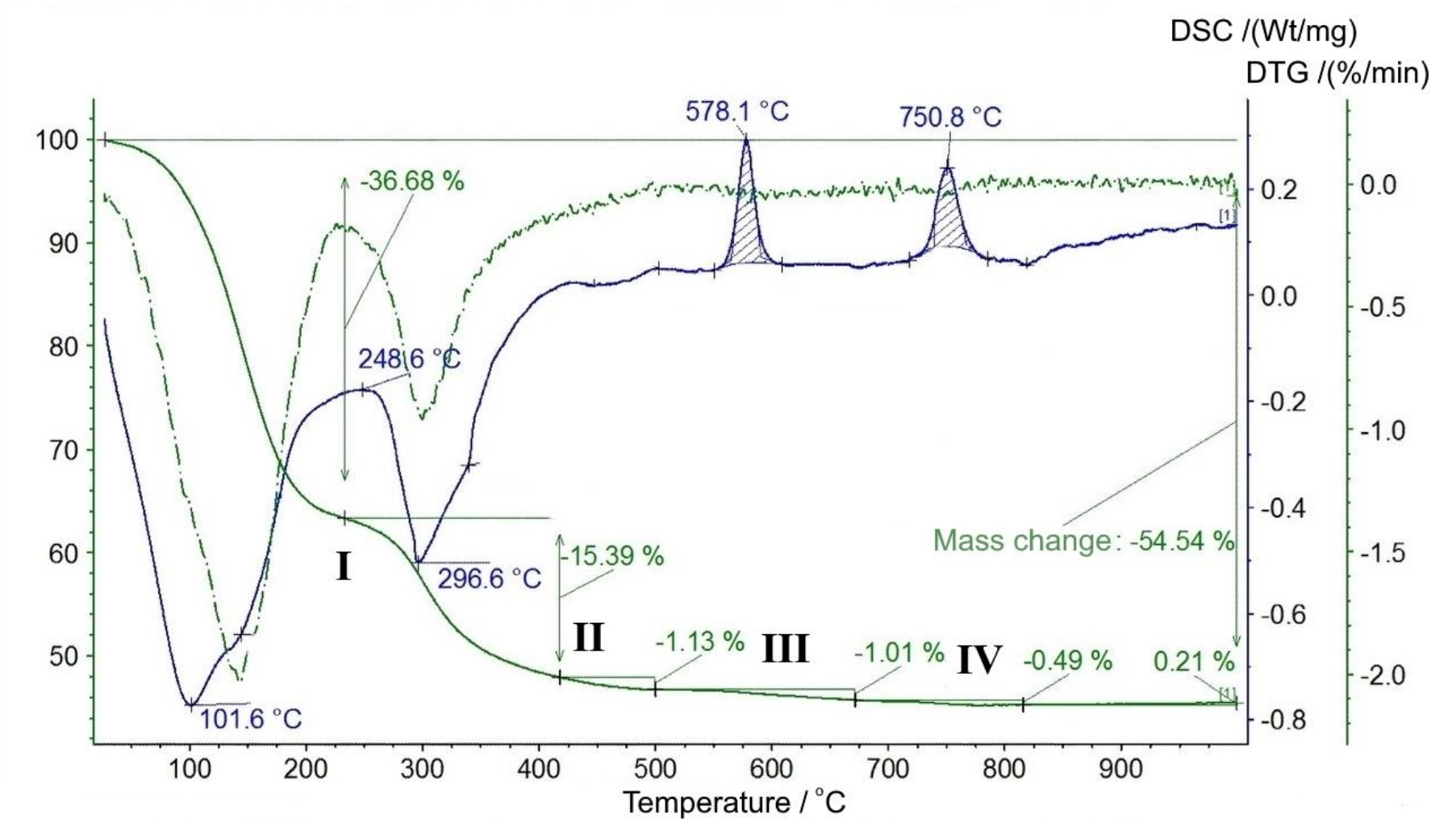


Figure 4 – TG/DSC analysis curve of a freshly prepared sample of the YIG precursor.

The next stage (II) proceeds with heat absorption in the temperature range 275–400 °C with the thermal decomposition of the solid solution to amorphous yttrium orthoferrite (YFeO<sub>3</sub>). The mass loss is 15%. The carbonate destruction with the formation of YFeO<sub>3</sub> is confirmed by the disappearance of the absorption bands corresponding to the stretching and deformation vibrations of the CO<sub>3</sub><sup>2-</sup> group and the appearance of an absorption band at 576 cm<sup>-1</sup>, which is related to the stretching vibration of the octahedral oxygen polyhedron of the perovskite structure in the IR spectrum of the precursor sample calcined at 520 °C (Figure 5). The exothermic effect of III with a mass loss of 2.15% corresponds to the formation of an amorphous phase of the composition of iron-yttrium garnet proceeding with further heating. According to X-ray phase analysis reflections corresponding to the cubic YIG syngony appear only when the sample is isothermally processed at 600 °C for 24 hours (Figure 2 (3)).

The exothermic effect of IV in the temperature range 740–770 °C corresponds to the amorphous phase crystallization into the structure of yttrium iron garnet, which is accompanied by a slight mass loss of 1.1% due to the removal of residual decomposition products from the pores during the formation of the crystal lattice.

The particle size of the YIG sample was calculated at 600, 800, and 1000 °C with the use of the Debye-Scherrer equation that relates the crystallite size to the width of the diffraction peaks of X-ray diffraction patterns. The results obtained in comparison with the particle size of a freshly prepared sample (according to TEM). According to the obtained results the average particle size increases as the calcination temperature of a freshly prepared YIG sample increases. The size of the particles of the freshly prepared sample (40 °C) and of the sample calcined at 600 °C differs inappreciably, while increasing temperature to 1000 °C results in particles enlargement to 42 nm.

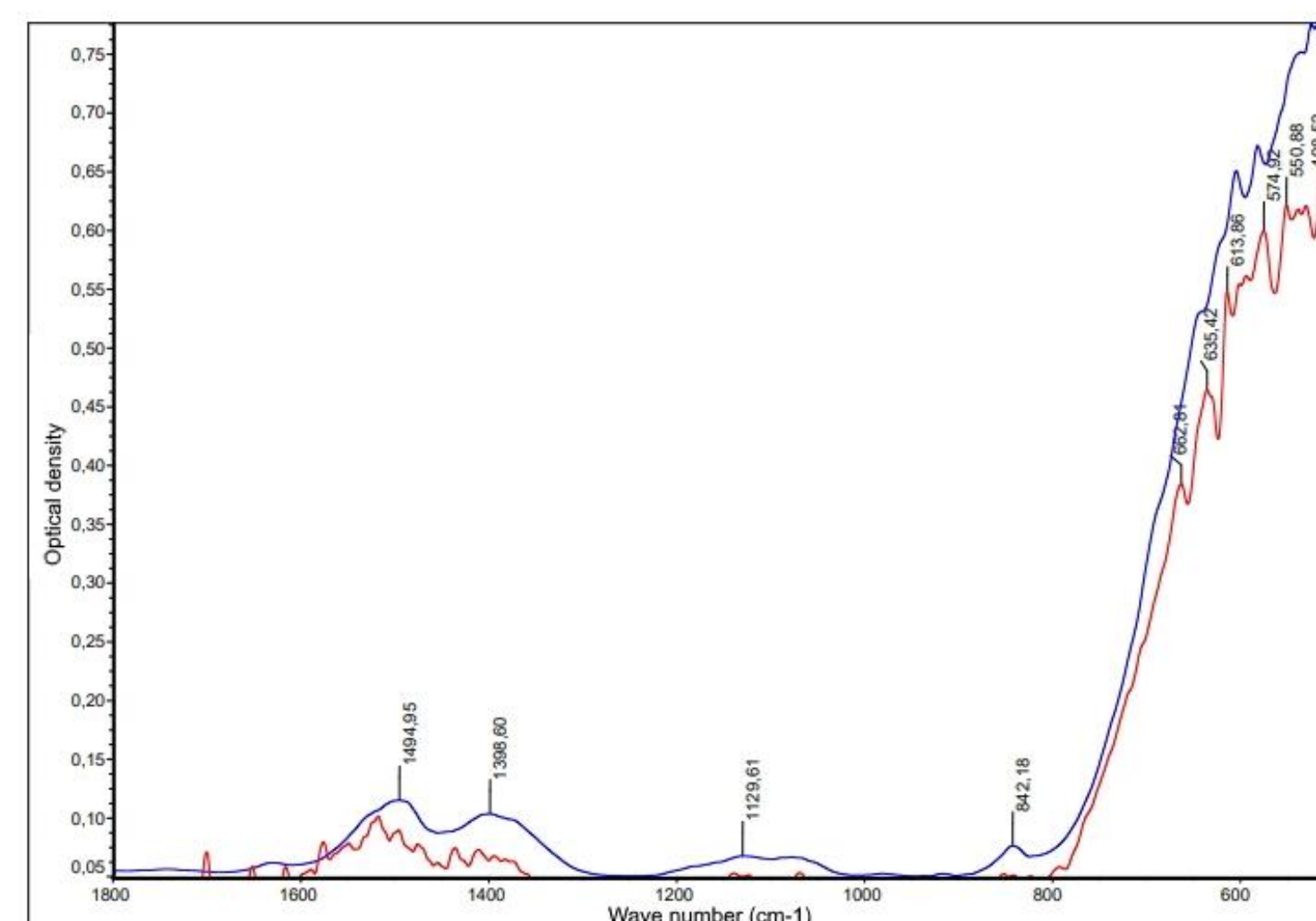


Figure 5 – The IR spectrum of a freshly prepared YIG precursor calcinated at 400 °C (blue) and 520 °C (red).

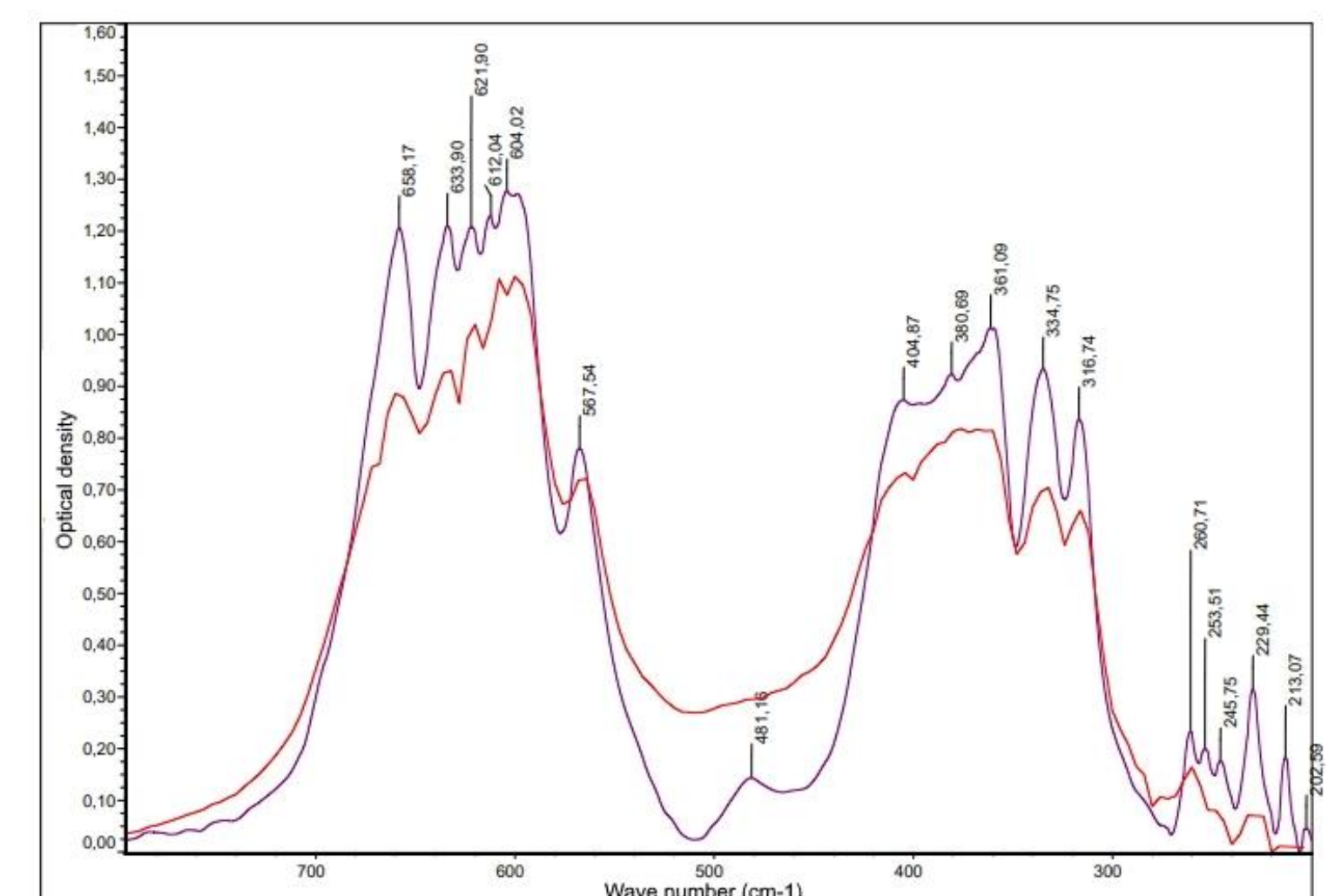


Figure 6 – The IR spectrum of a freshly prepared YIG precursor calcinated at 600 °C (red) and 800 °C (blue).

The calculation of Gibbs free energy (Figure 7) showed that the chemical feasibility of the YIG structure formation is preferable in comparison with YFeO<sub>3</sub>, since its thermodynamic stability increases with increasing temperature. It can be seen from the graph that, compared with yttrium orthoferrite, the formation of YIG is thermodynamically more favorable both in reaction (2) and in reaction (3).

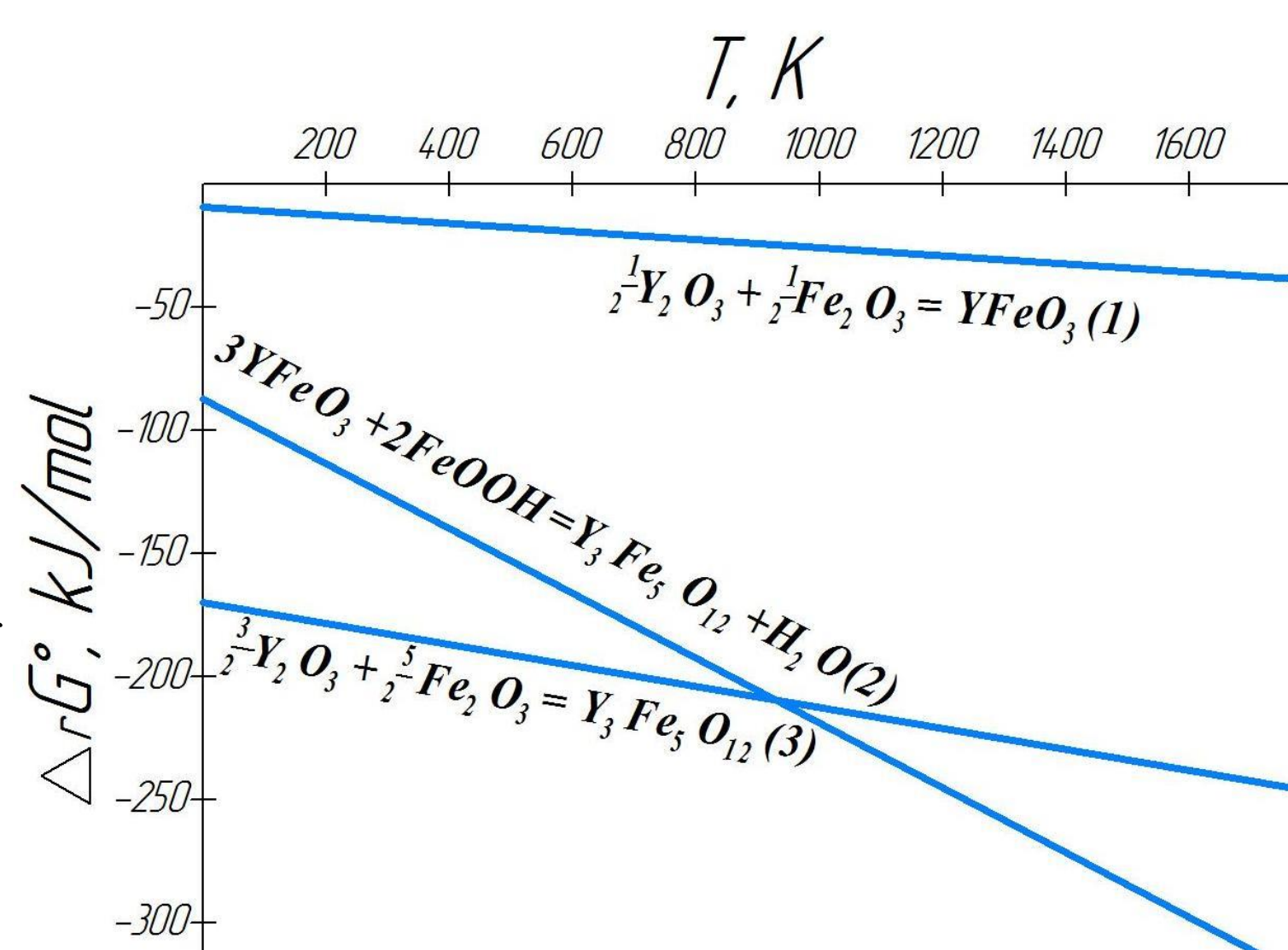


Figure 7 – Graphical representation of the change in the standard Gibbs energy of reactions (1), (2), and (3).

## CONCLUSION

Thus, both thermodynamic and kinetic approaches lead to the same results. The effect of supercritical CO<sub>2</sub> on the mechanical mixture of acetates in the quasi-equilibrium state causes an abnormally high mobility of the structure elements. As a result, it becomes possible to form the equilibrium phase of the YIG solid product directly (without the appearance of transition oxides) at temperatures much lower than during solid-phase synthesis. The temperature decrease in this case can be justified by a significant decrease in the activation energy and the active state of the solid solution obtained as a result of SAS.

This work was supported by the Ministry of Science and Higher Education (project of the Russian Foundation for Basic Research No 18-29-06013).