Mendeleev Commun., 2004, 14(4), 145–146

Synthesis of multicomponent ferrites by microwave treatment of nitrate mixtures

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DOI: 10.1070/MC2004v014n04ABEH001957

A systematic approach to the synthesis of ferrites by microwave-assisted decomposition of nitrate mixtures was developed to obtain single-phase multicomponent ferrites.

Microwave treatment provides non-contact heating, an inverted temperature gradient, direct energy transfer, and selective heating of reaction mixture components.[1]

However, only a few articles were dedicated to the microwave-assisted solid-state synthesis of complex oxides, for example, vanadates[2] and niobates.[3] This is probably due to the fact that many oxide phases are poor microwave susceptors at ambient temperatures. Usually, this problem is solved by addition of chemically inert compounds, for example, carbon or SiC, to the reaction mixture (so-called ‘hybrid’ microwave heating). The main demerit of this practice lies in almost inevitable product contamination with a suscepting phase, which is impermissible in the synthesis of functional materials.

Here, we present a systematic approach to the synthesis of multicomponent ferrites by microwave-assisted decomposition of nitrate mixtures. Note that this synthetic path, which leads to oxide product formation through decomposition of salt mixtures, has various advantages over a traditional ceramic procedure because oxide phases formed by salt mixture decomposition are homogeneously mixed and possess enhanced reactivity due to the high concentration of defects. At the same time, microwave treatment dramatically shortens the duration of synthesis due to uniform heating and ‘non-thermal’ effects.[4] This provides an opportunity to control the microstructure and functional properties of synthesised materials.

We found previously[5] that microwave irradiation can be successfully applied to the synthesis of binary ferrite materials from nitrate mixtures. In this work, a microwave synthesis of more chemically complex ferrites was carried out.

Analytical-grade $Mn(NO_3)_2\cdot 6H_2O$, $Fe(NO_3)_3\cdot 9H_2O$, $Co(NO_3)_2\times$ $\times 6H_2O$, $Ni(NO_3)_2\cdot 6H_2O$, $Cu(NO_3)_2\cdot 6H_2O$ and ZnO were used as starting reagents. The salts were mixed in stoichiometric proportions for the synthesis of $Cu_{0.5}Zn_{0.5}Fe_2O_4$, $Co_{0.5}Zn_{0.5}Fe_2O_4$, $Mn_{0.5}Ni_{0.5}Fe_2O_4$, and $Mn_{0.33}Ni_{0.33}Zn_{0.33}Fe_2O_4$, ground in an agate mortar, placed in alumina crucibles ($V = 80$ ml) and exposed to microwave irradiation for 15 min. Microwave treatment was carried out in a Samsung M1712R microwave oven (650 W, 2.45 GHz). Check runs were carried out by introducing nitrate mixtures into a muffle furnace for 15 min at a temperature reached during the microwave processing of the same mixture.

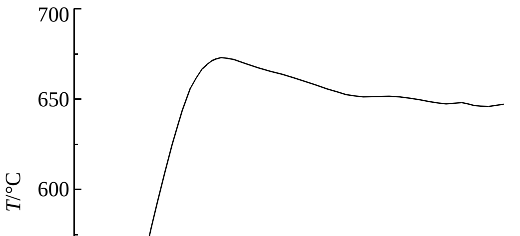

Figure 1 Typical time dependence of temperature during the microwave treatment of salt mixtures for spinel ferrite synthesis ($Co_{0.5}Zn_{0.5}Fe_2O_4$).

Table 1 Phase composition of microwave and thermally treated samples.

Initial mixture	Microwave treatment (15 min)	Thermal treatment (15 min)
$0.5Cu(NO_3)_2$ + $0.5ZnO$ + $2Fe(NO_3)_3$	100% $Cu_{0.5}Zn_{0.5}Fe_2O_4$	75% $Cu_{0.5}Zn_{0.5}Fe_2O_4$ 25% mixture of individual oxides
$0.5Co(NO_3)_2$ + $0.5ZnO$ + $2Fe(NO_3)_3$	100% $Co_{0.5}Zn_{0.5}Fe_2O_4$	75% $Co_{0.5}Zn_{0.5}Fe_2O_4$ 25% mixture of individual oxides
$0.5Mn(NO_3)_2$ + $0.5Ni(NO_3)_2$ + $2Fe(NO_3)_3$	100% $Mn_{0.5}Ni_{0.5}Fe_2O_4$	70% $Mn_{0.5}Ni_{0.5}Fe_2O_4$ 30% mixture of individual oxides
$0.33Ni(NO_3)_2$ + $0.33Mn(NO_3)_2$ + $0.33ZnO$ + $2Fe(NO_3)_3$	100% $Mn_{0.33}Ni_{0.33}Zn_{0.33}Fe_2O_4$	75% $Mn_{0.33}Ni_{0.33}Zn_{0.33}Fe_2O_4$ 25% mixture of individual oxides

The samples were characterised by X-ray powder diffraction (DRON-3M diffractometer, CuKα radiation). The X-ray diffraction patterns were analysed using the JSPDS database.

During the microwave treatment of all mixtures, nitrates rapidly melted and boiled in their crystal water for 2–3 min. After water evaporation, melted nitrate mixtures decomposed with the release of gaseous HNO_3 and NO_2. The final temperature reached during ferrite syntheses was 640–670 °C (Figure 1).

According to XRD data (Table 1), microwave treatment leads to the formation of single-phase multicomponent oxide products with the cationic composition corresponding to that of the initial mixtures. The degree of ferritization in check runs accounts for 70–75%, and complete transformation is achieved only after calcination in a muffle furnace for 10 h at 700 °C.

Therefore, microwave irradiation significantly accelerates the reactions of multicomponent ferrite formation. This is probably due to the fact that the temperature of the reaction mixture raises much more rapidly during microwave treatment than in the case of conventional thermal treatment. It is well known that microwave treatment leads to the uniform heating of the sample, whereas conventional heating results in a non-uniform heat distribution, and the reaction proceeds predominantly from the periphery of the reaction bulk to its centre. This results in the formation of individual oxide phase nuclei evenly distributed in the sample volume. These nuclei possess extremely high reactivity and their homogenious distribution largely eliminates diffusion barriers during a phase formation process. This supposition was confirmed by additional experiments. The samples of individual manganese, cobalt and copper nitrate hydrates were treated for 5, 10 and 15 min in microwave and conventional muffle ovens at the same temperature. It was shown that coherent scattering domain (CSD) sizes for oxide powders synthesised by microwave-assisted decomposition are 1.5–2 orders smaller. Moreover, it was found that the rate of CSD growth in a microwave field is significantly higher than during conventional thermal treatment. It is reasonable to suggest that widely discussed ‘non-thermal’ effects of microwave treatment,[4] which consist in the intensification of diffusion processes with the application of high-frequency electromagnetic fields, play a significant role in the enhancement of solid-state reactions in a microwave field.

Note that using microwave irradiation we obtained a single-phase ferrite that contains four cations ($Mn_{0.33}Ni_{0.33}Zn_{0.33}Fe_2O_4$)

in 15 min. Thus, the developed technique of salt–oxide mixture decomposition in a microwave field allowed us to synthesise oxide compounds of any chemical complexity.

Therefore, microwave treatment dramatically shortened the duration of the synthesis of multicomponent ferrites. This effect provides support to the discussed concept of the enhancement of diffusion processes under microwave irradiation caused by ionic currents on the crystallite interfaces.

This work was supported by the Complex Programme of the Russian Academy of Sciences ‘New Principles and Methods for Creating and Synthesis of Substances with Given Properties’, the Programme ‘Leading Scientific Schools’ (project no. 00-15-97435), the Russian Foundation for Basic Research (grant no. 02-03-33263) and the Programme ‘Universities of Russia’ (project no. UR.06.01.003).

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Received: 3rd June 2004; Com. 04/2282