Preliminary study on a new solid solution $Co_{2-x}Mg_xFeV_3O_{11}$: synthesis, thermal stability and IR spectra

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Physicochemical properties of solid solutions can be modified through the changes in their compositions and therefore they are very important for designing of new functional materials with desirable electric, magnetic, thermal or catalytic properties.

The aim of the presented work was to check whether in the system $Co_2FeV_3O_{11}$–$Mg_2FeV_3O_{11}$ a solid solution is formed and if it is so – the second main point was to investigate the effect of the composition change of the obtained phase on its thermal stability. Considering the approximate values of Co^{2+} and Mg^{2+} radii in MO_6 polyhedra [1] it can be expected that a substitutional solid solution $Co_{2-x}Mg_xFeV_3O_{11}$ should be formed. Both of the mentioned $M_2FeV_3O_{11}$ (M = Co, Mg) compounds contain isolated tetrahedra VO_4 in their structures [2,3]. It is known from literature that phases with such polyhedra in the structure are catalytically active inter alia in oxidative dehydrogenation of organic compounds [4]. Therefore, new solid solution formed in the system $Co_2FeV_3O_{11}$–$Mg_2FeV_3O_{11}$ could be considered as component of potential catalyst with modifiable properties.

Three mixtures of separately obtained $Co_2FeV_3O_{11}$ and $Mg_2FeV_3O_{11}$, weighed in the molar ratio of 0.5:1.5, 1:1, 1.5:0.5, were prepared for the preliminary investigation. The obtained samples, after homogenizing, were heated in air at 680ºC in two 20-h stages, with intermediate grinding. On the base of the XRD and DTA analysis results of the samples after their heating it has been stated that they were monophase, so the following reactions occurred:

$$(1\text{-}0.5x)\ Co_2FeV_3O_{11(s)} + 0.5x\ Mg_2FeV_3O_{11(s)} = Co_{2-x}Mg_xFeV_3O_{11(ss)} \qquad (\text{for } x = 0.5,\ 1,\ 1.5)$$

The phase of the composition $Co_{1.5}Mg_{0.5}FeV_3O_{11}$ has been also obtained as a result of reaction occurring between vanadates, i.e. during heating their mixture in two stages: 580ºC (20h) + 680ºC(20h), according to the equation:

$$0.75\ Co_2V_2O_{7(s)} + 0.25\ Mg_2V_2O_{7(s)} + FeVO_{4(s)} = Co_{1.5}Mg_{0.5}FeV_3O_{11(ss)}$$

whereas the phase of the composition $CoMgFeV_3O_{11}$ has been also obtained as a result of reaction between oxides and precursors of oxides, i.e. during heating their mixture in two stages: 580ºC (20h) + 590ºC(20h), according to the equation:

$$3MgCO_3\cdot Mg(OH)_2\cdot 3H_2O_{(s)} + 4\ CoCO_{3(s)} + 6\ V_2O_{5(s)} + 2\ Fe_2O_{3(s)} = 4\ CoMgFeV_3O_{11(ss)} + 7\ CO_{2(g)} + 4\ H_2O_{(g)}$$

Applying DTA method thermal stability of new solid solution was investigated. It has been stated that the obtained $Co_{2-x}Mg_xFeV_3O_{11(ss)}$ phase melts at a temperature depending on its composition and ranging from 860 (for x = 0.5), through 910 (for x = 1.0) to 960±5ºC (for x = 1.5), so the thermal stability of the new phase increases with increasing the degree of Mg^{2+} ions incorporation into the crystal lattice of $Co_2FeV_3O_{11}$. With the increase in replacement of Co^{2+} by Mg^{2+} ions, changes in IR spectra of solid solution were also observed, i.e. positions of IR absorption bands shift slightly to the higher wave numbers.

On the basis of the results obtained so far it can be concluded that in the system $Co_2FeV_3O_{11}$–$Mg_2FeV_3O_{11}$ a new substitutional solid solution is formed.
The work is being continued in order to establish the homogeneity range of $Co_{2-x}Mg_xFeV_3O_{11}$.

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