SONOCHEMICAL SYNTHESIS AND CHARACTERIZATION OF NANOSIZED COPPER ALUMINATE SPINEL

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In the present work, copper aluminate ($CuAl_2O_4$) nanoparticles were synthesised by sonochemical method. X-ray diffraction analysis revealed that the synthesised crystals are of cubic spinel structure. The analysis confirmed the presence of γ -Al_2O_3 phase in the synthesized product. An increase in the concentration of Cu ions relative to Al ions in the solution changes the color of the powder. This is associated with the change in the ratio of $CuAl_2O_4$ crystallites to γ-Al_2O_3 crystallites. The size of spinel crystallites were found to be 7-10 nm in size.

Keywords: sonochemical, spinel, nanoparticles, $CuAl_2O_4$, γ -Al_2O_3, X-ray diffraction
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INTRODUCTION

A wide range catalytic, electronic and optical properties allow the use of transition metal oxide spinels in various fields of science and technique. Among the spinel-structured materials, Cu-based spinels exhibit high activity in many applications, especially in catalytic processes. Compared with some metals, the use of aluminate spinels is more favorable in terms of environmental safety. Copper aluminate ($CuAl_2O_4$) spinels are characterized by thermal stability, mechanical resistance, hydrophobicity and low surface acidity. Usually, the synthesis of metal aluminates requires temperatures above 1000°C and several days. To overcome these disadvantages, more useful methods such as co-precipitation, hydrothermal synthesis and sol-gel have been widely used in the preparation of $CuAl_2O_4$ spinel in recent times [1-4]. However, the main shortcomings of the majority of the methods are the use of a wide variety of reagents, multi-steps and high energy requirements. Compared to other methods, the sol-gel method is considered more affordable technology for the synthesis of $CuAl_2O_4$ spinel, as it enables the production of particles with a homogeneous composition and small size at relatively low temperature [3,4]. The authors used diethanolamine as a new fuel for the sol-gel auto-combustion synthesis of nanocrystalline $NiAl_2O_4$, $CuAl_2O_4$ and $ZnAl_2O_4$ alumina spinels in their research [5]. The results of X-ray diffraction (XRD) analysis showed that the average crystal size of single-phase $CuAl_2O_4$ aluminate spinel obtained by this way was 62 nm after calcination at 1000°C. The high energy consumption and the large size of the obtained nanoparticles are the main disadvantages limiting the application of this method.

The main goal of this research was the synthesis of $CuAl_2O_4$ spinel with homogenous structure by sonochemical method. Both the crystalline structure and the sizes of the crystallites were determined. Raman sectroscopy analysis was carried out.

EXPERIMENTAL

Preparation of $CuAl_2O_4$ spinel

For the synthesis of nanoparicles of $CuAl_2O_4$ spinel containing 12% CuO 5 g dry $AlCl_3$ was dissolved in 50 ml deionized (DI) water. 0.32 g of $CuCl_2 \cdot 2H_2O$ salt was crushed in a mortar and after adding 50 ml of DI water was mixed in a ultrasonic bath with a frequency of 68 kHz for 1 hour. During this time, due to the effect of ultrasonic waves, the water temperature rised to 62ºC. At the end, the mixed solution turns into a completely clear blue liquid. The beaker containing the solution was heated on a magnetic stirrer (stirring at a speed of 1500 rpm) and 5.91 g of NaOH solution dissolved in 50 ml of DI water was gradually added to it dropwise for half an hour. As the amount of alkali increases, the solution turns light brown. The temperature of the solution was raised to 80ºC and was additionally mixed for 30 min. When the mixing process was stopped, rapid precipitation occurrred in the obtained gel-like solution. The precipitate was separated from the solution by centrifugation, washed repeatedly with DI water until pH was reached 8, and after drying at 80ºC for 2 hours, thermally treated at 800ºC for 5 hours. As a result, a light brown powder was obtained. Synthesis of nano-sized $CuAl_2O_4$ spinel crystals containing 25% CuO was carried out by the same method using 0.67 g of $CuCl_2 \cdot 2H_2O$ salt and brown powder was obtained. For comparison, the nanoparticles of γ-Al_2O_3 and CuO were synthesized.

The XRD analysis of the obtained powdered substances were carried out using a D2 Faser Diffractometer device with CuKα radiation (Bruker, Germany). The Raman spectra of the samples were recorded in EnSpectr R532 Raman spectrometer within the wavenumber range of 300-1000 cm-1 at

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room temperature. In order to avoid false signals in the spectrum, the powdered samples were placed on a Si substrate.

RESULTS AND DISCUSSION

Structural analysis

The results of XRD analyses of γ-Al_2O_3, CuO and $CuAl_2O_4$ (containing 12 və 25 % Cu) nanocrystals are shown in Figure 1. As we can see in the Figure, $CuAl_2O_4$ phases obtained with both percentages of Cu are spinel having cubic structure (lattice constant a = 8.05500Å). XRD analysis of CuO confirms that it has a monoclinic structure. The intense peaks corresponding to 31.7° and 45.6° belonging to γ-Al_2O_3 also appeared in the spectrum of the sample containing 12 mass% Cu. In the spectrum of the sample containing 25 mass% Cu, these peaks are slightly shifted to larger angles. These peaks are not seen in the spectrum of CuO. In the spectra of spinel structures, the intense peak observed at 67° in the spectrum of γ -Al_2O_3 shifts to a smaller angle as the concentration of CuO increases. This corresponds to the weak 65.7° in the spectrum of CuO. From the abovementioned, it can be concluded that two phases are formed in the synthesised nanocrystal structure including $CuAl_2O_4$ with a cubic spinel structure (JCPDS No. 33-0448) and cubic γ -Al_2O_3 phase (JCPDS no: 00-001-1303). The peaks related to γ-Al_2O_3 can be explained by the fact that the calcination temperature (800ºC) creates conditions for the formation of the γ -Al_2O_3 phase along with the $CuAl_2O_4$ phase. We also assume that the concentration of Cu ions in the chemical solution is more than 3 times lower than that of Al ions concentration, which may resulted in smaller number of the crystals formed in the $CuAl_2O_4$ phase and crystallization of the remaining Al ions in the γ-Al_2O_3 phase. At both concentrations, CuO phase (JCPDS No. 45-0937) was not recorded in the $CuAl_2O_4$ spectra.

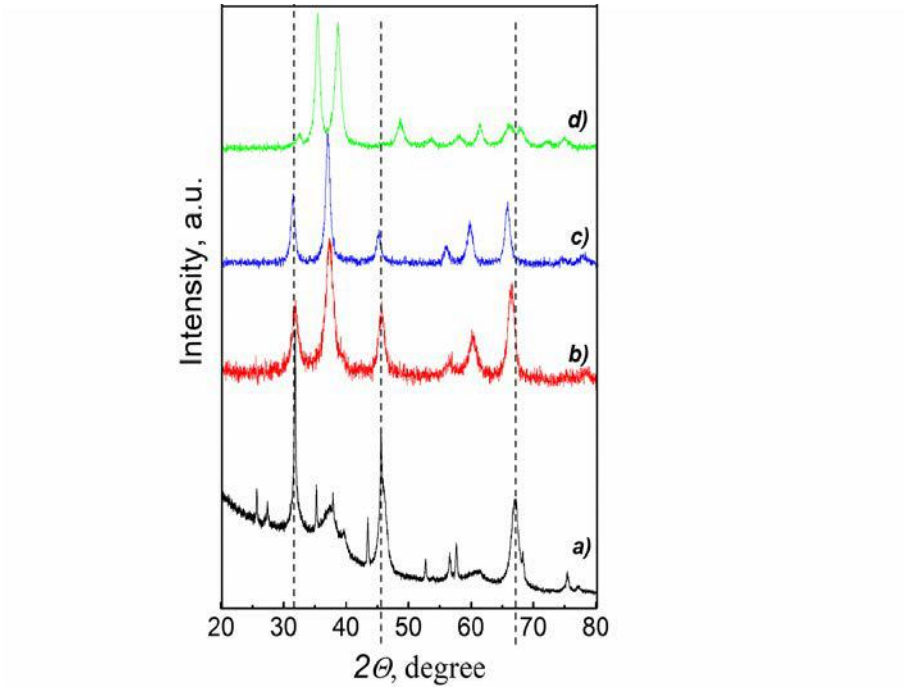

Fig. 1. XRD pattern of γ-Al_2O_3, CuO and $CuAl_2O_4$ (containing 12 və 25 % Cu)

The average crystallite size (D) of single-phase $CuAl_2O_4$ spinel crystals was calculated using Debye–Scherrer equation:

$$D = 0.9\,\lambda / \beta \cos\theta$$

where D is the average crystallite size, λ is the wavelength of the X-ray source (Cu Kα , 1.54 Å), β is the integral breadth of the diffraction peak, which was calculated from the full width at half maximum of the strongest diffraction peak (311), and θ is the Bragg's diffraction angle. According to the calculations, the average size of $CuAl_2O_4$ nanocrystals were are 10 and 7 nm for $CuAl_2O_4$ (12% Cu) and $CuAl_2O_4$ (25% Cu), respectively.

Figure 2 illustrates the nanocrystalline powders of CuO, $CuAl_2O_4$ (12% Cu), $CuAl_2O_4$ (25% Cu) and γ-Al_2O_3.

Raman analysis

The Raman spectrum of the samples obtained at room temperature in the range of 100-1000 cm-1 wavenumber is shown in Figure 3. The 400, 645 and 718 cm-1 peaks observed in the spectrum of $CuAl_2O_4$ containing 12% Cu were also observed in the spectrum of $CuAl_2O_4$ containing 25% Cu. These peaks belong to the γ-Al_2O_3 phase and are associated with vibrational modes of Al-O bonds [6]. A slight shift of the peaks confirms the formation of the $CuAl_2O_4$ phase [7].

Fig.2. Photoqraphs of a)CuO, b)$CuAl_2O_4$ (12% Cu), c)$CuAl_2O_4$ (25% Cu) and d)γ-Al_2O_3 crystals.

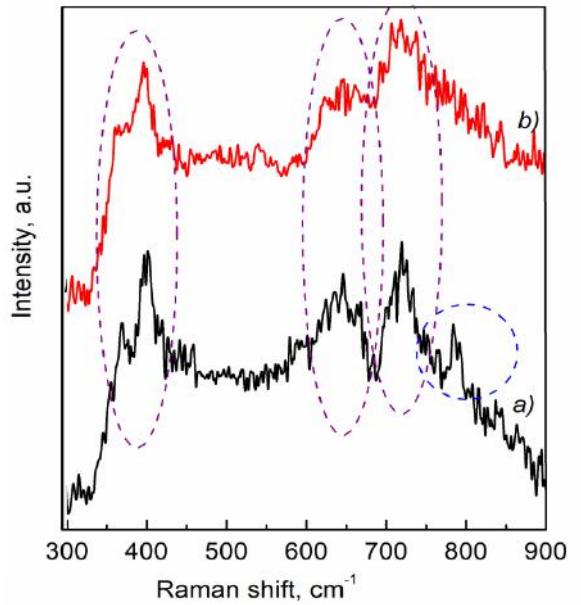

Fig.3. Room temperature Raman spectra of powders: a) $CuAl_2O_4$ (12% Cu) and b) $CuAl_2O_4$ (25% Cu)

CONCLUSION

$CuAl_2O_4$ phase was synthesized by sonochemical method with two different concentrations of Cu according to stoichiometry. XRD analysis showed that $CuAl_2O_4$ cubic spinel phase is present in the powdered substances obtained with both concentrations of Cu, and in addition, γ-Al_2O_3 phase was formed. The sizes of the as-synthesised nanoparticles are 7-10 nm. The results were also confirmed by Raman spectroscopic analysis.

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