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Synthesis of $MgAl_2O_4$ Nanopowders

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Abstract—A procedure has been developed for the synthesis of $MgAl_2O_4$ nanopowders with a characteristic particle size of 10–40 nm. Translucent hydrous xerogels have been synthesized as precursors to $MgAl_2O_4$. The synthesized magnesium aluminum spinel nanopowders are promising for the fabrication of optical ceramics.

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INTRODUCTION

Interest in the synthesis of magnesium aluminum spinel, $MgAl_2O_4$, stems from its unique physicochemical properties: high hardness (13.5 GPa), high melting point (2135°C), high thermal conductivity (15 W/(m K)), and chemical stability. Owing to this, it finds application in metallurgy, nuclear engineering, photonics, and other areas [1]. A number of applications require optically transparent ceramics. Various methods for the synthesis of $MgAl_2O_4$ powders have been reported in the literature: decomposition of precursors obtained by hydroxide coprecipitation from aqueous solutions of nitrates [1, 2] and chlorides [3]; reaction of a $Mg(NO_3)_2$ solution with a solid sodium aluminum hydroxide carbonate [4]; reactions of aluminum salts with ammonia solutions containing magnesium cations [3]; crystallization of $MgSO_4 \cdot Al_2(SO_4)_3 \cdot 22H_2O$ from a solution of magnesium and aluminum sulfates [3]; and mixing of hydrous magnesium and aluminum nitrates, followed by melting and decomposition [5].

The powders thus obtained were used to fabricate ceramics [2, 3]. The fabrication of ceramics using precursors allows one to reduce the process temperature in comparison with the sintering of $Al_2O_3 - Mg(OH)_2$ mixtures [6].

Even though a variety of approaches have been proposed for the fabrication of optical $MgAl_2O_4$ ceramics, process parameters have not yet been optimized.

This paper presents a continuation of our studies concerned with the synthesis of nanopowders of various compounds from aqueous solutions. Previously, we reported syntheses of magnesium, aluminum, and yttrium oxides from precipitates obtained by a similar technique [7, 8].

EXPERIMENTAL AND RESULTS

The starting chemicals used were analytical-grade magnesium oxide, OSCh 17-3 aluminum nitrate nonahydrate, analytical-grade nitric acid, a concentrated solution of analytical-grade NH_4OH, and distilled water. The synthesized powders were characterized by X-ray diffraction (XRD) (DRON-4 diffractometer, pyrolytic graphite monochromator, CuK_α radiation), thermal analysis (MOM Q-1500 D thermoanalytical system), and scanning electron microscopy (JEOL JSM-5910). The crystallite size D and lattice strain ε were determined by XRD on a URD-63 diffractometer. D and ε were calculated as described elsewhere [9]. Lattice parameters were determined using the Powder 2.0 program.

An extensive analysis of the literature prompted us to use coprecipitation from aqueous nitrate solutions with aqueous ammonia as the precipitant. This method offers the advantages of simplified apparatus, high reaction rates, and low cost. First, we prepared a 0.2 M magnesium nitrate solution and a 0.28 M aluminum nitrate solution, which were then mixed on a magnetic stirrer. To the resultant nitrate solution was added dropwise a 25% NH_4OH solution until precipitation. The curve describing the mixing process is presented in Fig. 1. As seen, precipitation begins at pH 4 and reaches completion near pH 9. The latter pH value fits well with the conclusion drawn by Sokol et al. [3] that, at pH 9, the precipitate has the stoichiometric cation composition.

The precipitates were characterized by thermogravimetry at a heating rate of 10°C/min in the temperature range 20–1000°C (Fig. 2). The temperature was monitored with a 5°C accuracy. The differential thermal analysis (DTA) curve in Fig. 2 shows a number of exo- and endothermic peaks in the range 200–

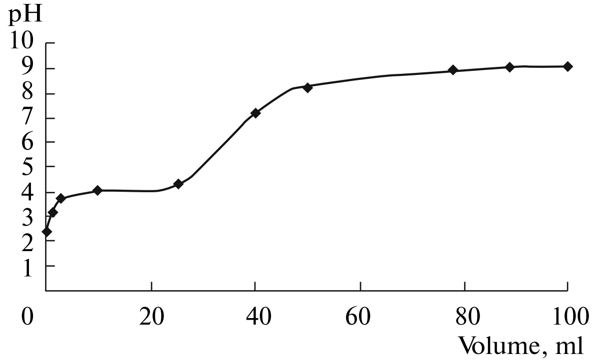

Fig. 1. Solution pH as a function of the added volume of NH_4OH solution.

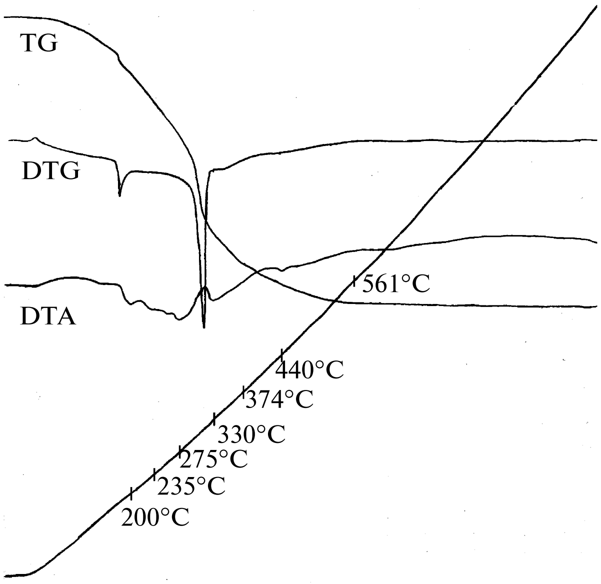

Fig. 2. Thermal analysis results for the precipitate used as a precursor to magnesium aluminum spinel.

Parameters of $MgAl_2O_4$ nanoparticles

t_{ann}, °C	D, nm	$\varepsilon \times 10^3$
565	11	20.3
800	41	20.0
1000	13	5.7

400°C, which are attributable to dehydration of the precipitate and $MgAl_2O_4$ crystallization. The sample weight stabilizes near 560°C. The total weight loss is 51.8%.

Based on the thermogravimetry data, we selected annealing temperatures for identifying phase transformations and evaluating the particle size and lattice strain of the powders. The samples were heated to the intended temperature at a rate of 10°C/min. The XRD data are presented in Fig. 3. Figure 3a shows the XRD pattern of the unannealed precipitate, which comprises amorphous and crystalline components. Heating leads to amorphization of the material (Figs. 3b–3e). Starting at 565°C, we observe formation of a cubic spinel phase. The lattice parameter of the powder heated to 1000°C was determined to be $a = 8.077(8)$ Å. This lattice parameter is close to the value given in the ICDD PDF database (#84-0377, $a = 8.080$ Å), suggesting that we obtained $MgAl_2O_4$. XRD data were used to evaluate the crystallite size and lattice strain of the samples heated to 565, 800, and 1000°C (table).

It can be seen from the table that, at the temperature where the sample weight stabilizes, the particle size is 11 nm and there is high lattice strain. Further heating markedly increases the particle size (by a factor of 4). At still higher temperatures, both D and ε drop sharply. This is accompanied by changes in the shape of XRD peaks. Similar behavior of the crystallite size and lattice strain was reported for yttrium oxide [8] and solid solutions between barium and rare-earth fluorides [10].

Working out the synthesis procedure, we obtained, like Ledovskaya et al. [1], translucent xerogels with a characteristic size of 3–5 mm. Their photographs are presented in Fig. 4. The translucent xerogels were similar in appearance to materials synthesized in an earlier study [10].

To determine the morphology and size of the synthesized particles, the translucent xerogels were examined by scanning electron microscopy (Fig. 5). Prior to examination, the samples were dried at 150°C (primary dehydration). In the micrograph in Fig. 5a, one can discern agglomerated particles about 20 nm in size, which are aligned to form chains.

In the micrograph of the $MgAl_2O_4$ sample heated to 1000°C (Fig. 5b) and then furnace-cooled, one can discern agglomerates of particles about 50 nm in size. The discrepancy between the scanning electron microscopy and XRD data (table) for 1000°C is most likely due to nanoparticle relaxation processes.

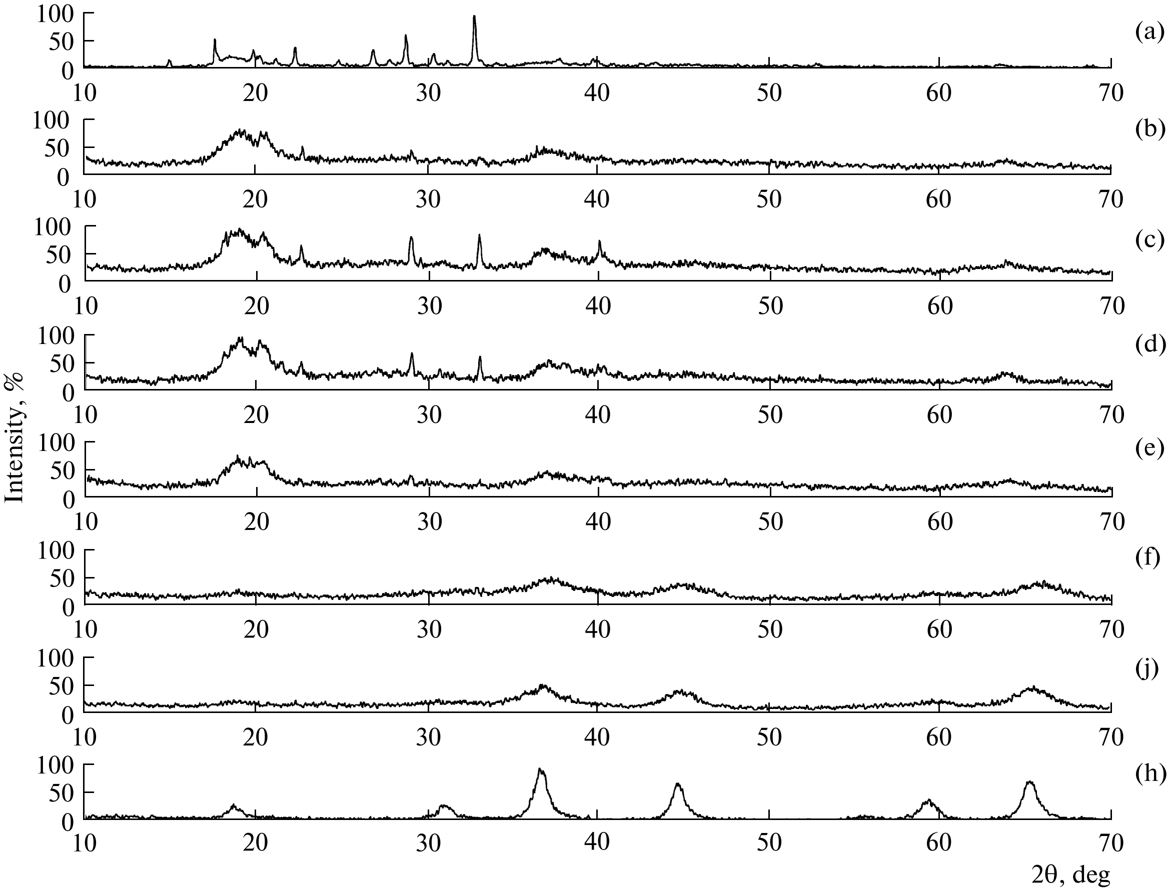

Fig. 3. XRD patterns of samples heated to (b) 220, (c) 235, (d) 275, (e) 330, (f) 565, (g) 800, and (h) 1000°C; (a) precipitate.

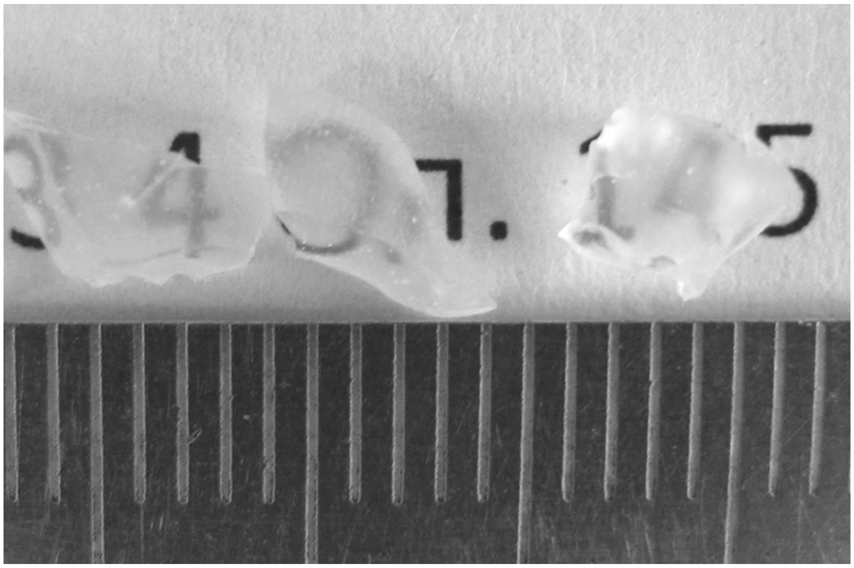

Fig. 4. Photographs of translucent xerogels used as precursors to magnesium aluminum spinel. The mean sample thickness is 2.3 mm.

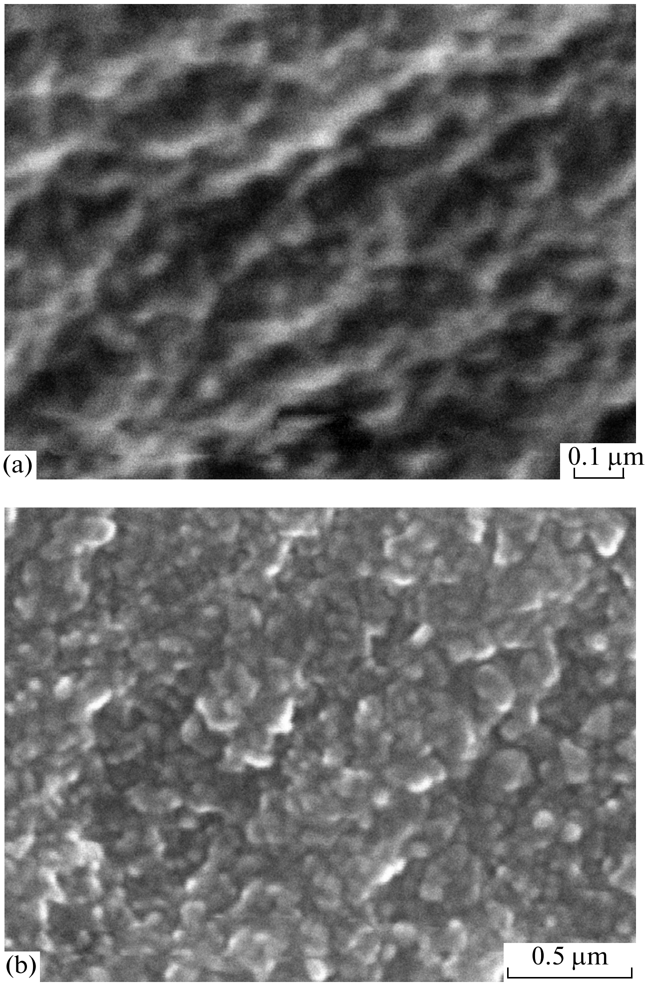

Fig. 5. Micrographs of powders heated to (a) 150 and (b) 1000°C.

CONCLUSIONS

$MgAl_2O_4$ nanopowders have been synthesized via precipitation from aqueous solutions. The present results demonstrate the possibility of producing translucent hydrous xerogels as precursors to $MgAl_2O_4$. The synthesized nanopowders are promising for the fabrication of optical $MgAl_2O_4$ nanoceramics.

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