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LETTERS
TO THE EDITOR

Features of the Synthesis of Aluminum–Magnesium Spinel Nanoparticles in the Potassium Chloride Melt

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The aluminum–magnesium spinel ceramics is transparent in visible and IR spectral regions and possesses mechanical strength and thermal stability characterized with high values of destruction viscosity, which allows it to be used in severe operating conditions under high thermal and mechanical loadings. The synthesis of a powdered material is one of stages of the ceramics preparation. Its future properties (namely, strength, hardness, porosity, and transparency) in many respects depend on the quality of this powder. A large number of methods of these materials reparation resulted from long-term research and development in nanotechnology. A sol–gel method widely applied to the preparation of nanocrystalline powders of metal oxides is noteworthy among such a variety.

The main requirements imposed on powders are size uniformity of particles, their shape, the absence of rigid agglomerates, and chemical and phase purity [1, 2].

There are a number of methods for the synthesis of nanocrystalline powders, the majority of which being insufficiently studied. Among them there is the sol–gel technology, which belongs to the youngest and most promising nanotechnologies. A disadvantage of such methods (based on polymeric gel decomposition) is the formation of a porous mass consisting of nanoparticles of synthesized oxides, which are formed in a strongly agglomerated state.

The aim of the present research is the synthesis of weakly agglomerated nanopowders using the example of aluminum-magnesium spinel ($MgAl_2O_4$). For this aim we have chosen the citrate gel version of the synthesis (the Pechini method).

As initial salts for the synthesis by the Pechini method we took solutions of magnesium and aluminum nitrates, to which a saturated solution of citric acid in the volume ratio of 1 : 1 was added. The equations of the corresponding reactions can be written as follows.

$$MgO + 2HNO_3 = Mg(NO_3)_2 + H_2O, \quad (1)$$

$$Al_2O_3 + 6HNO_3 = 2Al(NO_3)_3 + 3H_2O, \quad (2)$$

$$Me(NO_3)_3 + 3C_6H_8O_7 = [Me(C_6H_8O_7)_3](NO_3)_3. \quad (3)$$

When ethylene glycol was added to the formed metal complexes a polymeric dense transparent gel was obtained as a result of the etherification reaction. The gel was placed in a furnace in calcination crucibles heated up to a preset temperature and kept there for a certain time.

The approach to the development of the procedure for obtaining weakly agglomerated particles is based on [3] dedicated to the synthesis of lead metaniobate. Here the synthesis proceeds in an inert salt (sodium or potassium chloride) melt, in which niobium and lead oxides are soluble. In the course of the reaction the chloride melt dissolves reacting oxides, and the product of the reaction between them is precipitated. The resulting cake consists of product particles distributed in a solid chloride template. The product is readily separated from the chlorides by treating with water. As a result practically non-agglomerated eumorphic product particles are isolated.

Using the above-mentioned work as the base, we studied the version of the aluminum–magnesium spinel synthesis by a secondary calcination in a melt of an inert salt, which should prevent from sintering particles and their agglomeration. The following factors were taken into consideration in the salt choice: a temperature interval, in which the calcination will proceed (the salt should be nonvolatile and stable at the calcination temperature, but simultaneously it should be low-melting, as the synthesis should proceed in a salt melt); the salt should be easily removable from the system after calcination without the product contamination and should not react with synthesized oxides. We used KCl for the synthesis. Chemical inertness of the salt melt toward metal oxides was checked by means of thermodynamic calculations.

The procedure modification is as follows. A powder was prepared by the standard Pechini method. Resulting cake of aluminum–magnesium spinel was dispersed and then mixed in a mortar with potassium chloride in the ratio 1 : 1. The mixture was calcinated at a higher temperature. A water-soluble salt was removed from the sample by washing, and then the powder was dried. The conditions of the $MgAl_2O_4$ synthesis are defined by four key parameters: gel calcination temperature is 850°C, calcination time is 2 h; temperature of secondary calcination in the salt melt is 1000°C, and secondary calcination time is 2 h.

According to the X-ray phase data, the synthesized powders consist of the unique crystal phase of aluminum–magnesium spinel. To calculate changes in properties of nanocrystals from the X-ray data, we have analyzed line widths by the method described in [4]. Broadening of lines in the X-ray patterns occurs both because of the presence of small-size crystals and of lattice defects. The size of crystallites is 15–20 nm. The scanning electronic-microscopy study of the microstructure of powders has shown the presence of poorly agglomerated particles of size less than 200 nm.

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