Zol-gel synthesis of SiAlON materials dopped by rare-earth elements

S N Ivicheva, A S Lysenkov, N A Ovsyannikov and Yu F Kargin

Baikov Institute of Metallurgy and Materials Science of Russian Academy of Sciences, 119334, Moscow, Leninski pr., 49, Russia

E-mail: ivitcheva@mail.ru

Abstract. The phase composition and morphological features of sialons doped with REE (Eu, Tb, Ce) were studied by nitriding the mixed sol prepared on the basis of silicon and aluminum alkoxides without introducing the corresponding nitrides. It was established that as a result of nitriding of a REE doped Si-Al sol at 1650 °C, the β-SiAlON phases with a hexagonal crystal structure corresponding to β-Si3Al3O3N5 are formed. At a firing temperature of 1700 °C crystalline sialon types corresponding to the γ-phase with a monoclinic structure (Si2Al1O7N and Si6Al10O21N4) are formed. The effect of the addition of red-earth elements on the morphology of crystalline particles of the resulting sialon phases is shown.

1. Introduction

Complex nitride and oxonitride compounds, in particular, SIALON (SiALON) are promising matrices for doping with rare-earth ions and manufacturing phosphors and luminescent detectors of ionizing radiation [1-6]. Actual task is to study the influence of the method of synthesis of high-purity SiALON and the method of introducing doped REE ions on the luminescent properties of SIALONS.

Sol-gel methods for the synthesis of sialon materials make it possible to obtain high-purity and highly dispersed powders with a uniform introduction and distribution of sintering and dopants. Earlier [5, 6], the features of sialon synthesis with a nominal composition Si3Al3O3N5 were studied using silicon nitride or aluminum nitride and a mixture of silicon and aluminum nitrides as starting components using the corresponding silica or aluminum obtained by the sol – gel method [7].

The goal of this work was to obtain high-purity β-sialon (β-Si3Al3O5N5) doped REE (Eu, Tb, Ce, etc.) by nitriding the mixed sol prepared on the basis of silicon and aluminum alkoxides without introducing the corresponding nitrides.

2. Results and discussion

The silica obtained by its interaction with aluminate ions has a very strong specific interaction, which is proved by the extremely low solubility of aluminosilicate minerals, for example, such as alumina. It seems that the nitriding of highly dispersed mixed oxides will allow to obtain sialons with high functional characteristics. The special relationship between aluminum and silicon is probably explained by the fact that for both atoms the coordination number with respect to the oxygen atom can under appropriate circumstances have a value of 4 or 6, and also Al and Si have relatively close in magnitude ionic radii [8]. Therefore, the aluminate – ion Al(OH)4+ is geometrically similar to Si(OH)4 which promotes a closer interaction with the formation of a mixed oxide during subsequent nitriding.
of which it is possible to obtain high purity and uniformity of SiALON.

Interest in the use of aluminum and silicon alcoholates in the process of sialon synthesis is primarily due to the use of their hydrolysis products to obtain pure (by chemical and phase composition) and active highly dispersed silicon and aluminum oxides and more uniform distribution of REE, which are injected in the required amount into sol in the form of homogeneous acid solutions. Mixed oxides of aluminum and silicon obtained using alkoxotechnologies differ in structural and textural characteristics from traditional crystalline varieties and amorphous silicon and aluminum hydroxides obtained, for example, by the coprecipitation method. By varying the conditions of hydrolysis, one can influence the basic characteristics of the final product, including its particle size and phase composition. In addition, when forming the synthesis products, sol-gel methods allow one to obtain narrow-fractional spherical powders of micro- and nano-dimensions, which is especially important since the maximum contribution to the excess surface energy of the system, which is the driving force in the synthesis of ceramic material, increases significantly with decreasing particle sizes.

To prepare sols, alkoxides of silicon and aluminum were used: tetraethoxysilane \((\text{C}_2\text{H}_5\text{O})_4\text{Si}\) (TEOS), purity > 98% of Merck and aluminum sec-butoxide \(\text{Al(OCH(CH}_3\text{)}_2\text{CH}_2\text{CH}_3)_3\), prepared by reacting metallic aluminum with butyl alcohol in the presence of catalyst (compounds gallium). In the synthesis process, ethyl and isopropyl alcohols, mineral acids, oxides or nitrate salts of REE were also used. Gelation of a sol containing mixed hydrated particles of mixed oxides of silicon and aluminum doped with REE was carried out in air, the gels were aged at room temperature. Preheating and heat treatment to remove the products of hydrolysis of alkoxides of silicon and aluminum were not performed. The obtained Al-Si-xerogel powders were burned in corundum crucibles without preliminary pressing in a furnace with a graphite heater in a nitrogen atmosphere at temperatures of 1600-1700 °C for 2 hours.

![Figure 1. Photomicrograph SEM of the original x-ray amorphous mixed sol dried at room temperature](image)
To identify the phase and chemical composition of the initial xerogel powders and their calcination products (SiAlON), X-ray phase analysis was used. The morphology and structural features of the samples were studied using scanning electron microscopy. The change in the morphology of the mixed particles of silica and aluminum oxides before and after calcination at 1600 °C in nitrogen atmosphere is shown in microphotographs (SEM), Figure 1 and 2. The initial sol dried at room temperature is represented by agglomerates 2-5 µm in size from spherical nanoparticles 20-50 nm (Figure 1). After calcination at 1600 °C of the sol doped with Ce, the resulting ceramic sample consists of intergrowths of prismatic crystals of elongated shape with an average cross section of 1 µm and a length of 2-4 µm (Figure 2).

![Figure 2. Micrograph of the SEM of a SiAlON sample doped with Ce after calcination at 1600 °C in a nitrogen atmosphere](image)

According to X-ray analysis the sialon samples obtained by nitriding doped with REE mixed Si-Al sol at 1650°C are β-SiAlON powders with a hexagonal crystal structure corresponding to the Si$_3$Al$_3$O$_3$N$_5$ phase. However, on X-ray diffraction patterns, all X-ray reflections are shifted toward larger angles which is probably due to the introduction of rare-earth elements, which differ in size from silicon and aluminum ions. With an increase in the firing temperature to 1700°C according to XRD in addition to Si$_3$Al$_3$O$_3$N$_5$ other crystalline sialons Si$_2$Al$_3$O$_7$N (35-0023) and Si$_6$Al$_{10}$O$_{21}$N$_4$ (36-0832) are observed [JCPDS-International Center for Diffraction Data. All rights reserved PCPDFWIN v.2.4, 2003], characterized as a χ-phase with a monoclinic structure in which there is some deficiency in Si probably due to the volatility of SiO which can be formed in the reducing environment of the experiment. According to SEM data the appearance of the χ-phase of sialon is manifested by the
elongation of crystals and the appearance of whiskers penetrating the structure of crystallites (Figure 3).

Figure 3. Microphotographs of Tb doped SEM SiAlON after calcination at 1700 °C.

Acknowledgments
The work was supported by the Russian Foundation for Basic Research, project No. 17-03-00630a.

References
[1] Shyan-Lung Chung, Shu-Chi Huang, Wei-Chi Chou and Wira Wibisono Tangguh 2014 Current Opinion in Chemical Engineering 3 62
[2] Dhia A Hassan, Jian Xua, Yibin Chena, Langkai Lia, Renjie Zenga 2016 Materials Research Bulletin 79 69
[3] Young Jun Yun, Jin Kyu Kim, Ji Young Ju, Seul Ki Choi, Woon Ik Park, Ha-kyun Jung, Yongseon Kim, and Sungho Choi 2016 Inorganic Chemistry 55 8750
[4] Yuwaraj K Kshetri, Bhupendra Joshi, Soo Woon Lee 2016 Journal of the European Ceramic Society 36 4215
[5] Slesarev A I, Ivicheva S N, Lysenkov A S, Kargin Yu F, Solntsev K A, Ishchenko A V, Yagodin V V, Shul’gin B V 2017 Problemy spektroskopii and spektrometrii 38 3
[6] Yagodin V V, Ishchenko A V, Ivicheva S N, Lysenkov A S, Ovsyannikov N A, Kargin Yu F, Baibalova G F 2018 Problemy spektroskopii and spektrometrii 40 87
[7] S. N. Ivicheva, A. S. Lysenkov, N. A. Ovsyannikov, D. D. Titov and Yu. F. Kargin 2018 IOP Conference Series: Materials Science and Engineering 347 012046
[8] Ailer R K 1982 Chemistry of silica (Moscow: MIR) p 712