Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 41 (2015) 10616–10623

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

# Kinetics and formation mechanism of yttrium aluminum garnet from an amorphous phase prepared by the sol–gel method

Alexander M. Kutyin[a,b], Elena Ye. Rostokina[a,b,*], Evgeny M. Gavrishchuk[a,b], Victor V. Drobotenko[a,b], Alexander D. Plekhovich[a,b], Pavel A. Yunin[b,c]

[a]*G.G. Devyatykh Institute of Chemistry of High-Purity Substances, Russian Academy of Sciences, 49 Tropinina Str., Nizhny Novgorod 603950, Russia*
[b]*Lobachevsky State University, 23 Prospekt Gagarina, Nizhny Novgorod 603950, Russia*
[c]*Institute for Physics of Microstructures, Russian Academy of Sciences, GSP-105, Nizhny Novgorod 603950 Russia*

Received 5 March 2015; received in revised form 27 April 2015; accepted 28 April 2015
Available online 7 May 2015

## Abstract

Isothermal crystallization kinetics was studied for $Y_3Al_5O_{12}$ obtained from amorphous dispersed phases based on aggregately stable sols of yttrium aluminum hydroxides. To describe the formation of yttrium aluminum garnet from the amorphous phases, a mathematical model involving intermediate $Y_4Al_2O_9$ and $YAlO_3$ phases has been proposed. From the obtained experimental data on the phase composition of the crystallizing system, kinetic parameters of the crystallization process were determined, which allowed us to propose a probable mechanism of YAG crystallization from hydrosols of various composition. The actual mechanism of garnet formation depends not just on the temperature treatment conditions of the amorphous phase, but also on the type of the precursors. The optimization of the time–temperature regimes of YAG crystallization allowed preparation of samples with required properties. Thus, the sol–gel method involving sols of high stability towards aggregation is shown to be promising for the production of high-quality powders and optical ceramics of yttrium aluminum garnet.

*Keywords:* Sol–gel processes; YAG; Phase transformation kinetics; Computational model

## 1. Introduction

Ceramics based on yttrium aluminum garnet ($Y_3Al_5O_{12}$ or YAG) is a promising material for creation of active elements of high-power solid-state lasers in the near-infrared wavelength range [1–4]. In modern production technologies of ceramic materials with high optical characteristics, one of the most important stages is preparation of the appropriate nanopowders. For synthesis of high-quality YAG powders, the methods of "soft" chemistry are considered as very promising, with hydrothermal synthesis [5,6], combustion synthesis [7,8], sol–gel method [3,9–11], and co-precipitation method [12–14] being the most commonly used. In these methods, mixing of the reactants on the atomic scale increases the reaction rates and lowers the temperature of the powder synthesis, as well as the temperature of subsequent heat treatment for polycrystal formation. Many different precursors can be used, with their appropriate pre-purification, and a great variety of the routes of amorphous phase synthesis are possible. This allows efficient control of fundamental parameters of the process, such as the crystallization temperature, the final grain size, as well as morphology, dispersity and purity of the material. Among these approaches, the sol–gel method provides for the most of these opportunities, being a relatively simple method for synthesis of pure powders of uniform composition at relatively low temperatures.

Though YAG is a well-studied material, the available data on kinetics and mechanism of its crystallization are rather scarce. It was noted [15,16] that the high-temperature conversion of a mixture of aluminum and yttrium oxides in the solid-phase synthesis of yttrium aluminum garnet could proceed via

---

[*] Corresponding author at: G.G. Devyatykh Institute of Chemistry of High-Purity Substances, Russian Academy of Sciences, 49 Tropinina Str., Nizhny Novgorod 603950, Russia. Tel.: +7 908 739 4381.
*E-mail address:* lena_rostokina@mail.ru (E.Ye. Rostokina).

http://dx.doi.org/10.1016/j.ceramint.2015.04.161
0272-8842/© 2015 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

a chain of consecutive reactions $Y_4Al_2O_9$ (YAM) → $YAlO_3$ (YAP) → $Y_3Al_5O_{12}$ (YAG). It is generally assumed that the $YAlO_3$ phase is characterized by a distorted orthorhombic perovskite structure (YAP). However, the studies of kinetics and modeling of the yttrium aluminum garnet crystallization in these systems mostly considered only the final stage of the formation of the YAG phase, with little attention to the effects caused by various series-parallel reactions of the impurity phases [17–19,20(a),(b)].

Many studies of the yttrium aluminum garnet formation from the amorphous phase were carried out for single-phase systems, with crystallization of YAG directly from the amorphous phase in the absence of eventual impurity phases [4,7,21–23]. In these papers, the nature of the rate-limiting step and the mechanism of the processes were discussed basing on the kinetic (or dimensional) parameters, and the proposed interpretation varied considerably among the authors. Practically no studies of the kinetics of garnet crystallization in the diphasic gels were reported [24–26].

To clear up the YAG crystalline phase formation mechanism and determine the effective activation energy values, the dynamic methods are often used, such as differential thermal analysis (DTA) and differential scanning calorimetry (DSC) [10,21–23]. However, in complex systems with simultaneous crystallization of several phases multiple overlapping peaks are often recorded in the non-isothermal mode of thermal analysis, and many problems arise in identification of these phases.

Thermographic studies of YAG solid-phase synthesis under isothermal conditions, though they are more simple and informative, are carried out very rarely due to long time of the experiment at high temperatures [4,24,27]. However, with the sol–gel method the measurement temperature can be considerably decreased. This makes the isothermal modes more accessible and applicable for identification of the new phases and studies of the mechanism of their formation.

In our work, crystallization kinetics of YAG formation from amorphous dispersed phases based on aggregately stable yttrium aluminum hydroxide sols was studied under isothermal conditions. Our aim was to clear up the mechanism of YAG crystallization by analysis of the obtained experimental data and mathematical modeling of the processes of chemical and phase transformations in these systems.

## 2. Experimental

The starting materials for the synthesis of yttrium aluminum garnet samples were yttrium oxide ($Y_2O_3$, 99.99% purity), aluminum isopropoxide ($Al(i\text{-}OC_3H_7)_3$, 99.99% purity), nitric acid ($HNO_3$, 99.99% purity) and acetic acid ($CH_3COOH$, 99.9% purity).

The nanosized powder of yttrium oxide was obtained by self-propagating high-temperature synthesis (SHS) from yttrium acetate nitrates, as reported previously [28]. Yttrium hydroxyacetate sols ($Y(OH)_2(OOCCH_3)$) were prepared by the method described in [29]. Aqueous solutions of aluminum hydroxynitrates ($Al_n(NO_3)_3(OH)_{3n-3}\cdot 6H_2O$, where $n = 1$–6), were synthesized in the following way. The crushed crystalline aluminum isopropoxide was hydrolyzed by atmospheric moisture for two weeks with formation of amorphous $Al(OH)_3$ powder, which, in turn, was dissolved in water with addition of nitric acid (Al:$HNO_3$ ratio 1:0.5–3) at 90 °C and periodic stirring in an ultrasonic bath for 0.5–1 h. The boehmite sol (AlOOH) was obtained by peptization of boehmite powder by nitric acid (0.64 M) under stirring in an ultrasonic bath followed by heating in a water bath at 70–80 °C. As a result, a visually transparent sol was formed. The ratio of AlO(OH):$HNO_3$ was 1:0.07. The boehmite powder was synthesized by hydrolysis of aluminum isopropoxide in hot water at 80 °C, the $(i\text{-}PrO)_3Al$:$H_2O$ ratio was 1:100, as described in [30].

Yttrium–aluminum hydroxide hydrosols were prepared by mixing the appropriate starting reagents in a molar ratio of Y:Al = 3:5. The following methods were used:

I. SHS yttrium oxide powder was added to an aqueous solution of aluminum hydroxynitrate $Al_5(NO_3)_3(OH)_{12}$ during stirring in an ultrasonic bath. Subsequent heating of the slurry at 50 °C and periodic agitation in an ultrasonic bath for 3.5–4 h led to formation of stable slightly opalescent aluminum yttrium hydroxide sols, presumably of the composition $Y_3Al_5(NO_3)_3(OH)_{21}$ with concentration of 40 g/L (hereinafter, noted as yttrium aluminum garnet). The transition of $Y_3Al_5(NO_3)_3(OH)_{21}$ sol into gel occurred at concentration of 50–60 g/L.
II. Mixtures of boehmite and yttrium hydroxyacetate sols were treated in an ultrasonic bath until transparent aluminum yttrium hydroxyacetate sols $5AlOOH\cdot 3Y(OH)_2(OOCCH_3)$ with concentration of 80 g/L were obtained. Such sols are stable over time and turn into gel at concentration of 110 g/L.
III. Aluminum hydroxynitrate hydrosol $Al_5(NO_3)_3(OH)_{12}$ was mixed with yttrium hydroxyacetate sol ($Y(OH)_2(OOCCH_3)$) with subsequent treatment in an ultrasonic bath. As a result, transparent aggregately stable aluminum yttrium hydroxide sols $Al_5(NO_3)_3(OH)_{12}\cdot 3Y(OH)_2(OOCCH_3)$ with concentration of 60 g/L were obtained. Transition of aluminum yttrium hydroxyacetatenitrate sol into gel occurs at concentration of 175 g/L.

The obtained sols (methods I–III) were dried in a SNOL 20/300 LFN oven at 90–150 °C for 2 days to form xerogels. The obtained xerogels were milled in a planetary mill for 10 min and sieved through a laboratory sieve with the mesh size of 94 μm.

The obtained amorphous powders of aluminum yttrium hydroxides were annealed in a SNOL 6.7/1300 laboratory furnace in the temperature range of 850–1000 °C with different isothermal soaking times. The isothermal exposure time was measured from the moment of reaching the desired temperature. After completion of the aging, the furnace was rapidly cooled.

X-ray analysis of the synthesis products was carried out on a Bruker D8 Discover X-ray diffractometer with Cu Kα radiation, wavelength $\lambda = 1.5418$ Å. The measurements were carried out in a symmetric $\theta$–$2\theta$ geometry for the angular range $2\theta = 10$–$110°$ with a linear PSD LynxEye detector. All the samples were measured under identical experimental conditions. Qualitative phase analysis was carried out in Diffrac.EVA 2.0 program