

Sol-gel preparation and electrical behaviour of Ln: YAG (Ln = Ce, Nd, Ho, Er)

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Abstract: A sol-gel method has been developed to prepare pure yttrium aluminum garnet, $Y_3Al_5O_{12}$ (YAG), and rare-earth substituted ($Ce-Y_3Al_5O_{12}$, $Nd-Y_3Al_5O_{12}$, $Ho-Y_3Al_5O_{12}$, and $Er-Y_3Al_5O_{12}$) samples. The XRD patterns of the polycrystalline powders sintered at 1000 °C showed the formation of monophasic garnet materials. The micro-structural features in the polycrystalline samples were studied by scanning electron microscopy. A homogeneous distribution of rare-earth dopants in the YAG lattice was achieved in all of the cases. Electrical conductivity measurements were also performed on the compacts of sol-gel derived Ln-YAG samples. In contrast to the expected dielectric behaviour, the conducting properties of the examined specimens indicate metallic behaviour with the resistivity increasing gradually with increasing temperature.

Keywords: sol-gel synthesis, garnet crystals, rare-earth doping, electrical properties.

INTRODUCTION

Wet chemistry has been used for a long time for the preparation of oxide powders.¹ One of the main advantages of the sol-gel process for electronic applications is the easy deposition of thin films directly from the solution by techniques such as dipcoating, spin-coating or spray.² The sol-gel synthesis of metal oxides is based on the polymerization of inorganic molecular precursors in aqueous solution or metal alkoxides in non-aqueous media. Condensed species are formed during hydrolysis and condensation reactions leading to the growth of oxo/hydroxo oligomers, sols or gels which, on drying under ambient conditions, give a xerogel that still contains a large amount of water or other solvent. It is well known, that the morphology and physical properties of sol-gel derived ceramics strongly depend on the total chemical process.³

Compounds in the system $Y_2O_3 - Al_2O_3$ are promising materials for optical, electronic and structural applications. These oxides are attractive host materials for the development of advanced phosphors with their general chemical stability. The compound $3Y_2O_3 \cdot 5Al_2O_3$, commonly called a yttrium aluminum garnet ($Y_3Al_5O_{12}$, YAG), adopts

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the cubic garnet structure and, when doped with a transition metal or lanthanide element, is an important solid-state laser material widely used in luminescence systems, window materials for a variety of lamps, and for fiber-optic telecommunication systems.⁴⁻⁸ However, the discovery of advanced oxide phosphors with multiple superior qualities for display applications remains a difficult problem.^{9,10} The specific luminescence properties of multi-ary oxides are highly sensitive to changes in dopant composition, host stoichiometry, and processing conditions.^{11,12}

Lanthanide-doped yttrium aluminum garnet lasers are extensively used in research laboratories and in industry as a laser source, while different physical properties and microscopic processes and their effects on the laser performance continue to be under study.¹³⁻¹⁶ In the present work, the sinterability and microstructural evolution of lanthanide-doped yttrium aluminum garnet $\text{Ce-Y}_3\text{Al}_5\text{O}_{12}$, $\text{Nd-Y}_3\text{Al}_5\text{O}_{12}$, $\text{Ho-Y}_3\text{Al}_5\text{O}_{12}$, and $\text{Er-Y}_3\text{Al}_5\text{O}_{12}$ powders synthesized by an aqueous sol-gel process were investigated. The evaluated synthetic technique leading to Ln-YAG using an acetate-nitrate-glycolate intermediate illustrates the simplicity and superior potential of the proposed method.

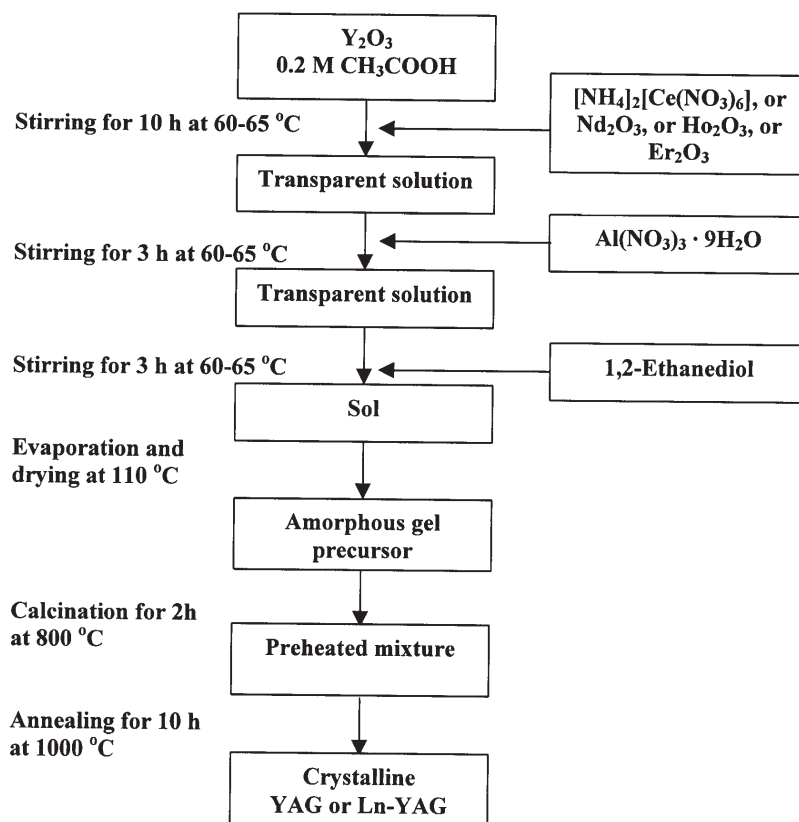


Fig. 1. Scheme of the steps involved in the sol-gel process used for the preparation of $\text{Y}_3\text{Al}_5\text{O}_{12}$ and Ln-doped (Ln = Ce, Nd, Ho, Er) $\text{Y}_3\text{Al}_5\text{O}_{12}$ ceramics.

EXPERIMENTAL

Five samples Ln:Y₃Al₅O₁₂ with different nominal composition, Y₃Al₅O₁₂ (YAG), Ce-Y₃Al₅O₁₂ (Ce-YAG), Nd-Y₃Al₅O₁₂ (Nd-YAG), Ho-Y₃Al₅O₁₂ (Ho-YAG), and Er-Y₃Al₅O₁₂ (Er-YAG) synthesized by a previously reported aqueous sol-gel method.¹⁷ The gels were prepared using stoichiometric amounts of analytical-grade Y₂O₃, [NH₄]₂[Ce(NO₃)₆], Nd₂O₃, Ho₂O₃, Er₂O₃ and Al(NO₃)₃·9H₂O as the starting materials. The mole ratio of Ln:YAG = 1:10 was selected for the all the doped garnet samples. In the sol-gel process, yttrium oxide (0.00375 mol; 0.847 g) was first dissolved in 0.2 M CH₃COOH at 60–65 °C. To this solution, ammonium cerium nitrate (0.00025 mol; 0.137 g) (Ce-YAG) dissolved in distilled water, or neodymium oxide (0.000125 mol; 0.042 g) (Nd-YAG), or holmium oxide (0.000125 mol; 0.047 g) (Ho-YAG), or erbium oxide (0.000125 mol; 0.048 g) (Er-YAG) dissolved in acetic acid were added. Then aluminum nitrate (0.0125 mol; 4.6875 g) dissolved in distilled water was added and the resulting mixtures were stirred for 3 h at the same temperature. In the following step, 1,2-ethanediol (2 mL) as a complexing agent was added to the above solutions. The acidic medium (pH ≈ 5) prevented the flocculation of metal hydroxides in the mixtures and no adjustment of pH was necessary. After concentrating the solutions by slow evaporation at 65 °C under stirring, the Y-Al-O and Ln:Y-Al-O acetate-nitrate-glycolate sols turned into transparent gels. The oven dried (110 °C) gels became light brown due to an initial decomposition of nitrates. The gel powders were ground in an agate mortar and preheated for 2 h at 800 °C in air. Since the gels are very combustible, slow heating (≈ 3–4 °C min⁻¹) especially between 100 and 400 °C was found to be essential. After an intermediate grinding in an agate mortar, the powders were additionally sintered for 10 h at 1000 °C in air. A schematic diagram of the processing steps involved in the sol-gel synthesis of the mixed-metal Y₂Al₅O₁₂ and Ln: Y₃Al₅O₁₂ garnet ceramics is shown in Fig. 1.

X-Ray powder diffraction (XRD) studies were performed on a STOE diffractometer operating with CuK α radiation. A scanning electron microscope (SEM) CAM SCAN S4 was used to study the morphology and microstructure of the ceramic samples. Energy dispersive X-ray (EDS) analysis was performed, under vacuum, in the specimen chamber of an EDS coupled SEM CAM SCAN S4. The electrical conductivities were measured on disk specimens (10 mm in diameter) of polycrystalline ceramics using the standard two-probe method as a function of temperature in the range 20–160 °C. The copper wire electrodes were attached to the sample pellets using a silver paste.

RESULTS AND DISCUSSION

In order to obtain the nanocrystalline Y₃Al₅O₁₂ phase, the appropriate Y(Ln)–Al–O precursor gels were calcined and sintered at 1000 °C in air. It is interesting to note that almost identical microstructures were observed for all the mixed-metal oxides regardless of the nature of the dopant. Typical scanning electron micrographs of all YAG and Ln-YAG specimens revealed very homogeneous samples consisting of differently shaped grains, with the formation of a continuous network of crystallites being evident. However, pores and voids was also detected, which probably result from escaping gases during calcination.¹⁸ The micrographs of the heat-treated powders also showed the formation of highly agglomerated, uniform, and crystalline particles with smooth surfaces. The SEM picture of a representative sample (Ho-doped YAG) is shown in Fig. 2.

Additionally, the Ln:Y:Al atomic ratios for the doped garnet samples were determined by EDS analysis. The average metal ratios for the different systems were calculated to be Ce : Y : Al = 1.2(1) : 37.2(3) : 61.6(3) (for Ce-YAG), Nd : Y : Al = 1.3(1) : 37.0(2) : 61.7(4) (for Nd-YAG), Ho : Y : Al = 1.2(1) : 36.9(5) : 61.9(5) (for Ho-YAG), and Er : Y : Al = 1.1(1) : 37.1(3) : 61.8(2) (for Er-YAG). The standard deviations of the distributions are given within the parentheses. These results show that the syntheses yielded homogeneous

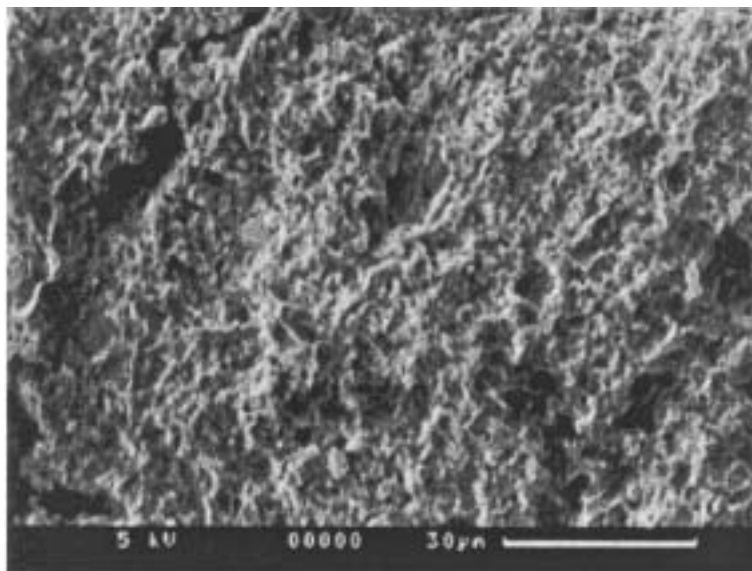


Fig. 2. Scanning electron micrograph of a Ho-doped $Y_3Al_5O_{12}$ ceramic sample.

ceramic materials, with composition near to the desirable metal ratio. Light or dark regions were not identified in the backscattered electron mode. Since the brightness of the specimen by BSE is homogeneous over the entire measuring area, most of the material is finely divided, *i.e.*, the distribution of its chemical elements is highly uniform.

These results were found to be consistent with the crystallization process observed by XRD measurements. It is interesting to note that almost identical XRD patterns were observed for all the Ln-doped mixed-metal oxides. The X-ray diffraction patterns for a representative sample (Er-doped YAG) is shown in Fig. 3.

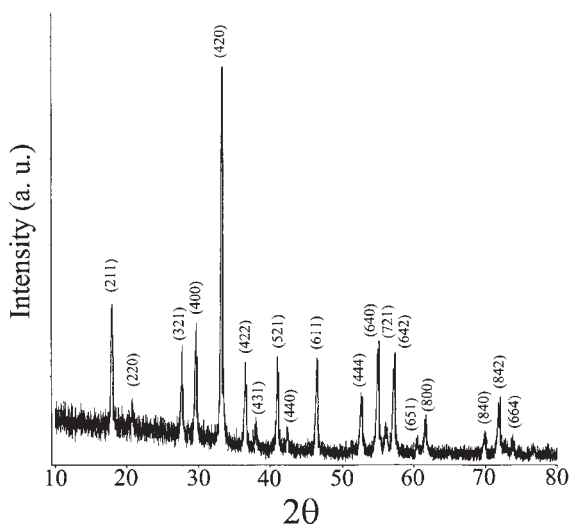


Fig. 3. X-Ray diffraction pattern of a Er-doped $Y_3Al_5O_{12}$ ceramic sample synthesized by the sol-gel method at 1000 °C.

Sintering at 1000 °C produced fully crystallized single-phase Er-Y₃Al₅O₁₂ with a well pronounced garnet crystal structure.^{19,20} The results are also in a good agreement with the reference data for Y₃Al₅O₁₂ (PDF [33–40]). The X-ray diffraction data of the garnet sample are presented in Table I. As can be seen, all single lines are indexed, and no unindexed lines could be observed. The most intensive lines are (420) – 100 %, (211) – 39 %, and (400) – 37 %. Therefore, it can be concluded that the sol-gel synthesis gave well-developed rare-earth doped YAG at 1000 °C and no formation of crystalline dopant oxide Ln₂O₃ was observed. The formation of a single mixed-metal Ln-Y₃Al₅O₁₂ phase with a homogeneous distribution of the dopant element already at 1000 °C emphasizes that this synthesis temperature is rather low for such kinds of ceramic materials.

TABLE I. X-Ray powder diffraction data of a Er-Y₃Al₅O₁₂ sample. Number of indexed lines = 19. Number of unindexed lines = 0

Miller indices			<i>d</i> - spacing /Å	Free parameter (intensity) / %
<i>h</i>	<i>k</i>	<i>l</i>		
2	1	1	4.999	38.9
2	2	0	4.328	5.9
3	2	1	3.273	29.6
4	0	0	3.062	37.0
4	2	0	2.738	100.0
4	2	2	2.500	26.9
4	3	1	2.401	6.1
5	2	1	2.236	27.8
4	4	0	2.164	5.0
6	1	1	1.987	27.7
4	4	4	1.768	14.8
6	4	0	1.698	29.9
7	2	1	1.667	5.8
6	4	2	1.637	29.4
6	5	1	1.555	4.2
8	0	0	1.531	7.8
8	4	0	1.369	5.7
8	4	2	1.299	14.7
8	4	0	1.234	4.6

The electrical conductivity measurements were performed on compacts of Ln-YAG which is known to be a typically high resistance material. Previously, however, it was demonstrated that the conducting properties of the examined Y₃Al₅O₁₂ specimen indicated metallic behaviour with the resistivity value increasing gradually with increasing temperature.¹⁷ Here the influence of lanthanide doping on the observed electrical conductivity of YAG was investigated (Fig. 4).

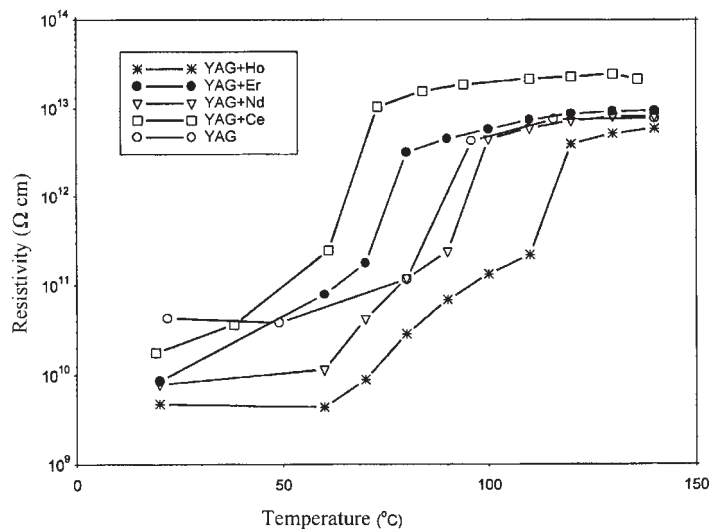


Fig. 4. Resistivity-temperature characteristics of $Y_3Al_5O_{12}$ and $Ln-Y_3Al_5O_{12}$ samples synthesized by the sol-gel method at $1000^\circ C$.

As can be seen, all of the samples clearly show the PTCR (positive temperature coefficient of resistivity) effect which is characterized by a rapid increase in the electrical resistance as the temperature is increased over the ferroelectric transition temperature (Curie point).^{21,22} The resistivity jump of all synthesized samples was about 2.5 orders of magnitude in the temperature range $20-140^\circ C$. However, the Curie point depends considerably on the nature of rare-earth element (Table II). In contrast to the observed electric behaviour of the YAG samples, resistivity measurements on alumina and yttria specimens prepared from individual gels showed the samples to be electrically insulating.

TABLE II. The approximate Curie points of the synthesized $Ln-Y_3Al_5O_{12}$ samples

Sample	$T_C/^\circ C$
$Y_3Al_5O_{12}$	75
Ce- $Y_3Al_5O_{12}$	57
Nd- $Y_3Al_5O_{12}$	65
Ho- $Y_3Al_5O_{12}$	60
Er- $Y_3Al_5O_{12}$	68

Electrical conduction in solids is generally determined by two parameters: carrier concentration and carrier mobility. Oxides, which are predominantly ionic compounds, are the most exploited high-temperature materials. In general, the overall transport properties of oxides are determined by defects formed in response to both impurities and deviations from stoichiometry.²³ However, the important question concerning the reasons of the observed unusual electrical behaviour of the garnet samples remains to be answered. We believe that the observed increased resistivity values at higher temperatures might result from

the trapping of charge carriers in the grain boundaries. For example, it has been reported for yttria stabilized tetragonal zirconia that compacts with crystallite size smaller than 50 nm show semi-conducting properties where as compacts with crystallite size greater than 50 nm show metallic behaviour.²⁴ Another noticeable feature is the high dielectric strength of the samples,²⁵ *i.e.*, they withstand high voltages (> 1000 V) without undergoing any degradation or becoming electrically conducting.

CONCLUSIONS

A sample sol-gel chemistry synthetic approach has been developed to obtain crystalline yttrium aluminum garnet by heat treatment of metal chelates at temperatures (1000 °C) lower than those required for the solid-state synthesis (> 1600 °C). Besides, homogeneously rare-earth doped YAG ceramics could easily be obtained by the proposed method. The as-synthesized Ln–Y₃Al₅O₁₂ samples exhibited a PTCR effect, having almost identical resistivity jump. The Curie point, however, of the samples appeared to be dependent on the nature of the dopant element. Some of the advantages of the proposed sol-gel synthesis method, *e.g.*, low sintering temperature (1000 °C) of Ln–YAG samples, excellent homogeneity and control of stoichiometry, high phase purity, were also demonstrated in the present study. Thus, the acetate-nitrate-glycolate sol-gel process offers unique opportunities for the synthesis of optical materials, since it is suitable for the production of thin/thick films, monoliths and fibers. Moreover, the proposed aqueous sol-gel method is inexpensive and thus appropriate for the large-scale production of new materials.

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ИЗВОД

СОЛ-ГЕЛ СИНТЕЗА И ЕЛЕКТРИЧНЕ КАРАКТЕРИСТИКЕ

Ln:YAG (Ln = Ce, Nd, Ho, Er)

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Развијена је сол-гел метода за добијање чистих итријум алуминијум граната, Y₃Al₅O₁₂ (YAG), као и супституисаних граната са ретким земљама (Ce-Y₃Al₅O₁₂, Nd-Y₃Al₅O₁₂, Ho-Y₃Al₅O₁₂, и Er-Y₃Al₅O₁₂). Рендгенограми поликристалних прахова синтерованих на 1000 °C показују стварање монофазног граната. Микроструктурне особине поликристалних узорака проучаване су скенирајућом електронском микроскопијом. У свим случајевима постигнута је хомогена дистрибуција допаната у YAG решеткама. Електрична проводљивост је мерена за све узорке Ln-YAG компактних узорака. Уместо очекиваног диелектричног понашања, испитани узорци показивали су металну проводљивост са специфичном отпорношћу која се лагано повећавала са температуром.

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