Lanthanide-doped YAG synthesis via sol–gel process: microstructural, electrical and magnetic properties

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Yttrium aluminium 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 have been prepared by a sol-gel method. The monophasic polycrystalline powders were obtained by sintering precusor gels at 1000 °C. The microstructural 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. The electrical conductivity measurements were performed on the compacts of sol-gel-derived Ln–YAG samples. In contrast to the expected dielectric behaviour, the conducting properties of the specimens indicated a metallic behaviour with the resistivity value increasing gradually on increasing the temperature. The magnetic properties of rare-earth doped specimens were found to be quite different from those of pure YAG. The magnetic susceptibility showed almost temperature-independent paramagnetism for rare-earth-doped YAG samples.

Key words: garnet crystals, rare-earth doping, microstructure, electrical and magnetic properties

INTRODUCTION

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. Yttrium aluminium garnet ($Y_3Al_5O_{12}$, YAG) adopts the cubic garnet structure, and when doped with a transition metal or lanthanide element, YAG 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 [1–5].

Lanthanide-doped yttrium aluminum garnet laser is extensively used in research laboratories and in industry as a laser source, while different physical properties as well as microscopic processes and their effects in laser performance continue to be under study [6–8]. Previously we have demonstrated that monophasic yttrium aluminium garnet powders with homogeneously distributed lanthanide elements within the garnet matrice can be successfully synthesized by an aqueous sol-gel process. The evaluated synthetic technique to Ln-YAG using acetate–nitrate–glycolate intermediate illustrates the simplicity and superior potential of the proposed method [9–11].

The purpose of this work was to study the specific microstructural, electrical and magnetic properties of the sol-gel-derived $Y_3Al_5O_{12}$ and Ln–$Y_3Al_5O_{12}$ (Ln = Ce, Nd, Ho and Er) garnet compounds.

EXPERIMENTAL

$Y_3Al_5O_{12}$ (YAG), Ce–$Y_3Al_{52}O_{12}$ (Ce–YAG), Nd–$Y_3Al_5O_{12}$ (Nd–YAG), Ho–$Y_3Al_5O_{12}$ (Ho–YAG), and Er–$Y_3Al_5O_{12}$ (Er–YAG) samples were synthesized by the previously reported aqueous sol-gel method [9, 11]. The gels were prepared using stoichiometric amounts of analytical-grade Y_2O_3, $[NH_4]_2[Ce(NO_3)_6]$, Nd_2O_3, Ho_2O_3, Er_2O_3 and $Al(NO_3)_3 \cdot 9H_2O$ as starting materials. The molar ratio of Ln : YAG = = 1:10 was selected for all doped garnet samples. 1,2-ethanediol as a complexing agent was used in the sol-gel process. The oven-dried gels were ground in an agate mortar and preheated for 2 h at 800 °C in air. After an intermediate grinding in an agate mortar the powders were additionally sintered for 10 h at 1000 °C in air.

A CAM SCAN S4 scanning electron microscope (SEM) was used to study the morphology and microstructure of the ceramic samples. The energy dispersive X-ray (EDS) analysis was performed in vacuum, in the specimen chamber of an EDS-coupled SEM. The electrical conductivities were measured

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on disk specimens (10 mm in diameter) of polycrystalline ceramics by the standard two-probe method as a function of temperature in the range 20–160 °C. Copper wire electrodes were attached to the sample pellets using a silver paste. The magnetic susceptibility behaviour of garnets was studied with a SQUID magnetometer (Quantum Design, MPMS) in the temperature region between 20 K and 300 K using a static field.

RESULTS AND DISCUSSION

Previously [11] we have demonstrated by X-ray diffraction analysis that sintering Y(Ln)-Al-O precursor gels at 1000 °C produced fully crystallized single-phase garnet materials. Here, the textural properties of the calcined powders were investigated by SEM, from which the typical morphologies were obtained. It is interesting to note that an almost identical microstructure was observed for all mixed-metal oxides regardless the nature of lanthanide dopant. The typical scanning electron micrographs of all YAG and Ln-YAG specimens revealed very homogeneous samples consisting of differently shaped grains, and the formation of a continuous network of crystallites was evident. However, pores and voids were also detected, which probably resulted from the gases escaping during calcination [12]. The micrographs of heat-treated powders also showed formation of highly agglomerated, uniform and crystalline particles with smooth surfaces. The SEM pictures for two representative samples (Ho- and Er-doped YAG) are shown in Figs. 1 and 2, respectively.

Additionally, the Ln:Y:Al atomic ratios for the doped garnet samples were determined by EDS analysis. These results showed that the synthesis yielded homogeneous ceramic materials with th composition close to the desirable metal ratio. In the backscattered electron (BSE) mode the light or dark regions could not be identified (Fig. 3). Since the brightness of the specimen by BSE was homogeneous over the entire measuring area, most of the material was finely divided, *i.e.* the distribution of its chemical elements was highly uniform.

The electrical conductivity measurements were performed on the compacts of Ln–YAG which is known to be a typical high-resistance material. Pre-

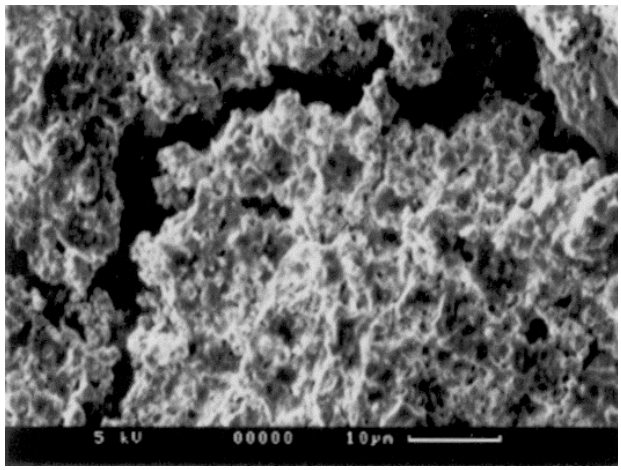

Fig. 2. Scanning electron micrograph of a Er-doped $Y_3Al_5O_{12}$ ceramic sample

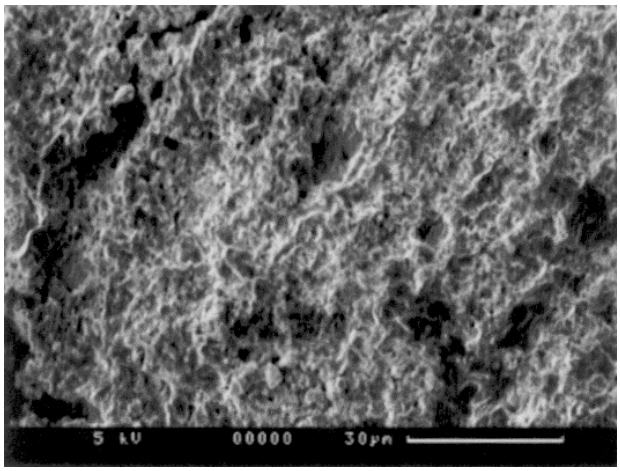

Fig. 1. Scanning electron micrograph of a Ho-doped $Y_3Al_5O_{12}$ ceramic sample

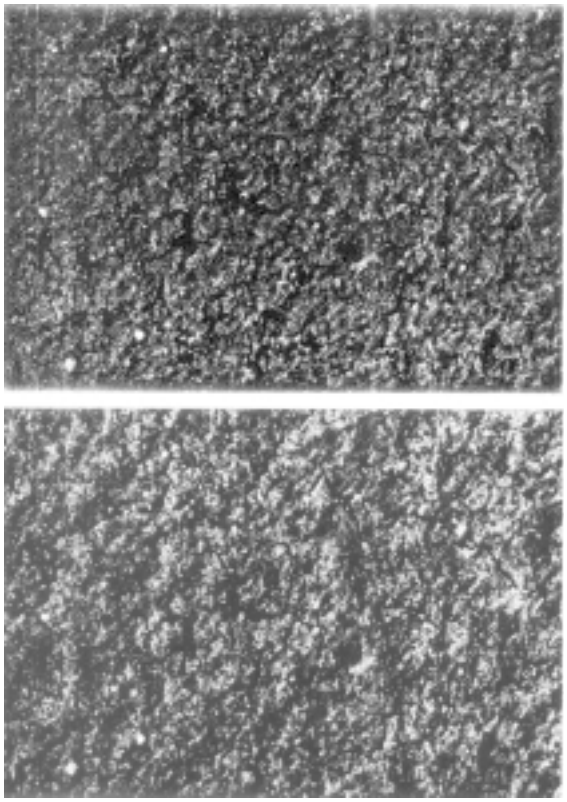

Fig. 3. Scanning electron micrographs of Ce-doped $Y_3Al_5O_{12}$ (a) and Nd-doped $Y_3Al_5O_{12}$ (b) garnets in backscattered electron mode

viously, however, we have demonstrated that the conducting properties of the examined $Y_3Al_5O_{12}$ specimen indicated a metallic behaviour with the resistivity value increasing gradually on increasing the temperature [9]. Here we investigated the influence of lanthanide doping on the observed electrical conductivity of the YAG (Fig. 4).

One can see that all of the samples clearly show the PTCR (positive temperature coefficient of resistivity) effect, which is characterized by a rapid increase in electrical resistance as the temperature is increased over the ferroelectric transition temperature (Curie point) [13, 14]. The resistivity jump of all synthesized samples was determined to be the 2.5 order of in about for the temperature range 20–140 °C. However, the Curie point depends considerably on the nature of the rare-earth element. In contrast to the observed electric behaviour of YAG samples, the resistivity measurements on the alumina and yttrium specimens prepared from individual gels revealed the samples to be electrically insulating (see Figs. 5 and 6, respectively).

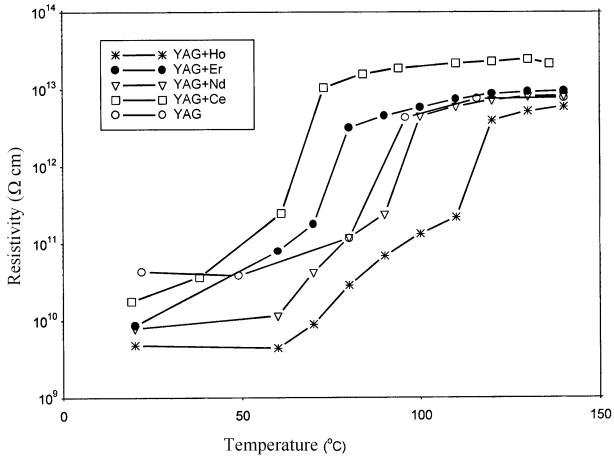

Fig. 4. Resistivity–temperature characteristics of Ln–YAG samples

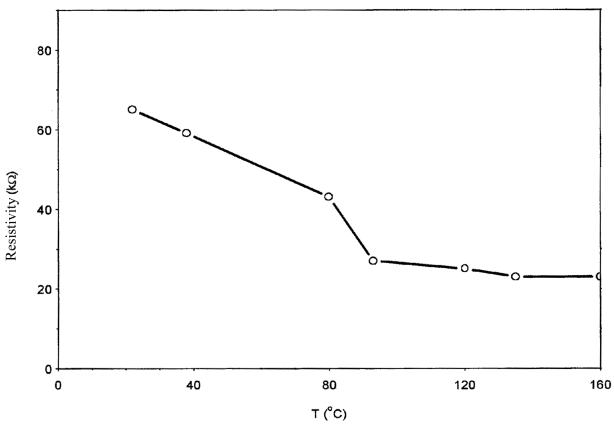

Fig. 5. Resistivity *vs.* temperature for aluminium oxide prepared by sol-gel method

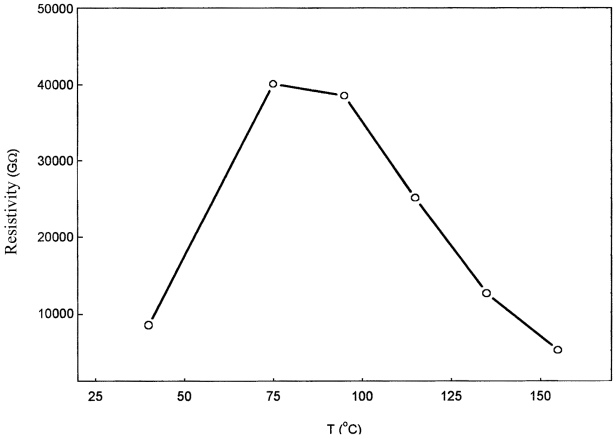

Fig. 6. Resistivity *vs.* temperature for yttrium oxide prepared by sol–gel method

The 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 the defects formed in response to both impurities and deviations from stoichiometry [15]. However, the important question concerning the reasons of such an unusual electrical behaviour in the garnet samples remains to be answered. We believe that he high resistivity values observed at a higher temperature might result from the trapping of charge carriers in the grain boundaries. For example, it has been reported for yttriuen-stabilized tetragonal zirconia that compacts with the crystallite size less than 50 nm show semi-conducting properties, whereas compacts with the crystallite size more than 50 nm show a metallic behaviour [16]. Another noticeable feature is the high dielectric strength of the samples [17], *i.e.* they withstand high voltages (>1000 V) without undergoing any degradation or becoming electrically conducting.

The temperature dependences of the magnetic susceptibility of the representative two Nd- and Er-doped YAG samples are shown in Figs. 7 and 8, respectively. The susceptibilities are very small. Down to about 75 K the susceptibilities are nearly temperature-independent with the room temperature values of ~0.001 emu/mol, initially suggesting diamagnetism [18, 19]. However, below 75 K the susceptibilities increase slightly, which might be attributed to the magnetism of the rare-earth atoms [20].

After correction for the diamagnetic momenta the monitored susceptibility data were treated with a modified Curie–Weiss law [21–23]:

$$\chi = \chi_o + C/(T-\Theta), \quad (1)$$

where χ is the molar susceptibility, χ_o is the temperature-independent susceptibility, C is the Curie–Weiss constant, which is related to the effective magnetic moment μ_{eff}, and Θ is the Curie–Weiss temperature.

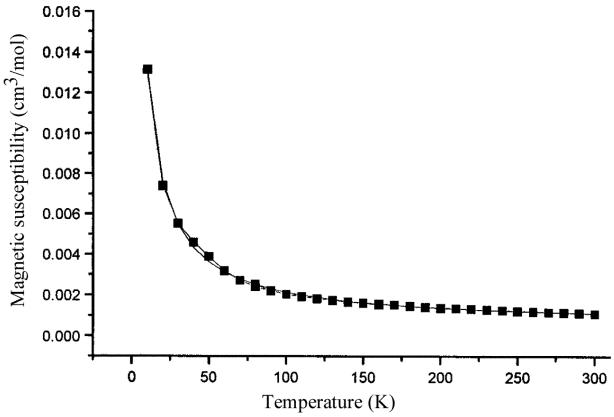

Fig. 7. Molar magnetic susceptibility of Nd-doped YAG plotted as a function of the temperature

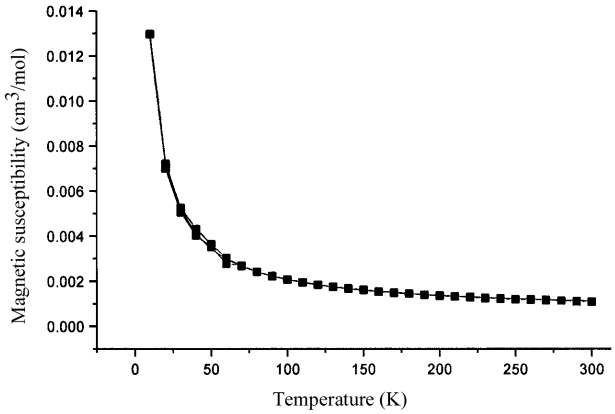

Fig. 8. Molar magnetic susceptibility of Er-doped YAG plotted as a function of the temperature

From the small Θ values (–2.7961 K for the Nd-doped YAG and –1.6900 K for the Er-doped YAG), we can conclude that the susceptibilities for both samples follow well the Curie–Weiss law and exhibit the Pauli paramagnetism [24], and only very small interactions between the responsible momenta occur [25]. From the calculated χ_o values (0.00058 cm^3/mol for the Nd-doped YAG and 0.00065 cm^3/mol for the Er-doped YAG), one can see that there is a temperature-independent positive contribution to the molar susceptibilities of the samples studied [26]. The calculated experimental magnetic momenta for one formula unit of Ln–YAG were found to be μ_{exp} = 1.13 Bohr magnetons (B. M.) for the Nd-doped YAG and μ_{exp} = 1.07 B.M. for the Er-doped YAG. Moreover, these values claculated for every temperature point are nearly constant in the whole temperature range (see Fig. 9). Thus, the susceptibility data clearly indicate that the synthesized Ln–YAG samples at low temperatures show a paramgnetic Curie-like increase attributed to the contribution of small amounts of dopants.

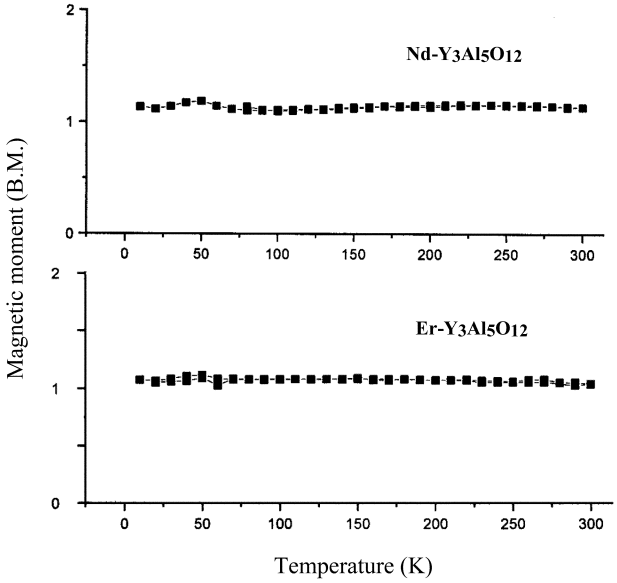

Fig. 9. Temperature dependence of the experimental magnetic moments for the Ln-doped $Y_3Al_5O_{12}$

CONCLUSIONS

Yttrium aluminium garnet, $Y_3Al_5O_{12}$, 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 have been prepared by a sol-gel method. The SEM and EDS results showed that the synthesis yielded homogeneous ceramic materials, with the composition close to the desirable metal ratio. In the backscattered electron (BSE) mode the brightness of the specimens was found to be also homogeneous over the entire measuring area. All the synthesized garnets showed a PTCR (positive temperature coefficient of resistivity) effect. The resistivity jump of all specimens was determined to be in the order of about 2.5 for the temperature range 20–140 °C. However, the Curie point was dependent on the nature of the rare-earth element. The temperature dependences of the magnetic susceptibility of the representative two Nd- and Er-doped YAG samples were also investigated. A Curie–Weiss fit to the data lead to a Curie–Weiss temperature Θ = –2.7961 K and Θ = –1.6900 K, and the magnetic momenta μ_{exp} = 1.13 B.M. and μ_{exp} = = 1.07 B. M. for the Nd- and Er-doped YAG samples, respectively.

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LANTANOIDAIS LEGIRUOTO YAG SINTEZĖ ZOLIŲ–GELIŲ METODU BEI MIKROSTRUKTŪRINIŲ, ELEKTRINIŲ IR MAGNETINIŲ SAVYBIŲ TYRIMAS

S a n t r a u k a

Zolių–gelių metodu susintetinti itrio aliuminio granatas ($Y_3Al_5O_{12}$) bei analogiški lantanoidais legiruoti (Ce-$Y_3Al_5O_{12}$, Nd-$Y_3Al_5O_{12}$, Ho-$Y_3Al_5O_{12}$ ir Er-$Y_3Al_5O_{12}$) pavyzdžiai. Nustatyta, kad gelius iškaitinus 1000°C temperatūroje, visais atvejais susidarė vienfaziai granatai. Skleidžiamuoju elektroniniu mikroskopu ištirti pavyzdžių morfologiniai ypatumai. Nustatyta, kad polikristaliniame itrio aliuminio granate legiruojantieji elementai pasiskirsto homogeniškai. Išmatavus gautų oksidų varžos priklausomybes nuo temperatūros, nustatytas šiems junginiams neįprastas metališkasis kitimo pobūdis. Staigus varžos padidėjimas pastebėtas esant nuo 20 iki 140°C temperatūrai. Nustatytos ir apibūdintos šių junginių magnetinės savybės.