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Short communication

Fabrication and scintillation properties of highly transparent Pr:LuAG ceramics using Sc,La-based isovalent sintering aids

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Abstract

The use of aliovalent sintering aids, especially TEOS, for scintillation ceramics preparation caused serious problems due to the need for charge compensation. Isovalent ions, on the other hand, do not cause such a problem and remain a new field to be explored. By using La_2O_3 and Sc_2O_3 isovalent sintering aids, we succeeded to produce Pr:LuAG ceramics with pure LuAG phase, good microstructure, and characterized by high optical quality with 80% transmittance in the visible range. Luminescence and scintillation properties were also investigated and turned out to be similar to those of previously studied transparent ceramics obtained with aliovalent sintering agents. Thermoluminescence data show the presence of several trapping states experiencing a disordered surrounding. It can be concluded that sintering aids, regardless of their valence, introduce local disorder due to their different radii with respect to that of the lattice ions resulting in the appearance of a UV emission and decrease of Pr^{3+} fast 5d–4f luminescence intensity. The aspects of energy transfer and trapping due to sintering aids in LuAG lattices are discussed.

Keywords: Pr:LuAG transparent ceramic; Isovalent sintering aids; Scintillation

1. Introduction

Scintillation materials with high light yield and fast decay time have been widely researched in recent years due to great demands for high energy physics, medical imaging as well as vast application for neutron detection [1]. Pr^{3+} doped $Lu_3Al_5O_{12}$ (LuAG) has shown promising properties as fast scintillator [2]. In 2005, Pr:LuAG single crystal was first introduced with a light yield 3 times higher than that of BGO, a fast decay time ($\sim$20 ns) and energy resolution reaching 4.6% at 662 keV [3–5]. Such a performance makes Pr:LuAG an important competitor for Positron Emission Tomography (PET), X-ray computing tomography (X-CT), and even Time-Of-Flight Positron Emission Tomography (TOF-PET) [2]. Taking into account the recent successful development of laser ceramics of cubic garnets such as Nd:YAG [6], also isomorph LuAG is presently considered for the realization of optical ceramics, in this case for scintillation application [7].

During the fabrication process of transparent ceramics, sintering aids have been widely used to improve transparency. In Nd:YAG laser ceramics, MgO [8] and TEOS [9] were widely used as sintering aids and great success has been achieved. Some studies were also devoted to Pr:LuAG transparent ceramics using the same TEOS [7] and/or MgO [10] as sintering aids. However, both of them are impurities which need charge compensation in their surroundings causing the occurrence of point defects (oxygen

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vacancies for Mg, dangling bonds and even defects related to a solid solution formation for Si [8]) acting as charge carrier traps. Such defects cause deterioration of the scintillation properties of transparent ceramics as recently revealed [10].

Therefore the finding of optimal sintering aids for ceramics aimed at scintillation application is still an open issue which motivates further studies. Some research efforts have been made on the doping of LuAG and YAG single crystals with isovalent ions such as Sc^{3+}, La^{3+} [11–13]. Positive results have been shown, namely that such codoping causes a speed-up of the scintillation response; this could be related to the fact that Sc^{3+} ions could simplify the excitation energy migration toward Pr^{3+} centers due to the good overlap of the Sc-related emission (Sc-trapped exciton) at around 275 nm with the 4f–$5d_1$ absorption band of Pr^{3+} center. Such isovalent oxide can form low temperature eutectic mixture with garnet. The expected lattice expansion due to ionic radii difference between Sc^{3+}, La^{3+} and lattice ions could justify an efficient role of such co-dopants as sintering aids. However, no results were reported until now concerning ceramics.

To our knowledge there is no report on the fabrication of good quality garnet transparent ceramics using solo isovalent rather than aliovalent oxides as sintering aids. Therefore, the aim of this work is focused on the ceramics fabrication using isovalent oxides as sintering aids in order to get highly transparent materials, evaluating also their luminescence and scintillation properties.

2. Experimental

We used the solid state reaction method for the fabrication of Pr:LuAG transparent ceramics. High purity commercial powders of Lu_2O_3, Al_2O_3 and Pr_6O_{11} ($>99.99\%$ purity) were weighted stoichiometrically together with different sintering aids. Two types of sintering aids were used. We used conventional aliovalent sintering aids containing MgO and TEOS with contents of 0.08 wt% and 0.2 wt% respectively, and isovalent sintering aids which combine 0.6 wt% La_2O_3 and 0.4 wt% Sc_2O_3. These concentrations allowed to produce samples with the best transparency. The starting powders were mixed by high energy ball-milling for 10 h using ethanol as medium. After ball-milling, the slurry was dried in the stove and mesh sieved, then pressed to dense compact by cold isostatic pressing (CIP) at 200 MPa. The compacts were vacuum-sintered at 1800–1840 °C for 20 h. After double face polishing, highly transparent ceramics were obtained.

The LuAG phase was identified by X-ray diffraction (XRD, Model D/MAX-2550V, Rigaku Co., Japan). The optical transmittance was measured by a spectrophotometer (Cary 5000, Varian Inc., USA). The microstructures were observed by electron probe micro-analyzer (EPMA) (Model JSM-6700, JEOL, Tokyo, Japan).

X-ray excited RL and wavelength resolved TSL measurements were performed with a homemade apparatus featuring a charge coupled device detector Jobin-Yvon Spectrum One 3000 coupled to a monochromator Jobin-Yvon Triax 180 with 100 grooves/mm grating operating in the 200–1100 nm interval. X-ray irradiations were performed by a Philips 2274 tube operated at 20 kV. For TSL, a 0.1 K/s heating ramp was adopted. The energy spectra were collected by coupling the samples optically to a photomultiplier (Hamamatsu, R878) supplied by -1200 V bias. The shaping time was 750 ns. All samples were irradiated by 662 keV gamma rays using a 137Cs source. Scintillation decays were measured at room temperature (RT) under ^{22}Na radioisotope excitation (511 keV) using the time-correlated single photon counting method (a modified 5000M model spectrofluorometer, Horiba Jobin-Yvon).

3. Results and discussion

By using the solid-state reaction method and same preparation conditions, high quality transparent Pr:LuAG ceramics were obtained with both aliovalent and isovalent sintering aids.

Fig. 1 shows the transmission of both samples. With the addition of isovalent sintering aids, we obtained ceramics with as much as 80% transparency in the visible range, which until now could be realized only with aliovalent sintering aids. The absorption spectra were identical for both samples. The absorption bands at 240 nm and 280 nm can be attributed to the two lowest $4f(^3H_4)$–$5d_{1,2}$ transition of Pr^{3+}. The sharp lines detected from 480 nm to around 600 nm are ascribed to the 4f–4f transition of Pr^{3+}. No additional absorption features caused by any sintering aids could be identified.

As diffraction patterns reported in Fig. 2 reveal, high optical quality transparent Pr:LuAG ceramics display pure LuAG phase in coincidence with the single-phase LuAG compounds (JCPDS no.73-1368). The use of either aliovalent sintering aids or isovalent sintering aids does not bring any new phase.

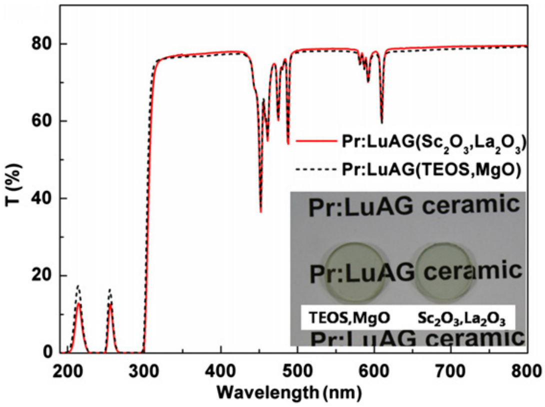

Fig. 1. Transmittance of Pr:LuAG ceramic samples with aliovalent sintering aids (TEOS, MgO), and isovalent sintering aids (La_2O_3, Sc_2O_3) (size:∅14 mm × 2 mm).

The investigation of the micro-structure of the polished Pr:LuAG ceramics with surface thermally etched at 1430 °C for 2 h in air were performed by SEM (Fig. 3). The samples displayed good and nearly pore-free microstructure with no second phase observed. However, from the images we note that the ceramic with TEOS and MgO doping have a mean grain size larger than that of the ceramic with Sc_2O_3 and La_2O_3 doping. It is known that TEOS acts as transient phase liquid sintering aid [9,14] while MgO [8] not only acts as sintering aid but also segregates at the grain boundaries impeding continuous grain growth at the final stage of vacuum sintering. From our present result we can suppose that similarly to Mg, Sc and La segregation at grain boundaries is also occurring, giving rise to a similar effect of grain growth limitation whose efficiency is even higher due to the higher content of Sc_2O_3 and La_2O_3 that was adopted with respect to TEOS and MgO. As a result, we get a relatively smaller grain size for Sc_2O_3 and La_2O_3 doping of LuAG ceramics.

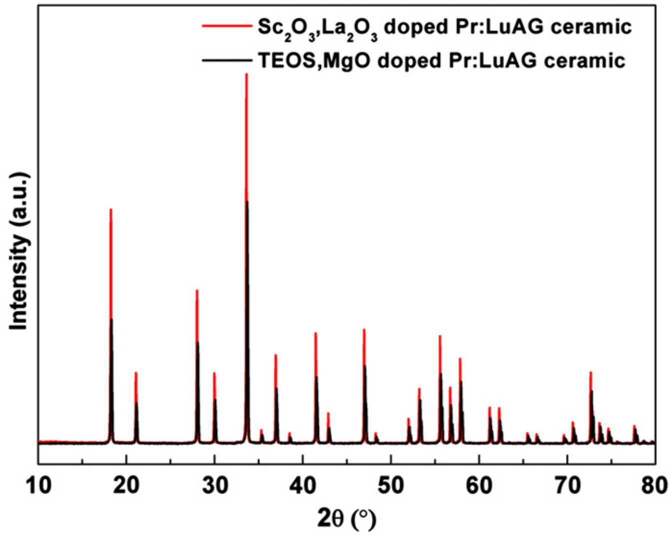

Fig. 2. X-ray diffraction patterns of Pr:LuAG ceramic samples with aliovalent sintering aids (TEOS, MgO), and isovalent sintering aids (La_2O_3, Sc_2O_3).

The actual sintering mechanism still remains an open field to be explored and can be further optimized. Given the fact that both samples were obtained with the same high optical quality and good microstructure, we compared their luminescence and scintillation properties.

Fig. 4 reports RL spectra of ceramic samples obtained with the use of alio- and iso-valent sintering aids. As a comparison, also the spectrum of a ceramic obtained without using any sintering agent is presented. All samples are characterized by a bright RL emission in the 300–400 nm region, coupled to less intense ones at both higher and lower wavelengths. The Sc^{3+} and La^{3+} ions have closed shell configuration and do not show any additional radiative transitions in the visible and UV spectral regions. The main emissions, with maxima at about 310 and 370 nm, are due to the interconfigurational transition among $5d_1$ and 4f Pr^{3+} levels, while those at longer wavelengths are related to radiative transitions among Pr^{3+} 4f–4f levels. A quantitative comparison among the spectra clearly evidences the effect of the different sintering aids on the Pr^{3+} RL characteristics: both alio- and iso-valent sintering aid strategies clearly results in a decrease of the Pr^{3+} 5d–4f emissions favoring the 4f–4f ones. This is more evident for the Sc_2O_3, La_2O_3 containing ceramic than for the TEOS, MgO containing one.

The emission in the 200–300 nm region, presented as an enlargement in the inset of Fig. 4, is somehow dependent on the used sintering aids. In fact, the emissions of the samples obtained without and with the aid of TEOS and MgO are characterized by the same spectral position and intensity ratio with respect to the main Pr^{3+} peaks; LuAG matrix emission in this wavelength region is related to the radiative recombination of self-trapped excitons (STE), the decay of which includes slower components in the microsecond range [16]. On the other hand, the ceramic synthesized with La_2O_3 and Sc_2O_3 clearly shows a red shift and an increase of the intensity of this emission: this shift has been previously connected [13,15] to the localization of excitons on or near Sc^{3+} or La^{3+} perturbed sites, in this case the trapped exciton (TE) decay time is about 600 ns.

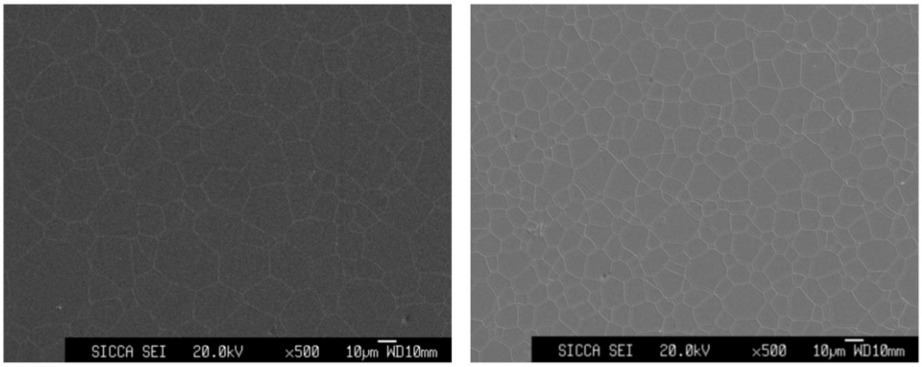

Fig. 3. Surfaces of Pr:LuAG ceramics with aliovalent sintering aids (TEOS, MgO) (left), and isovalent sintering aids (La_2O_3, Sc_2O_3) (right) after thermal etching at 1430 °C for 2 h.

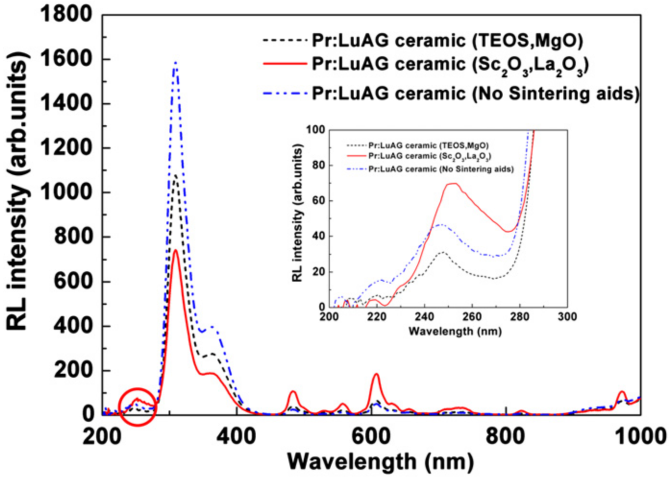

Fig. 4. Radio luminescence spectra of Pr:LuAG ceramics with aliovalent sintering aids (TEOS, MgO), and isovalent sintering aids (La_2O_3, Sc_2O_3) compared with ceramic without any sintering aids of the same size (Ø14 mm × 2 mm). Inset, enlargement of the 200–300 nm region.

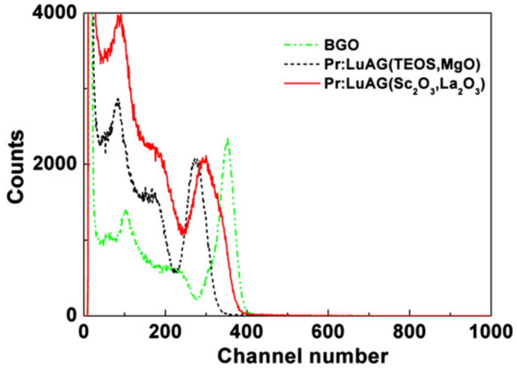

Fig. 5. Pulse-height spectra comparison of the 0.5 at% Pr:LuAG ceramic samples using aliovalent (TEOS, MgO) and isovalent sintering aids (La_2O_3, Sc_2O_3) with that of a BGO single crystal of the same size (Ø14 mm × 2 mm).

The relative light yield comparison with a BGO single crystal was performed for both samples in Fig. 5. The higher Compton contributions of our isovalent sintering aids doped sample is caused by longer collecting time in order to get the same counts with the aliovalent doped one, which is in accordance to its lower radio luminescence intensity. Despite of the steady state scintillation efficiency decrease observed by RL measurements in the ceramic prepared with isovalent sintering aids, the light yield within 750 ns time gate is comparable for both samples. This points to the presence of a more efficient energy transfer toward Pr^{3+} emission centers occurring with isovalent sintering aids with respect to that occurring using aliovalent sintering aids. Nevertheless, the presently used kind and concentration of isovalent sintering aids did not considerably enhance fast scintillation components within 750 ns time gate as shown below.

Scintillation decay and relative intensities of all components are reported in Fig. 6. Three exponential fit $I(t)$, see Eq. (1) below, is obtained by convolution of instrumental response (also in the figure) with $I(t)$ and applying a least square sum fitting procedure.

The decay fit is provided as a sum of exponential components:

$$I(t)=\Sigma A_i \exp\left[-t/\tau_i\right]+background, \quad i=1,2,3 \tag{1}$$

and the j-th component relative intensity is given by

$$Ij=A_j\tau_j/\Sigma A_i\tau_i \tag{2}$$

We observed basically no differences. Both samples feature a dominant component with 23–24 ns decay time which is close to the photoluminescence decay time of

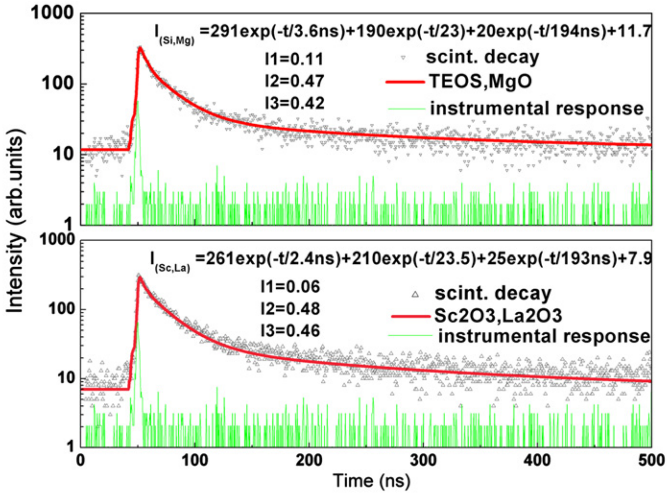

Fig. 6. Scintillation time decay of ceramic samples synthesized with different sintering aids. The solid curve is the convolution of the instrumental response (also shown) and of the function $I(t)$ given in the figure.

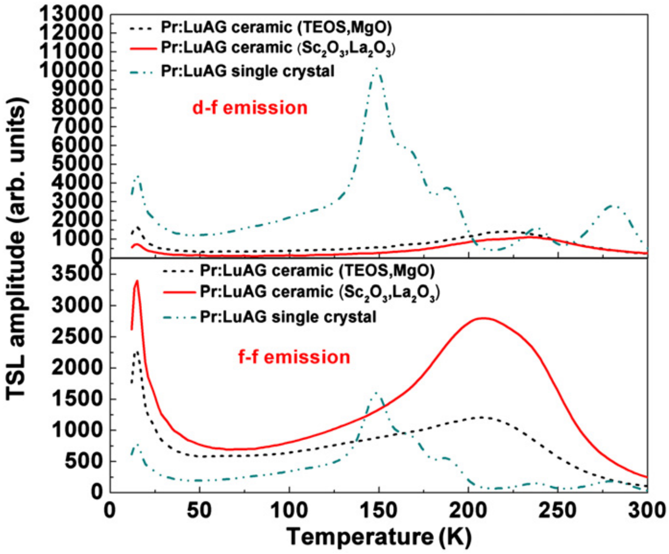

Fig. 7. TSL glow curves of single crystal and ceramic samples obtained from wavelength resolved measurements after integration in the 250–450 nm (Pr^{3+} d–f emission) and in the 450–770 nm (Pr^{3+} f–f transitions) intervals.

Pr^{3+} in LuAG single crystal host (20–21 ns) [3]. The shortest component with a few nanoseconds decay time is of unknown origin and may indicate some local structural distortions or energy transfer processes from the Pr^{3+} $5d_1$ level to nearby defects. The relative intensity of the slowest component is similar in both samples prepared with sintering aids. This component is due to a delayed recombination process introduced by sintering aids or grain boundaries [10].

Finally in Fig. 7 we performed low temperature TSL measurements comparing a Pr:LuAG single crystal with ceramics, in order to identify different recombination processes in the materials.

In the case of the single crystal, between 120 K and 200 K, both in the d–f and f–f emission regions, a triple peak structure is observed, which has been ascribed to antisite defects [15]. Such structure is not detected in both ceramic samples, confirming that there is a small, if not negligible, amount of such intrinsic defects in ceramics. Moreover, the TSL intensity ratio between 4f–4f and 5d–4f emission regions is much higher in the ceramics than that observed for the single crystal. Therefore, sintering aids, and especially the isovalent (La_2O_3, Sc_2O_3) ones, appear to favor the radiative recombination channel between electrons freed from traps and Pr^{3+} 4f excited levels [10]. We also note that the glow curves of ceramics are extremely broad in comparison with those of single crystal, suggesting the possible localization of traps in rather disordered surrounding, like grain boundaries, which broaden their energy levels. Considering that it is highly probable that both iso- and alio-valent sintering aids form only a solid solution in the garnet structure, the ionic radius mismatch between them and the matrix ions may give rise to further structural disorder. Similarly to what occurs in case of antisite defects, the different ionic radii of both alio- and iso-valent ions could also cause charge carrier trapping phenomena. On the other hand, we also have to consider that Si and Mg require charge compensation giving rise to the formation of defect complexes and color centers, which may behave as traps for charge carriers too. The rather close similarity between the ceramic glow curves could suggests that the two sintering strategies introduce the same kind of traps, irrespective of the actual valence of the ions. Indeed, the concentration of Sc and La ions used in order to obtain high transparency is much higher than those of Si and Mg, and thus possibly explaining the higher intensity of the glow curve of the isovalent SA containing ceramic with respect to that of the aliovalent one.

To have a clearer picture on the effect of the isovalent sintering strategy we plan to obtain new ceramics with much lower La and Sc concentrations, also dealt with as single sintering aid ions.

To sum up, in these single crystal or ceramic garnets structures, we have always to consider two different processes:

i) Localization of excitons around antisite defects or isovalent impurities with sufficiently different radius from the lattice ions (e.g. La or Sc ions in YAG or LuAG). These defects/impurities can give rise to UV emission bands peaking at characteristic different wavelengths.
ii) Localization of charge carriers around antisite and other defects which may give rise to electron traps. In the case of ceramics, different traps may arise with respect to single crystals due to structural disorder at the gain boundaries and interfaces.

4. Conclusions

The use of aliovalent sintering aids, especially TEOS, has enabled the garnet transparent ceramics to achieve great success in laser application. In scintillation ceramics, however, the employment of such classical sintering aids caused serious problems. We hereby demonstrate the preparation of high optical quality and high transparency Pr:LuAG ceramics by using isovalent sintering aids (La_2O_3, Sc_2O_3). It will extend the sintering aids choice for garnet ceramic fabrication for scintillation application. Even if we have not got clearly higher light output within 750 ns shaping time there is a clear sign of acceleration of energy transfer process from LuAG host toward Pr^{3+} emission centers.

At variance with aliovalent sintering aids, isovalent ones does not need for charge compensation. However, sintering aids of any kind can introduce a local structural disorder due to their different radii from the lattice ions and give rise to different kinds of traps. Higher concentration of isovalent sintering aids in our present sample caused deterioration of scintillation efficiency (radioluminescence intensity). Isovalent sintering aids can be used with lower concentration; moreover other isovalent ions such as Ga [16] can be considered to diminish the negative features described in this work. Their use is still considered promising to get highly transparent ceramics with improved scintillation performance.

Acknowledgments

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