Effects of Mg^{2+} and Si^{4+} Co-doping on the Microstructure and Luminescence Properties of Ce:YAG Ceramic Phosphors for High-Power LED/LD Lighting

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Date: 2023-02-01T00:00:00+00:00

Abstract

The effects of adding 0.04 wt%, 0.06 wt%, 0.08 wt%, 0.4 wt%, 0.6 wt% to 0.8 wt% MgO and tetraethyl orthosilicate (C8H20O4Si, TEOS) as sintering aids on the microstructure and luminescence properties of Ce3+-doped transparent Y3Al5O12 (Ce:YAG) ceramics were investigated during vacuum sintering. Comparative studies were conducted using X-ray diffraction, scanning electron microscopy/energy-dispersive spectroscopy, optical spectroscopy, photoluminescence spectroscopy, and electroluminescence spectroscopy. Both MgO and TEOS at a doping level of 0.8 wt% could obtain the dominant garnet phase, while the Ce:YAG ceramics doped with MgO exhibited finer average grain sizes (~5-10 m) and more uniform distribution compared to TEOS (~20-25 m). The addition of excessive MgO in Ce:YAG ceramics leads to MgO segregation, while excess TEOS results in Al2O3 segregation. Under the influence of MgO additive, a strong absorption peak appeared at 308 nm in Ce:YAG ceramics, which is attributed to the presence of Ce4+ due to the charge compensation effect of Mg2+. When 0.6 wt% TEOS was added, the optimal transmittance of Ce:YAG ceramics reached 80% @ 800 nm, and the luminous efficiency achieved a maximum of 106 lm/W. Experiments demonstrated that Si4+ exhibits superior optimization effects on luminous efficiency compared to Mg2+.

Full Text

Effect of Extra Added Mg^{2+} and Si^{4+} on the Microstructure and Luminescence Properties of Ce:YAG Ceramic Phosphors for High-Power LED/LD Lighting

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Keywords: Ce:YAG ceramic; Phosphors; White LED; Sintering aids

This study investigates the effects of varying amounts of MgO or tetraethyl orthosilicate ($C_8H_{20}O_4Si$, TEOS) as sintering aids—specifically 0.04 wt%, 0.06 wt%, 0.08 wt%, 0.4 wt%, 0.6 wt%, and 0.8 wt%—on the microstructure and luminescence properties of transparent Ce^{3+}-doped $Y_3Al_5O_{12}$ (Ce:YAG) ceramics fabricated via vacuum sintering. A comparative analysis was performed using X-ray diffraction, scanning electron microscopy/energy dispersive X-ray spectroscopy, optical and photoluminescence spectroscopy, and electroluminescence measurements. The dominant garnet phase was retained even with additions up to 0.8 wt% of either MgO or TEOS. However, MgO additions resulted in finer average grain sizes (~5–10 m) and more homogeneous distributions compared to TEOS (~20–25 m). High MgO concentrations caused MgO segregation in Ce:YAG ceramics, while excess TEOS led to Al_2O_3 segregation. A strong absorption peak at 308 nm was observed in MgO-assisted Ce:YAG ceramics, attributed to Ce^{4+} formation. The optimal transmittance of 80% at 800 nm was achieved with 0.6 wt% TEOS, which also exhibited a maximum luminous efficacy of 106 lm/W. Si^{4+} demonstrated superior optimization of luminous efficacy compared to Mg^{2+}, likely due to charge compensation effects.

1. Introduction

Ce:YAG is a classical luminescent material with a long history of investigation [1]. It serves as a highly efficient phosphor in white light-emitting diodes (LEDs) and laser diodes (LDs) [2], as well as a scintillator for high-resolution X-ray imaging [3] and high-energy physics applications [4], and even in solar cells [5]. The YAG matrix possesses excellent thermal conductivity (13.4 W/mK) and mechanical properties (Young' s modulus of 280 GPa) [6]. In recent years, bulk phosphors—including transparent ceramics [8–10], composite ceramics [11,12], glass ceramics [13,14], and single crystals [15]—have attracted global research interest for high-power LED/LD lighting [7,8] due to their superior thermal conductivity compared to organic epoxy resins or silicone. Among these, Ce:YAG transparent ceramics have been actively studied, from fabrication methods [9,16] to composition engineering [17,18], and are considered advantageous over glass ceramics or single crystals for their higher luminescent efficiency, lower fabrica-

tion temperature, scalability for mass production, and feasibility for composite structure design [19,20].

Sintering aids are commonly employed in transparent ceramic production. In the 1950s, Coble [21] pioneered the fabrication of translucent Al_2O_3 ceramics by adding small amounts of MgO as a sintering aid. In the 1980s, de With and van Dijk [22] first reported using SiO_2 doping to achieve translucent YAG ceramics. Since then, MgO and TEOS have been the most common sintering aids for YAG transparent ceramics, promoting densification, reducing scattering sources such as pores, and improving optical transmittance and homogeneity. Studies investigating MgO additions (0.01–0.15 wt%) in YAG transparent ceramics proposed a MgO solubility limit of 0.06 wt%, with Mg^{2+} substituting Al^{3+} sites and excess MgO precipitating as spinel secondary phases [23]. Research on MgO-assisted densification of YAG ceramics (0.03–0.18 wt%) revealed optimal transmittance at 0.03 wt% MgO, with higher concentrations causing significant grain growth, intragranular pores, and Mg-rich secondary phases that degraded optical properties [24]. The effects of TEOS on YAG transparent ceramics have also been reported, particularly for Nd:YAG laser ceramics [25,26]. TEOS decomposes into SiO_2, H_2O, and CO_2 at high temperatures, with Si^{4+} substituting tetrahedrally coordinated Al^{3+} sites when the solubility limit is not exceeded [26]. SiO_2 content increases both densification and grain growth rates at lower temperatures, with crystalline second phases forming when Si^{4+} solubility is exceeded.

Furthermore, as external additives beyond the chemical stoichiometry, sintering aids affect not only microstructure but also luminescence properties [27–29]. Mg^{2+} generally shortens scintillation decay but reduces luminescence efficiency in Ce^{3+}-doped $Lu_3Al_5O_{12}$ (LuAG) [30–32], $(Gd,Lu)_3Al_5O_{12}$ (GLAG) [33], $Gd_3(Al,Ga)_5O_{12}$ (GGAG), and Pr^{3+} scintillators [34–36]. Si^{4+} doping in Ce:YAG produces blueshifted emission attributed to decreased 5d level splitting of Ce^{3+} ions and significantly improved thermal stability [37]. Additionally, 5 wt% SiO_2-added Ce:YAG ceramic phosphors exhibited increased quantum efficiency (>15%) and higher thermal stability (10% improvement at 150 °C) compared to pristine Ce:YAG, attributed to denser microstructure and increased thermal activation energy from Si substitution of Al in the host lattice [38]. Moderate Si-codoping also effectively enhanced radiation hardness and scintillation properties of Ce:YAG crystals [39].

The combined effects of MgO and TEOS as compound sintering aids have been studied in YAG, LuAG [32], and GdYAG [40] systems. Ceramics with compound sintering aids exhibited better transparency and more homogeneous grains compared to single-additive systems [41]. High luminescence efficiencies of 93.6 lm/W (blue LED excitation) and 178.5 lm/W (blue LD excitation) were achieved in Ce:YAG ceramics with combined MgO (0.08 wt%) and TEOS (0.8 wt%) additives [42]. However, ionic interactions during YAG ceramic sintering have also been observed [43]. Due to similar ionic radii with Al^{3+}, both Mg^{2+} and Si^{4+} can dissolve into the

YAG matrix as substitutional ions. Ce:$Y_3Mg\ Al_{5\ 2}\ Si\ O_{12}$ (Ce:YAMSG) and Ce^{3+}:$Lu_3(Al,Mg)_2(Al,Si)_3O_{12}$ (Ce:LuAMSG) transparent ceramic phosphors have been developed [12,17,18,44,45]. The Mg^{2+}-Si^{4+} ion pair substitution can reduce sintering temperature, shrink the bandgap, enhance the crystal field, and lower the Ce^{3+} 5d level to produce luminescence redshift. However, this decreases the absolute quantum efficiency of Ce^{3+} emission and luminescence stability at high temperatures.

In summary, while previous works demonstrate the effects of MgO and SiO_2 on YAG and other aluminate garnet transparent ceramics, we note that MgO additions (0–0.2 wt%) were typically one order of magnitude lower than TEOS additions (0.5–1.0 wt%), likely due to the Mg^{2+} solubility limit of ~0.06 wt% in YAG [23]. Considering that appropriate amounts of second-phase particles can alter light propagation in ceramics to potentially increase excitation light absorption and emission extraction [40], we extended the addition range of both MgO and TEOS and focused on their effects as single sintering aids in vacuum-sintered Ce:YAG ceramics. By varying the additive amount by one order of magnitude, we characterized the resulting microstructure, optical, and luminescence properties to clarify the sintering aid mechanisms.

2.1. Ceramics Fabrication

Ce:YAG ceramics were fabricated via solid-state reaction and vacuum sintering. High-purity commercial powders of α-Al_2O_3 (>99.99%), Y_2O_3 (>99.99%), and CeO_2 (>99.99%) were weighed according to the stoichiometry of $(Ce_{0.005}Y_{0.995})_3Al_5O_{12}$, corresponding to 0.5 at.% Ce^{3+}-doped YAG. High-purity MgO powder and TEOS solvent were added as external additives beyond the Ce:YAG chemical stoichiometry. The TEOS decomposes into SiO_2, H_2O, and CO_2 at high temperatures, with SiO_2 acting as the final sintering aid. Additive amounts of 0.04 wt%, 0.06 wt%, 0.08 wt%, 0.4 wt%, 0.6 wt%, and 0.8 wt% were used. The as-sintered Ce:YAG ceramics were designated CYM and CYS, numbered according to MgO or TEOS additive amounts, respectively, with relative molar ratios to Ce^{3+} calculated and listed in Table 1 .

The powders were mixed using a high-energy ball mill at 200 rpm for 12 h with alcohol as the milling medium. The slurry was dried in air at 70 °C for 1–2 h and sieved through a 200-mesh screen. The resulting powders were calcined at 800 °C for 4 h in a muffle furnace to eliminate possible organic impurities. Ceramic green bodies (Ø25 mm × 2 mm) were formed by uniaxial pressing at 4 MPa followed by cold isostatic pressing at 200 MPa. The green bodies were sintered in a pressureless vacuum furnace at 1750 °C for 20 h, with vacuum reaching 10^{-4} Pa during the temperature hold. The as-sintered ceramics were cut and double-face polished to optical grade with dimensions of 4 × 4 × 0.5–0.8 mm^3 for further measurements.

2.2. Characterization

Ceramic phases were identified by X-ray diffraction (XRD) using an Ultima IV diffractometer (Cu Kα, 40 kV, 40 mA; Rigaku Corp., Japan) with a step size of 0.02° and scan rate of 2°/min in the 2 range of 10–80°. Grain morphology and elemental distribution maps were obtained using a high-resolution scanning electron microscope (HR-SEM S-3400 N) with energy dispersive X-ray spectroscopy (EDS) (Hitachi Ltd., Japan). Before SEM analysis, Ce:YAG ceramics were double-face polished and thermally etched in air at 1500 °C for 3 h. Grain size distributions were determined from thermally etched surfaces using the linear intercept method with a correction factor of 1.56 to convert average intercept length to real grain size. At least 300 grains were analyzed per sample.

Absorption spectra were measured using a UV–Vis–NIR spectrophotometer Cary 5000 (Varian Medical System Inc., USA) with automatic baseline subtraction. Photoluminescence emission (PL) and excitation (PLE) spectra were recorded on an F-4600 fluorescence spectrophotometer (Hitachi Ltd., Japan) at 1200 nm/min scan rate using a xenon lamp source. Electroluminescent (EL) properties—including EL spectra, correlated color temperature (CCT), CIE color coordinates, color rendering index (CRI), and luminous efficacy—were measured using a PM-80V1 spectroradiometer with an integrating sphere (Everfine Co., China), with ceramics excited by a commercial 445 nm blue LED chip. LD luminous flux was recorded using a YF-1000 high-accuracy array spectroradiometer (Everfine Co., China) with a 450 nm blue LD chip (1.4 W) focused on a $ $2 mm area.

3. Results and Discussion

Figure 1 [Figure 1: see original paper] shows photographs of the as-sintered 0.5 at.% Ce:YAG ceramics. All samples achieved visible transparency after double-face polishing. CYM ceramics gradually changed from yellow to orange with increasing MgO content, while CYS ceramics remained yellow. The darker color may be attributed to oxygen vacancies induced by divalent Mg^{2+} cations [29,46] or the reducing fabrication atmosphere [32]. Some studies suggest increased splitting of the Ce^{3+} 5d configuration from Al^{3+} substitution by Mg^{2+} [47], though crystal field strength variations may only affect hue. The detailed mechanism is elucidated through subsequent characterizations.

Figure 2 [Figure 2: see original paper] presents XRD patterns of the as-sintered 0.5 at.% Ce:YAG transparent ceramics with varying sintering aid amounts. All ceramics exhibited cubic YAG phase (PDF #033-0040). Enlarged views of prominent peaks show diffraction angles shifting to higher values relative to standard YAG, indicating decreased lattice parameters. Mg^{2+} did not significantly alter the host structure, and no detectable second phases appeared even at 0.8 wt% additions. This aligns with previous work demonstrating YAG's ability to accommodate Mg^{2+} over wide concentration ranges [48]. The weakened XRD intensity in 0.8 wt% TEOS-assisted ceramics (Fig. 2(b)) may result from

vitrification tendencies with heavy SiO_2 introduction [49,50]. However, XRD detection limits (~1%) mean trace impurities may exist, as SEM-EDS analysis later reveals Al_2O_3 and MgO segregations indicating local non-stoichiometry or second-phase formation (possibly spinel).

Figure 3 [Figure 3: see original paper] shows Ce:YAG ceramic grain morphology with different MgO sintering aid amounts. Grain size distributions and average grain sizes were calculated via linear intercept method from thermally etched surfaces. Ce:YAG ceramics with 0.08 wt% or 0.8 wt% MgO exhibited the most homogeneous grain size distribution and nearly pore-free microstructure. Minor micropores were observed at triple grain boundaries and within grains, acting as light scattering centers that degrade in-line transmittance [51,52]. Figure 3(b) presents grain morphology for TEOS-assisted ceramics. TEOS additives caused significant grain size increases, much larger than MgO cases, and produced very small porosity but poorer homogeneity. Si^{4+} thus effectively promoted densification and grain growth, leading to coarsening-dominated grain growth in Ce:YAG ceramics.

Figures 4 [Figure 4: see original paper] and 5 [Figure 5: see original paper] show elemental distribution maps for Ce:YAG ceramics with 0.04 wt% MgO (CYM1) and 0.06 wt% TEOS (CYS2) via SEM-EDS. Mg-rich regions were evident even at the lowest MgO addition (0.04 wt%), while Y, Al, and Ce distributed homogeneously. Al-rich rather than Si-rich regions were observed, suggesting Si^{4+} (26 pm at coordination number 4) is more competitive than Al^{3+} (39 pm) for tetrahedral site substitution [26]. The XRD peak shift to higher angles (Fig. 2(b)) supports this. Mg^{2+} (radius 89 pm, coordination number 8) likely occupies dodecahedral Y^{3+} sites (radius 101.9 pm), explaining the XRD peak redshift in Fig. 2(a).

Figure 6 [Figure 6: see original paper] compares grain size distribution histograms for CYM and CYS series. CYM grain sizes were generally smaller with narrower distributions than CYS, demonstrating Mg^{2+}'s more pronounced grain growth inhibition compared to Si^{4+}. Average grain size was ~20–25 m for TEOS additives versus ~5–10 m for MgO (Fig. 6(c)). Grain size evolution showed two stages: initial increase then decrease from 0.04–0.08 wt% MgO and 0.4–0.8 wt% MgO. While Mg^{2+} typically inhibits grain growth through solute drag [23,24], this work shows non-linear inhibition with concentration, possibly due to competing densification promotion [24,50]. Secondary phase average sizes were 2.5–4.5 m (CYM) and 2.5–7.5 m (CYS) (Figs. 6(a), 6(b)), generally exhibiting quasi-spherical morphology.

Figure 7 [Figure 7: see original paper] compares in-line transmittance and absorptance spectra in the visible range for 0.8 mm-thick Ce:YAG ceramics. CYS ceramics achieved optimal transmittance of ~80% at 800 nm, higher than CYM ceramics (70% at 800 nm). Two absorption bands at 350 nm and 450 nm make Ce:YAG suitable for blue LED/LD chip excitation. These transitions originate from the 2F5/2 ground state (spin-orbit split $4f^1$ configuration further split by cubic + tetragonal crystal field) to $5d^1$ excited states. The 2Eg ground level

under cubic crystal field splits into 2A1g and 2B1g levels, corresponding to 450 nm and 350 nm bands, respectively [54]. Notably, absorptance in the 250–450 nm range differed dramatically between series: CYM ceramics showed strong absorption below 350 nm with a distinct peak at ~308 nm. While Ce^{4+} charge transfer absorption peaks near 240 nm in Ce,Mg:LuAG ceramics [32,55] and a ~300 nm band was reported in Ce:LuAG without confirmed origin [56], Ce^{4+} is a d^0 and f^0 cation with only charge transfer bands unaffected by crystal field. Therefore, the 308 nm peak cannot be attributed to Ce^{4+} in Ce:YAG ceramics and requires further investigation.

Figure 8 [Figure 8: see original paper] shows PLE (λem = 530 nm) and PL (λex = 450 nm) spectra for CYM and CYS series at room temperature. All ceramics exhibited excitation bands at 350 nm and 450 nm characteristic of Ce^{3+} 4f-5d transitions. Broad emission peaking at ~530 nm appeared in all samples under 450 nm excitation, indicating Mg^{2+} addition does not alter the YAG bandgap or Ce^{3+} 5d levels. Defect states were reportedly absent in the YAG bandgap [57]. The emission originates from Ce^{3+} electron transition from 5d excited state to 2F5/2 and 2F7/2 ground states [54], confirming Ce^{3+} solid solution in the YAG matrix. CYM2 and CYS5, with optimal room-temperature PL intensities, were selected for thermal stability investigation from RT to 225 °C (Fig. 9 [Figure 9: see original paper]). PL intensity decreased with temperature, retaining 50% intensity at 225 °C. CYM2 showed nearly linear intensity decrease, while CYS5 exhibited two-step decrease with sharper reduction below 100 °C, requiring further mechanistic study.

Figures 10 [Figure 10: see original paper] and 11 [Figure 11: see original paper] show EL spectra and luminous efficacy of Ce:YAG ceramics under blue chip excitation (445 nm). CYM ceramics exhibited serious blue light leakage, while CYS ceramics efficiently absorbed blue excitation light with higher emission intensity. CYS ceramics showed overall luminous efficacy enhancement: 80–110 lm/W versus 20–70 lm/W for CYM ceramics. A reference Ce:YAG ceramic with compound sintering aids (0.08 wt% MgO + 0.8 wt% TEOS) [42] showed intermediate efficacy. Similar trends appear in Fig. 12 [Figure 12: see original paper], comparing luminous flux under 1.4 W blue LD excitation (450 nm). Table 2 summarizes EL parameters under 445 nm blue LED excitation. CYS ceramics showed slight emission redshift (~5–10 nm) compared to CYM ceramics. Maximum luminous efficacy occurred at 0.6 wt% additions: 106.4 lm/W for CYS and 68 lm/W for CYM. The high efficacy (~106.4 lm/W) and low CCT (3742 K) at 0.5 mm thickness are comparable to single-surface textured Ce:YAG ceramics (93.0 lm/W, 4144 K, 0.8 mm) [2] and transparent Ce:YAG ceramics (106–223 lm/W) [4].

Overall, red-light compensation and sufficient blue light absorption are crucial for improving luminous efficacy and lighting quality. CYS series ceramics demonstrated superior lighting performance, showing potential for future applications. The poorer PL and EL performance of CYM ceramics may result from insufficient blue light absorption, cation vacancies introduced by Mg^{2+},

and corresponding charge compensation that creates point defects and Ce^{4+} formation—for example, O^{2-} sites from charge imbalance [34] and reduced Ce^{3+} concentration [55], where Ce^{3+} is the effective luminescence activator.

4. Conclusions

In summary, Ce:YAG transparent ceramics were fabricated by solid-state reaction and vacuum sintering at 1750 °C for 20 h with MgO or TEOS added as external sintering aids across a wide range (0.04–0.8 wt%). Heavy MgO addition caused MgO segregation, while excess TEOS led to Al_2O_3 segregation, attributed to competitive ionic radius matching where smaller Si^{4+} and larger Mg^{2+} substitute Al^{3+} in tetrahedral sites. MgO distinctly inhibited grain growth but showed inferior luminous efficacy optimization compared to TEOS. Maximum luminous efficacy occurred at 0.6 wt% additions: 106 lm/W for TEOS and 69 lm/W for MgO, with in-line transmittance reaching 80%. This comparative study elucidates the effects of Mg^{2+} and Si^{4+} on luminescence performance, providing guidance for balancing optical transmittance and luminescence in Ce:YAG ceramics.

Declaration of competing interest: The authors declare no known competing financial interests or personal relationships that could have influenced this work.

Acknowledgement

The authors thank the National Natural Science Foundation of China (No. 62175249, 61475175), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDA22010301), and the Shanghai Science and Technology Commission Foundation (22511100300, 19DZ1100703, 18511110400). D. Yu. K. acknowledges support from the Russian Science Foundation (Project No. 20-73-10242).

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