Effect of activators and calcination on luminescence properties of åkermanite type phosphors

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Åkermanite type Ca₂MgSi₂O₇ phosphors activated with different types of rare earths have been synthesized through a solid state reaction method under weak reducing atmosphere and/or open atmosphere. The phase properties of the samples are characterized by X-ray diffraction and the effects of rare earth ions (Eu²⁺, Dy³⁺, Ce³⁺, Sm³⁺ and Pr³⁺/⁴⁺) and calcination atmosphere on the luminescence properties of the Ca₂MgSi₂O₇ host are investigated by using a photoluminescence spectrometer. The comparative results of SEM and laser particle size analysis reveal that the relatively regular morphology, smaller particle size and narrow size distribution can be achieved for the phosphor synthesized by the solid state reaction method including dry-milling below 170 mesh. In the photoluminescence investigations, all the activator ions show different emissions for Ca₂MgSi₂O₇ host lattice. The results show that the luminescence properties of rare earth ions activated Ca₂MgSi₂O₇ host are also highly dependent on the calcination conditions.

Keywords: Phosphors, åkermanite, Solid state reaction, Activators, Calcination, Luminescence, Rare earths

In recent years, as a new generation of long persistent phosphors, the rare earths-activated alkaline earth silicates and aluminates having high chemical stability, water resistance and color variation have been extensively studied due to a growing market demand for their applications in traffic signals, emergency exit routes, decoration, and textile printing, with ceramics, glasses, polymers or metals.

The host compound Ca₂MgSi₂O₇ belongs to the CaO-MgO-SiO₂ ternary system. Four Ca:Mg:Si:O compounds, such as monticellite (CaO-MgO-SiO₂:CaMgSiO₄), diopside (CaO-MgO-2SiO₂:CaMgSiO₄), åkermanite (2CaO-MgO-2SiO₂:Ca₂MgSiO₇), and merwinite (3CaO-MgO-2SiO₂:Ca₃MgSi₂O₈), exist in this system. The åkermanite type materials are one of the end-members of the melilite family of minerals (A₃B₅O₁₀, A: Ca/Na, B: Mg/Al/Fe(II), T: B/Al/Si). The Ca₂MgSi₂O₇ chosen for the present studies crystallizes in a tetragonal space group P₄₂/m in which the calcium ions are 8-fold coordinated, while both the Mg²⁺ and Si⁴⁺ ions are tetrahedrally surrounded by oxygen anions. Since in this structure type two SiO₄ tetrahedra share a corner, Åkermanite belongs to the family of sorosilicates. The Ca₂MgSi₂O₇ is also well known as a host for persistent phosphors, generally activated with several rare earth ions, such as Eu²⁺, Nd³⁺, Dy³⁺ or Mn²⁺. When Eu²⁺ and Mn²⁺ are used as dopant ions, the phosphors are potential candidates to be used in LEDs for the generation of white luminescence. In recent years, it has also been studied for biological and medical applications. Eu²⁺ doped Ca₂MgSi₂O₇ phosphors are known as efficient phosphors with good stability. The optical properties of Eu²⁺ doped CaMgSi₂O₆ have been reported by Jung et al. Moreover, the luminescence of M₂MgSi₂O₆: Eu²⁺ (M = Ca, Ba, Sr) and BaMg₂Si₂O₇: Eu²⁺ has also been reported. Furthermore, the long-lasting yellow color emitting phosphor, Ca₂MgSi₂O₇: Eu²⁺, Dy³⁺, where Dy³⁺ mainly acted as trap center, has been investigated. The phosphorescence behavior of Ca₂MgSi₂O₇ phosphors activated with different rare earths are expected to a different and observable when the samples are prepared in different atmosphere, although the origin of such differences is not fully understood, and no detailed studies have been repeated.

Therefore, it was decided to investigate the photoluminescence properties (PL) in Ca₂MgSi₂O₇: Eu/Dy/Ce/Sm/Pr synthesized in different atmospheres. With this goal in mind, a series of Eu₂O₃, Dy₂O₃, Ce₂O₃, Sm₂O₃, Pr₆O₁₁ separately added
to Ca$_3$MgSi$_2$O$_7$ as luminescent center and were prepared in N$_2$/H$_2$ and/or air (open) atmospheres, respectively. So, there are both similar results with previous researchs and also novel results of this structure with rare-earths.

**Material and Methods**

In the present study, the phosphors were synthesized via high temperature solid-state reaction method, also known as ceramic method. Using the base composition of Ca$_3$MgSi$_2$O$_7$:~0.5 mass% REO (Rare Earth Oxides-REO= Eu$_2$O$_3$, Ce$_2$O$_3$, Pr$_6$O$_11$, Sm$_2$O$_3$, Dy$_2$O$_3$), appropriate amounts of the high purity starting reagents, CaCO$_3$ (Merck, Suprapur, 99.95%), Mg(OH)$_2$ (Aldrich, 95%) and SiO$_2$ (Merck, highly dispersed suitable for use as excipient) and a small amount the fluxing agent, H$_3$BO$_3$ (Eti Maden, Turkiye, 99.9%), were thoroughly mixed and ground in a planetary mill (Fritsch/Pulverisette 5) at 250 rpm for 1.5 h in propanol-2 which was added to facilitate the grinding process and to enhance the particle mixing. Subsequently, the mixed slurry forms were dried in an oven at 100 °C for 5 h. Then, the mixed powders were heated in pure alumina crucibles using a tubular furnace (Protherm PTF 16/50/450) at 1100–1400 °C for 1-4 h under weak reducing atmosphere of 90–97% N$_2$ + 10–3% H$_2$ gas mixture. In addition, the powders were also heated using a open atmosphere furnace and then cooled down to the room temperature slowly. The synthesized phosphors were ground to powder form and screened to pass 170 mesh sieves prior to the characterization.

Simultaneous differential thermal analysis (DTA) and thermogravimetric (TG) analysis (Seiko Instruments Inc./Exstar TG/DTA 6200) at a heating rate of 10 °C/min from room temperature to 1350 °C were carried out to analyze the decomposition and the oxidation process of the precursor. The particle size analysis was done on a Malvern Instruments Mastersizer Hydro 2000G laser particle size analyzer. The morphology and particle size distribution of the calcined, dry-milled and sieved powders were designated with a Zeiss EVO 50 scanning electron microscope (SEM). A Rigaku Rint 2000 X-ray diffractometer, run at 40 kV and 30 mA (Cu-Kα radiation) in a step-scan mode (2°/2θ), was used to determine phases after calcination. The excitation and emission spectra of the synthesized phosphors were recorded on a fluorometer (Photon Technology International (PTI), QuantaMaster™ 30).

**Results and Discussion**

**Thermal analysis**

To examine the thermal stability of Ca$_3$MgSi$_2$O$_7$, which is composed of CaCO$_3$ and Mg(OH)$_2$ and SiO$_2$, DTA/TG analyses were carried out with the raw material mixture between 50 °C and 1350 °C (Fig. 1).

As shown by Fig. 1, the initial weight loss from the former precursor for about 2% from room temperature to 250 °C is due the evaporation of the physically absorbed water from the raw materials mixture. The first major weight loss step is found in the temperature range of 90–97% N$_2$ + 10–3% H$_2$ gas mixture. In addition, the powders were also heated using a open atmosphere furnace and then cooled down to the room temperature slowly. The synthesized phosphors were ground to powder form and screened to pass 170 mesh sieves prior to the characterization.

Fig. 1—TG and DTA results of the oxide/carbonate/hydrate mixtures prepared by ceramic method with identical target lattice composition of Ca$_3$MgSi$_2$O$_7$:0.006RE.
sharp drop of weight corresponds to the endothermic peak at 385 °C. The second endothermic peak appearing in the range 430–800 °C corresponds to the decomposition of magnesium hydroxide and regulation of the Mg(OH)$_2$ structure to that of pure MgO, accompanied by the loss of structural water. This rapid mass decrease corresponding to the endothermic effect was indicated in the TG results.

The second stage weight loss 510–790 °C is also related to the decomposition of CaCO$_3$ which occurs in a single step in a defined way due to carbon dioxide release, given rise to calcium oxide: CaCO$_3$(s) → CO$_2$(g) + CaO(s) corresponding to the endothermic peak at 765 °C in its DTA curve. The exothermal peak at 884 °C is believed to be the crystallization temperature for the first formation of Ca$_2$MgSi$_2$O$_7$ in the solid state-assisted process; also the precursor continues to crystallize at 1224 °C as indicated by a second clear exothermal peak. The TG curve exhibits a total mass loss of 26.50%, which is almost similar the calculated mass loss (26.48%) attributed to the complete dehydroxylation process of Mg(OH)$_2$ and CaCO$_3$.

**Particle size and characterization**

After calcination at optimum temperature of 1300 °C, for 2 h to get the dominant Ca$_2$MgSi$_2$O$_7$ phase, the samples were dry-ground and sieved under 170 mesh for characterization, e.g. SEM, XRD and PL. The comparative particle size distribution of Ca$_2$MgSi$_2$O$_7$ based phosphor samples, into which the rare earth ions were separately doped, were analyzed by laser particle size analysis. The particle size distribution of the Ca$_2$MgSi$_2$O$_7$ based phosphor samples was found to be $d(0.1): 2.535$ mm, $d(0.5): 15.390$ mm and $d(0.9): 63.256$ mm.

**X-ray diffraction (XRD) analysis**

Figure 3 depicts that the XRD patterns of the samples indicating the major peaks which can be indexed to Ca$_3$MgSi$_2$O$_7$ in a tetragonal structure (JCPDS 87-0052). This single-phase sample is well crystallized at 1300 °C for 2 h. Since no impurity phase was
observed in any of the samples, it clearly implies that the obtained samples are single phase and doping does not cause any significant change in the host structure or lattice distortions.

**Photoluminescence properties**

The excitation and emission spectra of Eu2O3 added Ca2MgSi2O7 phosphors, calcined in open atmosphere as well as weak reducing atmosphere are presented in Fig. 4.

Eu2O3 added Ca2MgSi2O7 phosphor calcined in weak reducing atmosphere has an emission band being at 532 nm in yellowish-green color region (Fig. 4(b)). The relative strong intensity of Eu2+ observed in its emission spectrum is due to the 4f to 5d transition of the Eu2+ ion because of the reducing atmosphere calcination conditions as reported in recent studies. Divalent europium ion (Eu2+) is one of a well known activator in phosphors for application in modern lighting, displays, and optical communications fields such as light-emitting diodes (LEDs), long-lasting phosphors (LLPs), fluorescent lamps and plasma display panels (PDPs). According to the structural studies, there is only one eight-coordinated Ca2+ site in the tetragonal Ca2MgSi2O7 lattice. It was predicted that Eu2+ and Mn2+ tend to substitute the Ca2+ and Mg2+ sites, respectively, because the ionic radii of Eu2+ (1.25 Å) and Mn2+ (0.66 Å) are compatible with those of Ca2+ (1.12 Å) and Mg2+ (0.75 Å). Also, the Si4+ site (0.26 Å) is too small for the Eu2+ and Mn2+ occupation to take place. When Eu replaces Ca in the Ca2MgSi2O7 phosphor, it will occupy two different kinds of lattice sites (Eu1 and Eu2) with coordination numbers of six or eight.

In the emission and excitation spectra of Eu3+-doped, or in other words, Eu2O3-activated Ca2MgSi2O7 calcined in oxidized atmosphere measured at room temperature (Fig. 5(b)), the following emission transitions were observed: $^5D_0 \rightarrow ^7F_1$ at 577 nm and $^2D_0 \rightarrow ^2F_2$ at 616 nm (611–620 nm), of which the $^5D_0 \rightarrow ^7F_1$ transition is stronger. Eu3+ ions emit a characteristic red light with several narrow lines due to the $4f \rightarrow 4f$ ($^5D_0 \rightarrow ^7F_i = 0, 1, 2, 3, 4$) transitions.

The luminescence spectrum of Eu3+ ion is slightly influenced by the surrounding ligands of the host material because the transitions of Eu3+ involve only a redistribution of electrons within the inner 4f sub-shell. The excitation spectra of these phosphor samples show that they can be well excited by near UV-light which is exactly as required by ultra-violet chip pumped multi-phosphor converted white LEDs.

Dy3+ ions have been often used as co-dopant in long afterglow phosphorescent pigments. When divalent alkaline earth ions, such as Ca2+ or Sr2+, are substituted by trivalent Dy3+ in the alkaline earth silicates and aluminates, various defects can be induced due to the charge compensation mechanism, among which alkaline earth ion vacancy (VM), is the principal one. VM is considered to be the hole trap, while Dy3+ occupying alkaline earth ion sites is a very probable source of electron trap. In the Eu2+ activated and the Dy3+ co-doped long afterglow phosphors, such as SrAl2O4: Eu2+, Dy3+, Y3+ or Sr2Al4O9: Eu2+, Dy3+, most of the excitation energy will be transferred from the host or the Dy3+ to the Eu2+. Thus, only 5d-5f emissions of Eu3+ can be observed. However, in the current study it is thought that in Dy3+ singly...
doped hosts, Dy\(^{3+}\) may be not only the supplier of traps but also an activator itself, as mentioned previously in the literature\(^5\).

The excitation and the emission spectra of the only Dy\(^{3+}\)-doped and also Dy\(^{3+}\)-doped with Ce\(^{3+}\)-co-doped Ca\(_2\)MgSi\(_2\)O\(_7\) samples are given in Fig. 5. Dy\(^{3+}\) ions, which show luminescence lines in the 470–500 nm region due to \(4F_{9/2} \rightarrow 6H_{15/2}\) transition and in the 570–600 nm region due to the \(4F_{9/2} \rightarrow 6H_{13/2}\) transition, have attracted much attention because of the white emission in the visible region of electromagnetic spectra. For the Dy\(^{3+}\) single-doped Ca\(_2\)MgSi\(_2\)O\(_7\):Dy\(^{3+}\) phosphor (Fig.5(a)), the excitation spectra for the emission at both 575 nm and 486 nm comprise a series of line spectra in the 250–430 nm region with the strongest line at 350 nm and some lines at 266, 296, 326, 362 and 389 nm, which are ascribed to the transitions from the ground state to excited states in the 4\(f\)^9 configuration of Dy\(^{3+}\); however these are not clearly assigned due to the dense and somewhat overlapping levels of 4\(f\) configuration of Dy\(^{3+}\) in the high energy region. The blue emission peaking at 486 and yellow emission peaking at 575 nm were observed and may be assigned to the \(4F_{9/2} \rightarrow 6H_{13/2}\) and \(4F_{9/2} \rightarrow 6H_{15/2}\) transitions of Dy\(^{3+}\), respectively\(^5,14\). The excitation spectra monitoring the 575 and 576 nm emissions consist of a series of lines in the 250–350 nm range with the strongest one at 350 and 326 nm. Also, it can be clearly seen that Ce\(_2\)O\(_3\) co-doping increases the luminescence intensity of the Dy\(^{3+}\)-doped host lattice, and requires to be investigated in detail.

The after glow process in the Ca\(_{x}\)MgSi\(_2\)O\(_{5+x}\):Dy\(^{3+}\) (\(x: 1, 2, 3\)) system has been described earlier by Chen \textit{et al.}\(^5\). According to this study, after irradiation with the ultraviolet light, most of the excitation energy associated with the excited carriers (electrons or holes) will be transferred via the host directly to the luminescence centers, Dy\(^{3+}\), followed by the Dy\(^{3+}\) 4\(f\) emissions as the immediate luminescence. However, part of the excitation energy will be stored when some of the excited carriers drop into the traps, instead of returning to the ground state. Later, with thermal excitation at proper temperature, these carriers will be released from the traps and transferred via the host to the Dy\(^{3+}\) ions, followed by the characteristic and persistent Dy\(^{3+}\) emissions. In practice, the electron traps and the hole traps may not be both equally abundant or important in terms of their contribution to the long afterglow emission\(^5\).

The excitation spectra (\(\lambda_{\text{exc}}: 341\) nm and 347 nm) of Ce\(^{3+}\)-doped Ca\(_2\)MgSi\(_2\)O\(_7\) host, calcined in open and weak reducing atmosphere has been observed as one broad band centered at 395 and 398 nm, respectively (Fig. 6).

The notable point is that main excitation and emission wavelengths are similar for synthesis in
both open and weak reducing atmospheres, but the Ce-activated phosphor synthesized in weak reducing atmosphere shows a broad blue asymmetric emission band at higher intensity, in addition to white light emission under UV-A excitation.

The asymmetric band could be excited by the spin orbit coupled into two levels of ground state. The asymmetry peak can be deconvoluted into two Gaussian profiles centering at ~390 and ~430 nm, which may be assigned to the transition from the lowest 5d level to $^2F_{5/2}$ and $^2F_{7/2}$, respectively. The energy difference between the spin-orbit splitting of the 4f ground state ($\Delta E = 1/\hbar\lambda_1 - 1/\hbar\lambda_2$) in Ca$_2$MgSi$_2$O$_7$:Ce$^{3+}$ is about 2254 cm$^{-1}$, which agrees with the theoretical value (2000 cm$^{-1}$). Ce$^{3+}$ doping in some hosts results in emission spectra near the ultraviolet region. The luminescent colours or wavelengths of these ions change widely from near UV to red region depending on the nature of the host lattices. Alkaline earth silicates, such as Ce$^{3+}$ activated Ca$_2$MgSi$_2$O$_8$ phosphor, gave rise to an efficient purple-blue emission under UV excitation and generated two kinds of emission centers in the host$^{14}$. Also, the long lasting phosphorescence was observed in Ce$^{3+}$ doped Ca$_2$Al$_2$SiO$_7$ at room temperature$^{18}$. Ce$^{3+}$ ion in åkermanite calcined in reducing atmosphere, which is in the $4f^1$ configuration, showed efficient white luminescence owing to the $4f$–5d transition. The $4f$–5d transition of Ce$^{3+}$ ions in solids is the parity allowed electric dipole transition having large oscillator strengths; such transitions produce efficient broad band luminescence. It has a larger Stokes shift than that of other rare earth ions due to the extended radial wave functions of the 5d state. Because of the favourable spectroscopic properties of Ce$^{3+}$ and the ability to incorporate Ce$^{3+}$ into different host materials, cerium activated materials have received renewed interest$^{18}$.

Generally, lanthanides exhibit the 3+ oxidation state, since they lose two 6s electron and one 5d(4f) electron to attain the lowest ionization energy. However, due to the presence of either half filled or completely filled or empty 4f sub shell, Ce, Pr, Nd, Tb, and Dy can also present the 4+ oxidation state, i.e. Ce$^{4+}$ ($4f^0$), Pr$^{4+}$ ($4f^1$), Nd$^{4+}$ ($4f^2$), Tb$^{4+}$ ($4f^0$), and Dy$^{4+}$ ($4f^8$)$^{19}$. Praseodymium oxides have attracted in the recent years because of their optical, electronic, and chemical properties. The PrO$_x$ system has a similar series having the general formula, Pr$_2$O$_{2n-2}$ with n = 4, 5, 6, 7, 9, 10, 11, 12, 18. The Pr$^{3+}$ oxide phase, i.e., Pr$_2$O$_3$, has also a hexagonal structure. This structure is characteristic for stoichiometric Pr$^{4+}$ oxide ($\alpha$-PrO$_2$). The phases intermediate between Pr$^{3+}$ and Pr$^{4+}$ oxides (β-Pr$_2$O$_{11}$, δ-Pr$_1$O$_{20}$, ε-Pr$_2$O$_9$, ζ-Pr$_2$O$_{16}$, τ-Pr$_2$O$_{12}$, Pr$_2$O$_{10}$ and Pr$_2$O$_8$) are classified into the oxygen-deficient modifications of the fluorite structure. Since the most stable phase of the neighboring rare earth oxide (REO) praseodymia is Pr$_6$O$_{11}$, exhibiting a mixed valence state (Pr$^{4+}$/Pr$^{3+}$) and the highest oxygen exchange activity among all rare earth oxides at atmospheric pressure and room temperature$^{20}$, Pr$_6$O$_{11}$ has been used as the source of Pr$^{3+}$ or Pr$^{4+}$-ions in the present study.

The excitation and emission spectra of Pr$_6$O$_{11}$-doped Ca$_2$MgSi$_2$O$_7$ phosphor which is calcined under open atmosphere is presented in Fig. 7(a). There are
three excitation peaks at 447 nm ($^3H_4\rightarrow^3P_2$), 468 nm ($^3H_4\rightarrow^3P_1$) and 483 nm ($^3H_4\rightarrow^3P_0$) and the strongest peak is at 447 nm. Significantly, the sharp emission peak at 600 nm and the half peak which is joined to the main peak can be seen in Fig. 7 (b). The main emission peak corresponds to $^1D_2\rightarrow^3H_4$ transition of Pr$^{3+}$. In the Ca$_2$MgSi$_2$O$_7$ crystal lattice, the praseodymium ions are substituted for the Ca$^{2+}$ ions, both as trivalent (Pr$^{3+}$) and tetravalent (Pr$^{4+}$) states and the red color is exclusively caused by the Pr$^{4+}$ ions since the calcination atmosphere is appropriate to maintain Pr$^{4+}$ ions in Pr$_6$O$_{11}$. Pr$_6$O$_{11}$-added, or more clearly Pr$^{3+}$-doped phosphors with full color luminescence have received substantial interest because the Pr$^{3+}$ ions exhibit different emissions according to the host lattice in which they are incorporated, e.g., red (from the $^1D_2$ level), green (from the $^3P_0$ level), blue (from the $^3S_0$ level) and ultraviolet (from the 4f–5d state)$^{21}$. The phosphorescence of 640 nm (red) and 553 nm (green) emission in the sample synthesized in weak reducing atmosphere is derived from $^3P_0\rightarrow^3H_6$ and $^3P_0\rightarrow^3H_5$ transitions of Pr$^{3+}$ under 299 nm UV excitation (Fig. 7(b)).

$\text{Pr}_6\text{O}_{11}$ (i.e. Pr$^{3+}$/Pr$^{4+}$) source for the present study is composed of Pr$_2$O$_3$ and Pr$_2$O$_5$, and the Pr$_6$O$_{11}$ doping process of can be defined by Eqs (1-3).

$$\text{Ca}_2\text{MgSi}_2\text{O}_7 + 2\text{Pr}^{3+} \rightarrow 2\text{Pr}^{4+} + 2e' + \frac{3}{2}\text{O}_2 \uparrow \quad ... \ (3)$$

$Pr^{4+}$ represents vacancy with two positive charge when Pr$^{4+}$ ion takes up the Ca$^{2+}$ site. $Pr^{3+}_{Ca}$ represents a vacancy with a positive charge when Pr$^{3+}$ ion takes up a Ca$^{2+}$ site. $V_{Ca}$ is the vacant site of a Ca$^{2+}$ site and $e'$ is a quasi-free electron.

Previous works have shown that RE$^{3+}$ ions are randomly distributed over the same cationic sites of Ca$^{2+}$ in the Ca$_2$MgSi$_2$O$_7$ host.$^6$ According to Kröger-Vink notation, Pr$^{5+}$ occupies the position of Ca$^{2+}$ on PrO$_2$ doping. Cation vacancy is generated to compensate charge for the non-equivalence substitution as in Eq. (1). When Pr$_2$O$_3$ is added to the host, the Pr$^{3+}$ ions occupy the Ca$^{2+}$ sites with the cation vacancies created to compensate charge as seen in Eq. (2). The $Pr^{3+}_{Ca}$ vacancy may also be compensated by the quasi-free electron, which is generated from the 5d band of Pr$^{3+}$ (Eq. (3))$^{18}$. The presence of Pr in Ca$_2$MgSi$_2$O$_7$ requires to be investigated in detail by X-ray absorption nearedge spectroscopy (XANES) to determine valences of both 3+ and 4+ or one of them.

The rare earth Sm$^{3+}$ with a 4f$^{5}$ electron configuration is often regarded as an efficient activator or co-activator to enhance luminescence intensity. It has complex energy levels and various possible transitions between f levels exhibit a strong orange-red fluorescence. The transitions obtained between these f levels are highly marked and the spectral lines are sharp.$^{23}$

![Fig. 7—Excitation and emission spectra of Ca$_2$MgSi$_2$O$_7$:0.006Pr$^{3+}$/Pr$^{4+}$ synthesized in (a) open atmosphere and (b) weak reducing atmosphere.](image-url)
The results show that Ce different ionic states occupying in the same host lattice. The study shows that the rare earth ions visible white light emission from the åkermanite type phosphor. The excitation spectra of Sm-

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