Phase Equilibria in the Calcia-Gadolinia-Silica System

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Abstract

The phase equilibria in the CaO-Gd₂O₃-SiO₂ system were investigated by heat treating precursor-derived powders at 1400°C and 1600°C, determining the resulting phase assemblages, and measuring the compositions of the liquid and solid solution phases. The stable ternary phases at 1400°C include silico-carnotite (Ca₃Gd₂Si₃O₁₂), Ca/Gd-cyclosilicate (Ca₃Gd₂Si₆O₂₆), and the apatite solid solution field extending from Gd_{9.33}(SiO₄)₆O₂ to Ca_{2.75}Gd_{7.25}(SiO₄)₆O_{1.625}. Of these, only apatite remains stable to 1600°C. The high-temperature α- and α'-Ca₂SiO₄ polymorphs exhibit moderate Gd₂O₃ solubility. The results are compared to the equilibria for the related CaO-Y₂O₃-SiO₂ system. The implications for understanding the interaction between rare earth containing thermal barrier coatings (TBCs) and silicate deposits (CMAS) are discussed.

Keywords: ceramics, rare earth compounds, phase diagrams, silicates, apatite

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1 INTRODUCTION

Phases in the ternary $\text{CaO-GdO}_{1.5}^{\text{a}}\text{-SiO}_2$ (CGS) system are of interest for their luminescent properties [1], as ionic conductors for solid oxide fuel cells [2,3], and as prospective thermoelectric materials [4]. The crystallization of CGS phases from multi-component oxide melts also plays an important role in mitigating thermal barrier coating (TBC) degradation caused by molten silicate deposits (CMAS) in modern turbine engines [5,6]. In this context, $\text{GdO}_{1.5}$ (or other rare earth oxides, $\text{REO}_{1.5}$) from the coating react with CaO and SiO_2 in the deposit to rapidly precipitate an apatite phase, blocking open gaps in the coating structure and significantly slowing melt infiltration [5]. The dynamics of these reactions are determined by the solubility of the $\text{REO}_{1.5}$ in the melt and the driving force to precipitate apatite relative to other reaction products. Information about the phase relationships and solid solution homogeneity ranges in the CGS system is needed for optimizing system performance in functional applications and for interpreting the reaction sequences that effectively mitigate CMAS degradation.

Although the properties and behavior of individual CGS phases have been studied, there has not been a comprehensive assessment of the system to identify all of the ternary phases and their equilibrium relationships. The current study, an experimental investigation of the ternary CGS phase equilibria at 1400°C and 1600°C, addresses this need. The details of the solid-state equilibria at 1400°C are relevant to the design and processing of functional materials. Meanwhile, the experiments at 1600°C provide insight into the liquid-solid equilibria and the extent of the liquid field compared to related systems. These details are relevant to ongoing efforts to expand thermodynamic databases to include expected CMAS reaction products.

This study builds upon a recent investigation of the related $\text{CaO-YO}_{1.5}\text{-SiO}_2$ (CYS) system [7]. Although some similarities are observed, the exchange of Y^{3+} for Gd^{3+} (with a ~4% increase in ionic radius [8]) impacts the stability and homogeneity ranges of the phases. This investigation therefore focused on elucidating the differences between the two systems. The discussion of the results highlights the findings that are unique to the CGS system.

^a Molar concentrations of single cation formula units (i.e. $\text{GdO}_{1.5}$ rather than Gd_2O_3) are used to more readily relate stoichiometric changes to the underlying crystal chemistry. Where appropriate, the compact notation C = CaO, S=SiO₂, and G=GdO_{1.5} is used (e.g., $\text{C}_3\text{G}_2\text{S}_3 = \text{Ca}_3\text{Gd}_2\text{Si}_3\text{O}_9$).

2 BACKGROUND ON PHASE EQUILIBRIA

The known CGS phases are listed in Table 1. The current understanding of the binary and ternary phase equilibria are provided in the following sections. Additional background about the structures and crystal chemistry of the ternary phases is provided in the earlier article focused on the CYS system [7].

2.1 End Members and Binary Subsystems

CaO is stable with a single polymorph until it melts at 2613°C. There are five $\text{GdO}_{1.5}$ polymorphs. The transformations $\text{B-} \leftrightarrow \text{A-} \leftrightarrow \text{H-} \leftrightarrow \text{X-GdO}_{1.5}$ occur at 2170°C, 2208°C, and 2360°C, respectively; the temperature of the $\text{C-} \leftrightarrow \text{B-GdO}_{1.5}$ transition around 1200°C is less well defined due to slow reaction kinetics [9]. The equilibrium phases for SiO_2 include α - and β -quartz, HP-tridymite, and β -cristobalite with transitions at 574°C, 867°C, and 1470°C before melting at 1723°C [10]. However, SiO_2 exhibits a variety of metastable polymorphs [11] and rather than following the equilibrium sequence amorphous SiO_2 typically crystallizes as β -cristobalite and transforms to α -cristobalite upon cooling.

There are four ternary CaO- SiO_2 phases: CaSiO_3 , $\text{Ca}_3\text{Si}_2\text{O}_7$, Ca_2SiO_4 , and Ca_3SiO_5 [12]. All four are stable at 1400°C; at this temperature CS and C_2S exhibit the pseudo-wollastonite (C2/c) and α' (Pnma) structures, respectively. At 1600°C the α - C_2S ($\text{P6}_3/\text{mmc}$) structure is stable while CS and C_3S_2 , which melt congruently at 1544°C and 1464°C, respectively, should not be observed. In the related CYS system the α' - and α - C_2S structures have significant (~10 mol%) $\text{YO}_{1.5}$ solubility [7,13] but $\text{YO}_{1.5}$ is effectively insoluble in the lower-temperature larnite and γ - C_2S polymorphs. Similar behavior is expected for the CGS system. There is a liquid miscibility gap above ~1700°C in the range 72 mol% to 98 mol% SiO_2 [14,15].

Three binary $\text{GdO}_{1.5}$ - SiO_2 phases are reported [16]. The disilicate ($\text{Gd}_2\text{Si}_2\text{O}_7$, $\alpha \rightarrow \delta$ at ~1450°C [17]) and the monosilicate (Gd_2SiO_5) are line compounds. The third binary phase, $\text{Gd}_{9.33}(\text{SiO}_4)_6\text{O}_2$, is the CaO-deficient end member of the solid solution range for the apatite phase based on the $\text{Ca}_2\text{Gd}_8(\text{SiO}_4)_6\text{O}_2$ stoichiometry. Additional details about the structure and stability range for apatite are provided in Section 2.2. A liquid miscibility gap is reported above ~1700°C in the SiO_2 -rich side of the $\text{GdO}_{1.5}$ - SiO_2 system [16].

There is a single binary compound, CaGd_4O_7 , in the $\text{CaO-GdO}_{1.5}$ system [18]. Although the structure has not been extensively characterized, this phase is reportedly similar to B-type $\text{GdO}_{1.5}$ [9]. It is hypothesized that CG_4 arises as a distinct phase due to the ordering of the anion vacancies introduced as CaO dissolves into B- $\text{GdO}_{1.5}$. CG_4 melts around 2200°C but the low temperature stability limit is unclear, possibly due to difficulties distinguishing the phase from B- $\text{GdO}_{1.5}$. One report indicates that CG_4 is stable to temperatures as low as 1500°C [19] while other studies concluded that CG_4 decomposes to a mixture of CaO and $\text{GdO}_{1.5}$ below 1600°C [20], 1650°C [18], or 1700°C [21]. There are also conflicting reports about the solubility of $\text{GdO}_{1.5}$ and CaO in one another. Barry et al. found that CaO dissolves up to 11 mol% $\text{GdO}_{1.5}$ in the range 1600°C to 2100°C and that CaO is virtually insoluble in B-type $\text{GdO}_{1.5}$ at 1850°C . Conversely, Gulamova et al. found negligible $\text{GdO}_{1.5}$ solubility in CaO but report that $\text{GdO}_{1.5}$ dissolves 6 mol% CaO at 1700°C and 3.5 mol% CaO at 1400°C [21].

2.2 Ternary Phases

Two ternary CGS phases have been reported. These are the silicocarnotite phase, $\text{Ca}_3\text{Gd}_2(\text{SiO}_4)_3$, [1] and the apatite phase, nominally $\text{Ca}_2\text{Gd}_8(\text{SiO}_4)_6\text{O}_2$ [22]. Based on the equilibria in other $\text{CaO-REO}_{1.5}\text{-SiO}_2$ systems, the ternary system may also include $\text{Ca}_3\text{Gd}_2(\text{Si}_3\text{O}_9)_2$, a monoclinic cyclosilicate structurally similar to pseudo-wollastonite [23], and an orthorhombic cuspidine-type phase [7,24], $\text{Ca}_2\text{Gd}_2\text{Si}_2\text{O}_9$, which would be related to the monoclinic rare earth aluminates (e.g. $\text{Gd}_4\text{Al}_2\text{O}_9$). Experience in the $\text{CaO-YO}_{1.5}\text{-SiO}_2$ system [7] indicates that $\text{C}_3\text{G}_2\text{S}_3$ and $\text{C}_3\text{G}_2\text{S}_6$ should be line compounds while in apatite and cuspidine can exhibit solid solution homogeneity ranges enabled by ionic substitutions.

The apatite structure is described by the general formula $\text{M}^{\text{I}}_4\text{M}^{\text{II}}_6(\text{SiO}_4)_6\text{X}_2$. Using this nomenclature, M^{I} and M^{II} correspond to columns of cation sites along the c-axis of the hexagonal unit cell. The M^{I} and M^{II} sites are coordinated by 9 and 7 oxygen atoms, respectively. The X site, located within a ring of M^{II} columns, hosts anions not covalently bound in the Si tetrahedra. In the CGS system the X sites are occupied by oxygen, Gd^{3+} occupies the M^{II} site, and the M^{I} site can be occupied by a combination of Ca^{2+} and Gd^{3+} . Without introducing vacancies or interstitials, charge balance is achieved for the case where M^{I} contains two Ca^{2+} and two Gd^{3+} , $(\text{Ca}_2\text{Gd}_2)\text{Gd}_6(\text{SiO}_4)_6\text{O}_2$ (or, more simply, $\text{Ca}_2\text{Gd}_8\text{Si}_6\text{O}_{26}$) [4]. CaO and $\text{GdO}_{1.5}$ may be substituted for one another according to $\text{Gd}_{8+x}\text{Ca}_{2+y}(\text{SiO}_4)_6\text{O}_{2+3x/2+y}$. The apatite composition space enabled

by these substitutions is plotted in Figure 1(a). Increasing the Ca:Gd ratio ($x = -y$, $x < 0$) introduces oxygen vacancies on the X sites to maintain charge balance. In the CaO-rich direction the substitutions are limited to the case where every M^I site is occupied by Ca (i.e. $\text{Ca}_4\text{Gd}_6(\text{SiO}_4)_6\text{O}$, $x = -2$). Alternatively, increasing the relative Gd content ($x > 0$) requires either cation vacancies ($x = -2y/3$) or oxygen interstitials ($x = -y$). The terminal CaO-free compositions could therefore be in the range from $\text{Gd}_{9.33}(\text{SiO}_4)_6\text{O}_2$ to $\text{Gd}_{10}(\text{SiO}_4)_6\text{O}_3$.

Prior studies have examined the apatite stability over this notional range. The $\text{Gd}_{9.33}(\text{SiO}_4)_6\text{O}_2$ stoichiometry is generally accepted as stable [3,4,25]. Nakayama et al. [2] studied the properties of material identified as $\text{Gd}_{10}(\text{SiO}_4)_6\text{O}_3$, although they note the presence of G_2S impurities and don't provide clear evidence differentiating their predominant phase from $\text{Gd}_{9.33}(\text{SiO}_4)_6\text{O}_2$. Slater et al. later reported that $\text{Gd}_{10}(\text{SiO}_4)_6\text{O}_3$ is not stable but found that the ionic conductivity increases for compositions on the $\text{GdO}_{1.5}$ -rich side of $\text{Gd}_{9.33}(\text{SiO}_4)_6\text{O}_2$ [3]. Based on these results they conclude that oxygen interstitials could be incorporated up to $\text{Gd}_{9.67}(\text{SiO}_4)_6\text{O}_{2.5}$. Qu et al. also found that $\text{Gd}_{10}(\text{SiO}_4)_6\text{O}_3$ is not stable but conclude that the CGS apatite is stable over the full range of compositions permitted by vacancy incorporation (i.e. $\text{Ca}_4\text{Gd}_6(\text{SiO}_4)_6\text{O}$ to $\text{Gd}_{9.33}(\text{SiO}_4)_6\text{O}_2$) [4].

3 EXPERIMENTAL METHODS

Powders corresponding to the compositions listed in Table 2 were synthesized from ethanol-based solutions of gadolinium nitrate (99.9%, Alfa Aesar, Ward Hill, MA), calcium nitrate (99.9%, Fisher Scientific, Pittsburgh, PA), and tetraethyl orthosilicate (TEOS, reagent grade, Fisher Sci.) via dropwise addition into an aqueous ammonium hydroxide/carbonate solution. The resulting Gd- and Si-hydroxide and Ca-carbonate precipitates were washed in ethanol and pyrolyzed in air at 1000°C.

The oxide powders were pressed into 6 mm diameter, 1.5 mm thick pellets and wrapped in platinum foil prior to equilibration in air. Specimens in sub-solidus phase fields were annealed in zirconia boats (machined from FBD, Zircar Zirconia, Florida, NY) in a zirconia furnace tube (McDanel Advanced Ceramics, Beaver Falls, PA) for 200h at 1400°C or 100h at 1600°C. Zirconia hardware was used to prevent contamination by alumina. The longer time at 1400°C helped grow the grains to a sufficient size for composition analysis. The specimens were polished using diamond lapping films, thermally etched at the equilibration temperature for 1h,

and quenched into air. Compositions forming a liquid phase at 1600°C were suspended from platinum wire in a box furnace (to facilitate fast extraction), held for 5h, and water quenched prior to mounting in epoxy, cross sectioning, and polishing. An alcohol/glycol lubricant was used for specimens containing water-sensitive phases (e.g., CaO).

The equilibrated specimens were characterized using a combination of x-ray diffraction (XRD, Panalytical Empyrean, Westborough, MA), scanning electron microscopy (SEM, XL30 Sirion FEG, FEI, Hillsboro, OR), and transmission electron microscopy (TEM, Technai G2 Sphera, FEI). When grains were sufficiently large, phase compositions were measured by wavelength dispersive spectroscopy (EPMA, SX-100, Cameca, Madison, WI). The compositions of fine-grained phases were measured using energy dispersive spectroscopy in the TEM (TEM-EDS, Oxford Inca, Concord, MA). Multiple grains of each phase were measured; typical standard deviations were less than 1 mol%. Internal standards were used to assess the accuracy of these measurements. The errors in the EPMA and EDS data were generally of order 1% and 5% of the measured values, respectively.

4 RESULTS AND DISCUSSION

4.1 *General Phase Relationships at 1400°C and 1600°C*

The experimentally determined equilibrium phase assemblages and compositions are reported in Table 2 and Table 3, respectively. This data is plotted as two- and three-phase fields in Figure 2 (a, b) and was used to construct the 1400°C and 1600°C isothermal sections in Figure 2 (c, d). At 1400°C $C_3G_2S_3$ and $C_3G_2S_6$ were confirmed as stable phases; both phases melt between 1400°C and 1600°C. Apatite was observed at 1400°C and 1600°C. Cuspidine, hypothetically $C_2G_2S_2$ based on the equivalent $C_2Y_2S_2$, was not observed at either temperature. The small liquid field discovered at 1400°C expands considerably at 1600°C where it shares phase fields with SiO_2 , apatite, and $(Ca,Gd)_2SiO_4$. The details of the temperature-dependent shifts in phase stability and the solution homogeneity ranges are discussed in the following sections.

4.2 *Apatite Homogeneity Range*

Specimens with compositions located on both sides of $Gd_{9.33}(SiO_4)_6O_2$ between G_2S_2 and G_2S (ID 1 and 2, respectively) were used to confirm the width of the apatite field along the

GdO_{1.5}-SiO₂ binary. The equilibrium microstructures at 1400°C, not shown, and 1600°C, Figure 1(b, c), contained apatite and either G₂S₂ and G₂S. The measured apatite compositions corresponding the SiO₂-rich and SiO₂-lean sides of the binary apatite field, plotted in Figure 1(a), are within ~1 mol% of one another and are centered near Gd_{9.33}(SiO₄)₆O₂. This result confirms that apatite stoichiometries that would require oxygen interstitials are thermodynamically unfavorable.

The microstructures of specimens with the composition corresponding to Ca₄Gd₆(SiO₄)₆O (ID 4, the CaO-rich end of the notional apatite field) are shown in Figure 1(d-f). Neither specimen is single-phase apatite. At 1400°C the specimen contains apatite and a significant fraction of silico-carnotite (C₃G₂S₃). At 1600°C apatite is in equilibrium with (Ca,Gd)₂SiO₄ and liquid. For both temperatures the measured terminal GdO_{1.5}-lean apatite composition is approximately Ca_{2.75}Gd_{7.25}(SiO₄)₆O_{1.625} (~17 mol% CaO, Figure 1(a)), located roughly midway between the defect-free Ca₂Gd₈(SiO₄)₆O₂ stoichiometry and Ca₄Gd₆(SiO₄)₆O. These observations indicate that the apatite stoichiometry Ca₄Gd₆(SiO₄)₆O has a higher free energy than the multi-phase assemblages.

The present findings are consistent with reports that the CaO solubility is limited to $y < 1$ for apatite containing either NdO_{1.5} (a larger cation) or YO_{1.5} (a smaller cation) [7,26] but contradict the report that Ca₄Gd₆(SiO₄)₆O ($y = 2$) and Ca₃Gd₇(SiO₄)₆O_{1.5} ($y = 1$) can be formed at 1600°C [4]. However, XRD, which was used for phase identification in the earlier CGS apatite work, would have limited sensitivity to detect the presence of glass and the partially decomposed (Ca,Gd)₂SiO₄ phase described in the next section. In fact, in the current investigation only reflections corresponding to the apatite phase were clearly discernable in the XRD spectrum for specimen ID 4 equilibrated at 1600°C.

The remaining three-phase triangles defining the relationship between apatite and other phases (e.g., ID 7-10) all join the apatite phase near Ca₂Gd₈(SiO₄)₆O₂, suggesting a strong thermodynamic preference for the defect-free stoichiometry compared to those requiring vacancy formation.

4.3 *GdO_{1.5} Solubility in Ca₂SiO₄*

The α' - and α -C₂S polymorphs appear to dissolve GdO_{1.5}. However, conclusive analysis of the nature of these phases at high temperature is complicated by their tendency to transform to

GdO_{1.5}-free C₂S polymorphs upon cooling. After quenching, the initial GdO_{1.5}-bearing C₂S grains in sub-solidus samples exhibit dark bands indicating the nucleation of a lower-temperature C₂S phase, Figure 3 (a,b,d). In specimens containing a liquid phase the partial transformation upon quenching produces a mottled appearance, Figure 3 (c) and Figure 6 (e). The compositions reported in Table 3 and used to construct Figure 2 represent area measurements for these partially transformed regions. The maximum values indicate that α' -/ α -can dissolve up to 8 mol% and 14 mol% GdO_{1.5} at 1400°C and 1600°C, respectively. The addition of GdO_{1.5} corresponds to a reduction in the CaO content, suggesting that Gd³⁺ substitutes for Ca²⁺ (i.e. (Ca,Gd)₂SiO₄). The measured SiO₂ contents rise slightly at the higher GdO_{1.5} contents indicating that the formation of cation vacancies maintains charge balance in the structure.

4.4 *Equilibria in the CaO-GdO_{1.5} Binary*

Specimens 11 and 12 provide information about the CaO-GdO_{1.5} binary equilibria. At 1400°C the XRD patterns for these samples, Figure 4, indicate that only CaO (ICSD 98-007-5786) and B-GdO_{1.5} (ICSD 98-063-6103) are stable along this binary. At 1400°C CaO dissolves up to 3 mol% GdO_{1.5} while B-GdO_{1.5} dissolves up to 7 mol% CaO. The XRD spectra for the specimens annealed at 1600°C reveal the presence of CaGd₄O₇ (ICSD 98-002-0818) instead of B-GdO_{1.5}. However the composition measurements indicate that grains identified as CG₄ were generally CaO-lean relative to the stoichiometric composition. This may indicate that CG₄ exhibits a small homogeneity range extending toward the GdO_{1.5} corner.

4.5 *Homogeneity Ranges for Other Phases*

At 1400°C the composition measurements indicate that C₃G₂S₃ and C₃G₂S₆, Figure 5 (a-c), are effectively line compounds with homogeneity ranges extending less than 1 mol% from their nominal stoichiometries. The binary G₂S and G₂S₂ phases exhibited less than 0.1 mol% CaO solubility while CS dissolves less than 0.2 mol% GdO_{1.5}. C₃S can dissolve up to 3mol% GdO_{1.5}; like C₂S, the CaO concentration in C₃S drops with increasing GdO_{1.5} content, consistent with the proposed (C,G)₃S formula.

4.6 *Liquid Field at 1600°C*

The shape of the liquid field at 1600° was assessed by measuring the glass compositions for the six specimens containing a liquid phase. The microstructures shown in Figure 6(a-d), IDs

5, 6, 9, and 14, each contained single-phase liquid. The compositions at the SiO₂-rich side of the liquid field, Figure 6(e,f) showed evidence of separation into SiO₂-rich and -lean liquids. The microstructure for specimen ID 15, Figure 6(f), the phase separated liquid only appeared in regions away from the crystalline SiO₂ grains. This observation suggests that the phase separation is either metastable at 1600°C or that it occurs upon cooling. Therefore, the average composition of the two phase regions was used in constructing the liquid phase field in Figure 2(d).

4.7 Comparison with the CaO-YO_{1.5}-SiO₂ System

The substitution of GdO_{1.5} for YO_{1.5} in the CaO-REO_{1.5}-SiO₂ system impacts the stability of the ternary phases and the homogeneity ranges for the solution phases. Compared to the CYS system [7], key differences in the CGS system include (i) the absence of cuspidine at 1400°C and 1600°C, (ii) decreased high temperature stability of silico-carnotite, (iii) an increased range of stable apatite compositions, and (iv) reduced GdO_{1.5} solubility in the predominantly CaO + SiO₂ liquid. These differences, which arise because Gd³⁺ is ~4% larger than Y³⁺ [8], are discussed in the following paragraphs.

In the YO_{1.5} system cuspidine is based on the monoclinic Y₄Al₂O₉ (YAM) phase. YAM accommodates substitution of Si⁴⁺ for Al³⁺ up to ~18mol% SiO₂ [27] or coupled substitutions of Ca²⁺ for Y³⁺ and Si⁴⁺ for Al³⁺ leading to the AlO_{1.5}-free end member with the approximate stoichiometry Ca₂Y₂Si₂O₉ [7,24]. The same phase was expected in the CGS system because the CYS cuspidine phase is quite stable (m.p. > 1700°C) and because Y₄Al₂O₉ and Gd₄Al₂O₉ have similar melting points [28,29] and exhibit similar SiO₂ solubility limits [27]. However, the recent CYS investigation revealed that YO_{1.5} substitutes into the structure more readily than CaO leading to stable compositions with Y:Ca ratios slightly greater than one [7]. The associated excess oxygen likely occupies a nominally vacant interstitial site. One possible explanation for this behavior is that the cation sites are slightly undersized to accommodate Ca²⁺, making it energetically more favorable to incorporate the interstitial oxygen than to maintain the 1:1 Y:Ca stoichiometry. In this case, substitutions involving the larger Gd³⁺ would be less favorable. However, additional details of the solid solution structures are needed in order to more definitively assess the reasons for the differences in stability.

The melting point of silico-carnotite was reduced from 1732°C in the CYS to below 1600°C in the CGS system. This observation is generally consistent with the previously reported trend that this phase become less stable as the RE^{3+} size is increased [1].

The homogeneity range for apatite, Figure 1(a), covers a wider range of RE:Ca ratios in the $\text{GdO}_{1.5}$ - than $\text{YO}_{1.5}$ -based system. This suggests that the stability of the stoichiometries requiring vacancies for charge balance increases for the larger Gd cation. This conclusion is consistent with data indicating that the enthalpy of formation for the CaO-free apatite stoichiometry increases with the size of the rare earth cation [25]. However, both systems show a tendency to form apatite near the defect-free $\text{Ca}_2\text{RE}_8(\text{SiO}_4)_6\text{O}_2$ stoichiometry rather than along the length of the homogeneity range. Additionally, in both systems the equilibria with the liquid phase only involve apatite compositions with CaO concentrations greater than or equal to $\text{Ca}_2\text{RE}_8(\text{SiO}_4)_6\text{O}_2$.

$\text{GdO}_{1.5}$ is less soluble than $\text{YO}_{1.5}$ in the liquid phase. The CGS liquid dissolves up to 14 mol% $\text{GdO}_{1.5}$ at 1600°C whereas the liquid in the CYS system can dissolve over 25 mol% $\text{YO}_{1.5}$. Additionally, apatite is the only $\text{GdO}_{1.5}$ -rich phase that exists in equilibrium with this liquid while, depending on the Ca:Si ratio, apatite, Y_2S_2 , and $\text{C}_3\text{Y}_2\text{S}_3$ all share equilibrium fields with the liquid in the CYS system. This behavior is likely influenced predominantly by the driving force to precipitate the crystalline phases (e.g., apatite). The equilibrium $\text{REO}_{1.5}$ solubility limit should vary inversely with the magnitude of the free energy of formation for the crystallizing phase. The collective evidence from calorimetry [25] and the phase equilibria suggests that there is a stronger driving force to precipitate apatite in the CGS system compared to the CYS system. The apparently smaller formation energy for the CYS apatite leads to a higher (and more variable) $\text{YO}_{1.5}$ solubility limit in the liquid phase.

The ease of incorporating the RE^{3+} into the melt structure likely plays a secondary role in determining the solubility limit. $\text{YO}_{1.5}$ and $\text{GdO}_{1.5}$ are known to be modifiers in the glass structure [30]. The solubility of $\text{YO}_{1.5}$ and $\text{GdO}_{1.5}$ in pure amorphous SiO_2 is low. CaO additions partially de-polymerize the SiO_2 making it easier to incorporate Y^{3+} and Gd^{3+} . However, in silicate liquids Y^{3+} is typically coordinated by six non-bridging oxygens (NBOs) while the larger Gd^{3+} has a higher coordination number [30,31]. The higher Y^{3+} field strength also exerts a stronger influence on the local structure. Thus, for a given fraction of NBOs (i.e. the ‘openness’

of the melt structure, determined by the modifier content) Y^{3+} should be more readily accommodated than Gd^{3+} .

4.8 *Implications for TBC Reactivity with CMAS*

Efforts to develop improved thermal barrier coatings materials for mitigating CMAS degradation aim to maximize the volume of rapidly crystallizing phases (V_{crys}) formed per volume of dissolved thermal barrier coating (V_{TBC}). In this context apatite is a desirable reaction product because it contains a high fraction of melt constituents ($CaO + SiO_2$) and precipitates rapidly upon TBC dissolution [5,32]. Systems favoring the crystallization of slower-growing silicates including garnet [6,33] and cuspidine [34] or which have a high $REO_{1.5}$ solubility in the melt do not arrest melt infiltration as effectively as those that only form apatite and have low solubility limits in the melt [6].

Efforts to make quantitative comparisons between the behaviors of TBC materials based on tests with individual ‘representative’ deposits are complicated by the wide variations in the anticipated deposit compositions. It is more effective to develop an understanding of the reactions by examining the underlying phase equilibria. The long-term goal, advanced by this and related studies, is to develop a thermodynamic database capable of accurately predicting the reactions occurring in higher-order (6+ component) systems. However, in the absence of such a tool preliminary assessments can be made based on the phase equilibria in the sub-systems containing the important phases involved in the reactions (i.e. apatite and a liquid containing predominantly CaO and SiO_2). Comparisons between the 1600°C isothermal sections for the CGS and CYS systems provides several insights into the differences in behavior for $GdO_{1.5}$ - and $YO_{1.5}$ -based coating materials upon reaction with silicate deposits containing varied Ca:Si ratios:

- (i) The ratio of $V_{crys}:V_{TBC}$ for apatite precipitation is determined in part by the ratio Ca:RE in the apatite phase. The phase equilibria indicate that although the stable Ca:Gd range for apatite is wider than Ca:Y, the apatite compositions that exist in equilibrium with the melt for both systems fall in a smaller subset at the CaO-rich end of the homogeneity range. This finding is consistent with measurements of the equilibrium apatite compositions upon reaction between prospective TBC systems and C(M)AS melts [35].
- (ii) Although ternary phases beside apatite are stable in the CGS system, the absence of the cuspidine phase, lower melting temperature for $C_3G_2S_3$, and lack of an equilibrium between

GdDS and the liquid phase at 1600°C suggest that apatite is more likely to be the predominant reaction product for a $\text{GdO}_{1.5}$ - compared to $\text{YO}_{1.5}$ -based TBC. This means that for an equivalent $\text{REO}_{1.5}$ concentration in the coating materials, coatings containing $\text{GdO}_{1.5}$ would be more likely to form apatite than those containing $\text{YO}_{1.5}$.

- (iii) The lower solubility limit of $\text{GdO}_{1.5}$ in the melt compared to $\text{YO}_{1.5}$ implies that the dissolution of $\text{GdO}_{1.5}$ -based TBC would saturate the melt and initiate apatite precipitation more readily than an equivalent $\text{YO}_{1.5}$ -based TBC.

The differences between the phase equilibria for the $\text{YO}_{1.5}$ - and $\text{GdO}_{1.5}$ -CaO-SiO₂ systems are not likely to influence to comparative behavior of rare earth stabilized TBC materials (i.e. 7YSZ vs. equivalent $\text{GdO}_{1.5}$ -stabilized tetragonal ZrO₂). The differences will be more pronounced for coatings with higher $\text{REO}_{1.5}$ content. Specifically, $\text{Gd}_2\text{Zr}_2\text{O}_7$ should offer improved resistance to molten silicate degradation compared to $\text{Y}_4\text{Zr}_3\text{O}_{12}$. This conclusion is consistent with RE cation-size-dependent reaction behavior between thermal barrier oxides and representative multi-component silicate melts [6,35].

5 CONCLUSIONS

This study elucidated the CaO- $\text{GdO}_{1.5}$ -SiO₂ phase equilibria at 1400°C and 1600°C. Key findings include:

- At 1400°C silicocarnotite ($\text{C}_3\text{G}_2\text{S}_3$) and cyclosilicate ($\text{C}_3\text{G}_2\text{S}_6$) are stable line compounds while apatite exhibits a solid solution homogeneity range. Of these, only apatite is stable at 1600°C.
- Although the crystal chemistry of the apatite phase permits compositions in the range $\text{Ca}_4\text{Gd}_6(\text{SiO}_4)_6\text{O}$ to $\text{Gd}_{9.33}(\text{SiO}_4)_6\text{O}_2$, the most CaO-rich compositions are not stable relative to the equilibrium with other phases. Specifically, the stable range extends from $\text{Ca}_{2.75}\text{Gd}_{7.25}(\text{SiO}_4)_6\text{O}_{1.625}$ to $\text{Gd}_{9.33}(\text{SiO}_4)_6\text{O}_2$.
- Ca_2SiO_4 dissolves up to 8.5 mol% $\text{GdO}_{1.5}$ at 1400°C and up to 14 mol% $\text{GdO}_{1.5}$ at 1600°C. The Gd^{3+} likely substitutes onto the Ca^{2+} sites with corresponding cation vacancy formation to maintain charge balance.
- At 1600°C the liquid can coexist with crystalline SiO₂, apatite, and (C,G)₂S. The wide range of liquid compositions stable in contact with apatite indicates that the latter phase is

likely to be the predominant crystallization product for reactions between $\text{GdO}_{1.5}$ -based TBCs and $\text{CaO}+\text{SiO}_2$ based melts.

The insights from this work aid in developing new phase stable oxides for functional applications and contribute to developing phase equilibrium-based tools for designing improved thermal barrier coatings.

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TABLES

Table 1: Binary and Ternary CaO-SiO₂-GdO_{1.5} Phases

Formula	Abbreviation	Phase Name	Space Group
CaO	C	Lime	Fm3m
SiO ₂	S	α -, β -Quartz HP-Tridymite β -Cristobalite	P3 ₂ 21, P6 ₂ 22 P6 ₃ /mmc Fd3m
GdO _{1.5}	G	C	Ia $\overline{3}$
		B	C2/m
		A	P $\overline{3}$ m1
		H	P6 ₃ /mmc
		X	Im $\overline{3}$ m
CaSiO ₃	CS	Wollastnite (β)	P $\overline{1}$
		Parawollastonite (2M)	P12 ₁ /c1
		Pseudowollastonite (α)	C2/c
Ca ₃ Si ₂ O ₇	C ₃ S ₂	Rankinite	P12 ₁ /c1
Ca ₂ SiO ₄	C ₂ S	Larnite	P12 ₁ /c1
		Calcio-Olivine (γ)	Pnma
(Ca,Gd) ₂ SiO ₄	(CG) ₂ S	α -Ca ₂ SiO ₄ α' -Ca ₂ SiO ₄	P6 ₃ /mmc Pnma
(Ca,Gd) ₃ SiO ₅	C ₃ S	Hatrurite	R3m
Gd ₂ Si ₂ O ₇	G ₂ S ₂	Gadolinium Disilicate (α)	P $\overline{1}$
		Gadolinium Disilicate (δ)	Pna2 ₁
Gd ₂ SiO ₅	G ₂ S	Gadolinium Monosilicate (X2)	P2 ₁ /c
CaGd ₄ O ₇	CG ₄	Calcium Gadolinium Oxide	C2/m
(Ca,Gd) ₄ Gd ₆ (SiO ₄) ₆ O ₂	Ap	Apatite	P6 ₃ /m
Ca ₃ Gd ₂ Si ₃ O ₁₂	C ₃ G ₂ S ₃	Silicocarnotite (SC)	Pnma
Ca ₃ Gd ₂ Si ₆ O ₁₈	C ₃ G ₂ S ₆	CaGd-cyclosilicate (CyS)	C2/c

Table 2: CaO-SiO₂-GdO_{1.5} Compositions and Phase Relationships

ID	Nominal Composition ^a	Observed Phase(s)	
		1400°C ^b	1600°C
1	G ₆₄ S ₃₆	G ₂ S ₂ + Ap	G ₂ S ₂ + Ap
2	G ₅₅ S ₄₅	G ₂ S + Ap	G ₂ S + Ap
3	C ₂₄ G ₃₇ S ₄₀	CS + C ₃ G ₂ S ₃ + Ap	Liq + (CG) ₂ S + Ap
4	C ₂₅ G ₃₈ S ₃₈	C ₃ G ₂ S ₃ + Ap	Liq + (CG) ₂ S + Ap
5	C ₃₈ G ₂₅ S ₃₈	C ₃ G ₂ S ₃	Liq + (CG) ₂ S + Ap
6	C ₅₄ G ₁₀ S ₃₆	(CG) ₂ S + CS + SC	Liq + (CG) ₂ S
7	C ₃ G ₆₄ S ₃₃	G ₂ S + Ap + GdO _{1.5}	G ₂ S + Ap + GdO _{1.5}
8	C ₃ G ₄₅ S ₅₂	G ₂ S ₂ + Ap + SiO ₂	G ₂ S ₂ + Ap + SiO ₂
9	C ₁₅ G ₂₅ S ₆₀	CyS + Ap + SiO ₂	Liq + Ap + SiO ₂
10	C ₂₀ G ₅₀ S ₃₀	(CG) ₂ S + Ap + GdO _{1.5}	(CG) ₂ S + Ap + GdO _{1.5}
11	C ₆₀ G ₃₀ S ₁₀	CaO + C ₃ S + GdO _{1.5}	CaO + C ₃ S + CG ₄
12	C ₆₃ G ₁₀ S ₂₅	(CG) ₂ S + C ₃ S + GdO _{1.5}	(CG) ₂ S + C ₃ S + CG ₄
13	C ₃₀ G ₁₀ S ₆₀	Liq + SiO ₂ + C ₃ G ₂ S ₆	Two Liqs
14	C ₃₂ G ₂₀ S ₄₈	CS + C ₃ G ₂ S ₆ + Ap	Liq + Ap
15	C ₂₇ G ₇ S ₇₀	--	Two Liqs + SiO ₂

^a Compositions are reported as mole percent of the constituent oxides based on a single cation formulas.

Table 3: Composition Measurements for Solution Phases ^a

Phase	ID	Composition (mol%) ^a					
		1400°C			1600°C		
		CaO	SiO ₂	GdO _{1.5}	CaO	SiO ₂	GdO _{1.5}
Apatite	1	0	40	60	0.0	39.6	60.3
	2	0.0	38.6	61.4	0.0	38.8	61.2
	3	15.2	36.7	48.1	16.6	37.4	46.0
	4	17	38	45	17	38	45
	5	--	--	--	16.9	37.3	45.8
	7	12	38	50	11	38	51
	8	12	38	50	11	38	51
	9	13	37	50	13.0	36.5	50.5
	10	13	37	50	13.6	37.4	49.0
	14	15	37	48	13.6	36.7	49.7
(Ca,Gd) ₂ SiO ₄	3	--	--	--	49	37	14
	5	--	--	--	50	37	13
	6	57.7	34.0	8.3	54	35	11
	10	61	34	5	59.2	34.6	6.2
	12	65.3	33.3	1.5	62	33	5
CaGd ₄ O ₇	11	Phase			16	1	83
	12	not stable			14	1	85
(Ca,Gd) ₃ SiO ₅	11	73	25	2	70	28	3
	12	72.7	26.6	0.8	71	26	3
Silicocarnotite	3	37.2	36.4	26.4	Phase not stable		
	4	38	38	25			
	6	38.1	37.1	24.8			
Cyclosilicate	9	27	55	18	Phase not stable		
	13	27.8	53.9	18.3			
	14	27.6	53.9	18.6			
GdO _{1.5}	10				0.7	0.1	99.3
	11	8	0	92	Phase not stable		
	12	7	0	93			
CaO	11	97	0	3	98	0	2
Liquid	5	--	--	--	48.3	45.7	6.1
	6	--	--	--	48	45	7
	9	--	--	--	26.7	59.5	13.8
	13	38	59	3	27.9	60.8	11.3
	14	--	--	--	35.6	52.5	11.9
	15	--	--	--	29.6	61.3	9.2

^a Values reported to 0.1 mol% and 1 mol% precision measured by EPMA and TEM/SEM-EDS, respectively.

FIGURES

Figure 1: The theoretical range for ionic substitutions in apatite, governed by $\text{RE}_{8+x}\text{Ca}_{2+y}(\text{SiO}_4)_6\text{O}_{2+3x/2+y}$, is shown with dashed lines and light shading in (a), adapted from Qu et al. [4]. The $\text{GdO}_{1.5}$ -based apatite is stable (b,c) in the CaO-free limit but (d-f) does not extend to the CaO rich limit of $\text{Ca}_4\text{Gd}_6(\text{SiO}_4)_6\text{O}$. Previously reported data for the $\text{YO}_{1.5}$ -based apatite homogeneity range is overlaid in (a) for comparison [7].

Figure 2: $\text{CaO-GdO}_{1.5}\text{-SiO}_2$ ternary isothermal sections. The experimental data, Table 2 and Table 3, define the three-phase triangles and tie lines at (a) 1400°C and (b) 1600°C that were used to construct the (c,d) complete diagrams with inferred tie lines.

Figure 3: BSE micrographs showing the as-quenched microstructures of the $(\text{Ca,Gd})_2\text{SiO}_4$ phase. The imaging conditions were selected so that each phase is clearly visible. As a result, the relative brightness of $(\text{C,G})_2\text{S}$ varies.

Figure 4: The XRD patterns for (a) ID 11 and (b) specimen ID 12 indicate that CaGd_4O_7 is stable at 1600°C but not 1400°C.

Figure 5: BSE micrographs showing the structure of the 1400°C specimens used to determine the stability and homogeneity range for the cyclosilicate ($C_3G_2S_6$). The darkest phase in (a) is SiO_2 and the bright phase in (a) and (c) is apatite.

Figure 6: BSE micrographs of specimens containing liquid phase at 1600°C. The magnification of all micrographs is equivalent.