

## Cerium – Magnesium – Oxygen

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### Introduction

The liquidus line in the system MgO–CeO<sub>2</sub> which is part of the liquidus surface of the ternary Ce–Mg–O system was experimentally obtained by [1932War] for the first time. [1976Pre] used X-ray diffraction and optical pyrometry to establish phase configurations and liquidus temperatures of alloys along the same MgO – CeO<sub>2</sub> section. They synthesized their specimens from chemically pure cerium dioxide and magnesium carbonate. By wet ball milling they obtained a homogeneous mixture of the component powders from which their specimens were formed by a heat treatment in the temperature range of 1200–1600°C with subsequent and rapid cooling. According to [1976Pre], no ternary compound exists in the system but a eutectic reaction occurs between MgO and CeO<sub>2</sub>. In the Ce<sub>2</sub>O<sub>3</sub>–MgO system [1971Lop] investigated specimens of 4:1, 1:1 and 1:2 compositions by XRD and DTA techniques. New phases were not observed in this system and the additions of MgO did not change the temperature of the polymorphic transformations in Ce<sub>2</sub>O<sub>3</sub>. The mixtures of MgO with 5 and 10 mass% of CeO<sub>2</sub> were investigated at 1800–2000°C by measurement of vapor pressure in the study of [1983Gvo]. The specimens were heat treated at 1570°C and characterized by XRD and electron microprobe analysis. Again no ternary compounds were found but the formation of a solid solution was indicated. Thermodynamic parameters to describe the CeO<sub>2</sub>–MgO system by the CALPHAD method were assessed by [1997Zha]. In the year 2005 solid solutions based on CeO<sub>2</sub> were synthesized and characterized by [2005Che, 2005Iva].

Details on the experimental and theoretical investigations of the ternary Ce–Mg–O system are summarized in Table 1.

### Binary Systems

The edge binary systems of the ternary Ce–Mg–O are accepted from different works. The Ce–Mg phase diagram is accepted from the critical evaluation made by [2002Gro] in the MSIT Evaluation Program. For Mg–O the phase diagram from thermodynamic assessments of [1993Hal] is considered to be best. The phase diagram of the Ce–O system is accepted from the thermodynamic assessment by [2006Zin] up to a temperature of 1800°C. In the Ce<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub> region the melting behavior is not well determined. For CeO<sub>2</sub> a melting temperature of 2750°C results from the evaluation of experimental data by [2006Zin]. However, thermodynamic calculations using the Calphad technique show a peritectic melting of CeO<sub>2</sub> with the formation of gas at 2293°C [2006Zin]. The reason for this discrepancy could be in both, in the Calphad modeling of liquid phase and in the experimental uncertainty. It was noticed by several investigators that the CeO<sub>2</sub> compound became oxygen deficient under heating [1932War, 1976Pre, 2006Zin] and neither the type of melting nor the actual composition could be determined [2006Zin].

### Solid Phases

The crystallographic characteristics of the binary phases are given in Table 2, ternary phases are not reported in this system. [1976Pre] found CeO<sub>2</sub> to dissolve up to 8 mol% MgO at 2100°C by measuring the lattice parameters. The formation of CeO<sub>2</sub> based solid solutions was also confirmed by [2005Che, 2005Iva]. The investigation of [1983Gvo] demonstrated that vapor pressures of Mg and Ce cations over mixtures containing 5 and 10 mass% CeO<sub>2</sub> were smaller than over pure MgO and CeO<sub>2</sub>. This indicates the formation of a solid solution which is more stable than mechanical mixtures of oxides. The formation of the solid solution was also confirmed by microprobe analysis and XRD investigation which indicated the increase of MgO lattice parameters. However, the solubility of CeO<sub>2</sub> was probably less than 5 mass% MgO. Electron microprobe analysis indicates that the CeO<sub>2</sub> phase segregates along the grain boundaries and the pore surfaces.

### Quasibinary Systems

The MgO-CeO<sub>2</sub> quasibinary system was experimentally studied by [1932War, 1976Pre]. [1983Gvo] studied the MgO rich compositions of the system. The phase diagram of the MgO - CeO<sub>2</sub> system is presented in Fig. 1 according to [1976Pre] accounting data of [1983Gvo]. The diagram is of simple eutectic nature. Because [1983Gvo] did not determine how much CeO<sub>2</sub> will actually dissolve in MgO the solubility limit is shown by a dashed line in Fig. 1. According to [1976Pre] the invariant equilibrium  $L \rightleftharpoons \text{MgO} + \text{CeO}_2$  exists at 2100°C, the eutectic composition is 70 mol% MgO and 30 mol% CeO<sub>2</sub>. The temperature of the eutectic reaction obtained earlier by [1932War] was 140°C higher, while the composition was the same. There is no indication for the formation of a CeO<sub>2</sub>-based solid solution in the early work of [1932War]. In the present evaluation we rely on the data of [1976Pre] because these authors provided a more detailed description of an appropriate experimental procedure.

[1971Lop, 1976Lop] state that the MgO-Ce<sub>2</sub>O<sub>3</sub> phase diagram is also of eutectic type. The temperature and the composition of the eutectic were experimentally determined by [1971Lop, 1976Lop] to be 1920°C and 50 mol% Ce<sub>2</sub>O<sub>3</sub>. Obviously Ce<sub>2</sub>O<sub>3</sub> does not form a solid solution with MgO since the temperatures of polymorphic transformations were not changed by additions of MgO.

### Thermodynamics

A thermodynamic modeling of the MgO-CeO<sub>2</sub> system was performed by [1997Zha]. These authors described the CeO<sub>2</sub> based solid solution by a Substitutional Model and applied the Associate Model with 2MgO·CeO<sub>2</sub> species to describe the liquid phase. The eutectic composition and temperature, were reproduced in the calculations very well, as well as the composition of CeO<sub>2</sub> solid solution. However the concave shape of the liquidus line in the MgO rich region can not be reproduced by the associate model and not by the substitutional model with Redlich-Kister polynomials.

### Notes on Materials Properties and Applications

Ce-Mg-O is seen as a candidate system to deliver inert matrix material processing nuclear waste. This process of separating the radionuclides from the spent fuel with subsequent fission or transmutation in reactors or accelerators can lead to a considerably reduced long term radiotoxicity. One way to handle the fuel for transmutation is its dispersion in inert matrix material of appropriate properties, in particular of high melting temperatures. Ce and Pu form as fission products in nuclear reactors. High refractory oxides such as aluminium oxide and MgO are appropriate candidate matrix materials for heterogeneous transmutation. Ce substitutes Pu in its compounds, such as PuO<sub>2</sub>, forming solid solutions [1997Zha]. That is why phase relations in the Pu-Ce-Mg-O system are important for the waste management from nuclear power generation.

Ce-Mg-O is of interest as catalyst and catalyst support for methane combustion reaction [2005Che, 2005Iva]. The CeO<sub>2</sub> based solid solutions were synthesized and characterized using XRD and adsorption spectroscopy (X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy) by [2005Iva]. The Mg<sup>+2</sup> ions enter the cubic lattice of the CeO<sub>2</sub> to form solid solution. This structure (fluorite) according to [2005Che] is favorable to enhance catalytic activity. The formation of nano size particles and good redox ability of Ce-Mg-O materials are also key factors supporting catalytic properties [2005Che].

### Miscellaneous

New material made from Ce-Mg-O nanoparticles with high thermal stability and high surface area was synthesized by [2004Che, 2005Che]. The average crystalline size was from 10 to 20 nm. It was demonstrated by XRD that at all studied Mg/Ce ratios, from 1/9 to 9/1, only fluorite type of solid solutions form. The cell parameters decrease slightly with increasing Mg contents. The smaller Mg<sup>+2</sup> ions entering the CeO<sub>2</sub> lattice decrease the lattice parameter and increase the peaks intensity. It is obvious from the phase diagram of the MgO-CeO<sub>2</sub> system that fluorite solid solutions are metastable at the studied conditions. However they are thermally stable and do not decompose under heating at the studied temperatures up to 1000°C [2004Che].

[1995Gvo] theoretically calculated the solubility of ceria in MgO and the critical temperature at which the solid solution decomposes. These calculations were based on theoretical semi-quantitative approaches introducing cerium cations into the crystal lattice of magnesium oxide.

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**Table 1:** Investigations of the Ce-Mg-O Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1932War]	pyrometry	2240-2600°C MgO-CeO <sub>2</sub> 0-91 mol% MgO
[1971Lop]	XRD, DTA	1500-2300°C Ce <sub>2</sub> O <sub>3</sub> -MgO 4:1, 1:1 and 1:2
[1976Pre]	DTA, XRD, optical pyrometry	CeO <sub>2</sub> (DTA 20-900°C), CeO <sub>2</sub> solid solution at 1200-1600°C (XRD of quenched samples), the MgO-CeO <sub>2</sub> system (melting determination by optical pyrometry) at 2100-2700°C
[1983Gvo]	XRD, electron microprobe, mass-spectrometry	MgO with 5 and 10 mass% CeO <sub>2</sub> , heat treatment at 1750°C, vapor pressure measurement at 1800-2000°C
[1997Zha]	CALPHAD	Phase diagram MgO-CeO <sub>2</sub> 1800-2900°C
[2004Che]	Thermal analysis TG-DTA, transmission electron microscopy (TEM), XRD, Raman spectroscopy, BET surface area technologies	25-700°C TG-DTA, 600-1000°C calcination, compositions Mg/Ce=1/9, 1/1, 9/1.
[2005Che]	XRD, thermo-gravimetric analysis (TG), DTA, atom force microscopy (AFM), catalytic activity test	25-700°C TG-DTA, 650°C calcination, compositions Mg/Ce=1/9, 1/1, 9/1
[2005Iva]	XRD, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR)	5-25 mol% Ce <sub>2</sub> O <sub>3</sub> at 450 and 750°C

**Table 2:** Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Mg) < 650	<i>hP2</i> <i>P6<sub>3</sub>/mmc</i> Mg	<i>a</i> = 320.944 <i>c</i> = 521.07	at 25°C [Mas2] 0.066 at.% Ce at 540°C, 0.014 at.% Ce at 400°C [2002Gro]
(δCe) 798 - 726	<i>cI2</i> <i>Im<math>\bar{3}m</math></i> W	<i>a</i> = 412	[Mas2]
(γCe) 726 - 61	<i>cF4</i> <i>Fm<math>\bar{3}m</math></i> Cu	<i>a</i> = 516.10	[Mas2] from 0 to 8.2 at.% Mg [2002Gro]
(βCe) 61 - (−177)	<i>hP4</i> <i>P6<sub>3</sub>/mmc</i> αLa	<i>a</i> = 386.10 <i>c</i> = 1185.7	at 25°C [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
( $\alpha$ Ce) < –177	<i>cF4</i> <i>Fm<math>\bar{3}m</math></i> Cu	$a = 485$	at –196°C [Mas2]
MgO < 2827 ± 10	<i>cF8</i> <i>Fm<math>\bar{3}m</math></i> NaCl	$a = 421.12$	[1993Hal]
CeO	<i>cF8</i> <i>Fm<math>\bar{3}m</math></i> NaCl	$a = 508.9$	[V-C2] 1.5 GPa, 700°C
A-Ce <sub>2</sub> O <sub>3–x</sub> < 2065	<i>hP5</i> <i>P<math>\bar{3}2/m1</math></i> A-La <sub>2</sub> O <sub>3</sub>	$a = 389.1 \pm 1$ $c = 605.9 \pm 1$	O/Ce = (3–3)/2, stoichiometric composition Ce <sub>2</sub> O <sub>3</sub> in [2006Zin] transition temperature from [2006Zin] lattice parameters and space group from [1985Bae]
H-Ce <sub>2</sub> O <sub>3</sub> 2065–2140	<i>hP5</i> <i>P6<sub>3</sub>/mmc</i> H-La <sub>2</sub> O <sub>3</sub>		[2006Zin] transition temperature from [2006Zin]
X-Ce <sub>2</sub> O <sub>3–x</sub> 2240 - 2140	<i>cI26</i> <i>Im<math>\bar{3}m</math></i> LaYbO <sub>3</sub>		[2006Zin] melting point from [1985She] Exist up to 2140°C [2006Zin]
C-Ce <sub>2</sub> O <sub>5±x</sub> 612–1403	<i>cI96</i> <i>Ia<math>\bar{3}</math></i> Mn <sub>2</sub> O <sub>3</sub>	$a = 1111.1 \pm 2$	O/Ce=(5±x)/3, stoichiometric composition Ce <sub>3</sub> O <sub>5</sub> in [2006Zin]
Ce <sub>7</sub> O <sub>12</sub> < 1048	<i>hR57</i> <i>R<math>\bar{3}</math></i> UY <sub>6</sub> O <sub>12</sub>	$a = 1035.09 \pm 0.02$ $c = 963.85 \pm 0.02$	lattice parameters recalculated from [2006Zin]
Ce <sub>9</sub> O <sub>16</sub> < 632	-	-	[2006Zin]
Ce <sub>19</sub> O <sub>34</sub> < 607	triclinic	$a = 662.7$ $b = 1147.8$ $c = 1012.3$ $\alpha = 100.9^\circ$ $\beta = 90.0^\circ$ $\gamma = 95.5$	[2006Zin]
Ce <sub>40</sub> O <sub>72</sub> < 582	-	-	[2006Zin]
Ce <sub>62</sub> O <sub>112</sub> < 487	-	-	[2006Zin]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
Ce <sub>11</sub> O <sub>20</sub> < 459	<i>aP</i> 31 <i>P</i> $\bar{1}$ Tb <sub>11</sub> O <sub>20</sub>	$a = 675.7 \pm 3$ $b = 1026.0 \pm 5$ $c = 673.2 \pm 3$ $\alpha = 90.04 \pm 4^\circ$ $\beta = 99.80 \pm 4^\circ$ $\gamma = 96.22 \pm 4^\circ$	[2006Zin]
CeO <sub>2-x</sub> 2750	<i>cF</i> 12 <i>Fm</i> $\bar{3}m$ CaF <sub>2</sub>	$a = 541.12 \pm 10$ $a = 532.0$	[2006Zin] at 4 at.% Mg [1976Pre]
Mg <sub>12</sub> Ce (I) < 616	<i>tI</i> 26 <i>I4/mmm</i> Mn <sub>12</sub> Th	$a = 1033$ $c = 596$	[2002Gro]
Mg <sub>12</sub> Ce (II)	<i>oI</i> 338 <i>Immm</i> Mg <sub>12</sub> Ce(II)	$a = 1033$ $b = 1033$ $c = 7750$	[Mas2, 2002Gro]
Mg <sub>10.3</sub> Ce 621 - 611	<i>hP</i> 38 <i>P</i> 6 <sub>3</sub> / <i>mmc</i> Ni <sub>17</sub> Th <sub>2</sub>	$a = 1031$ $c = 1032$	[V-C2, 2002Gro] composition is given as Ce <sub>2</sub> Mg <sub>17</sub>
Mg <sub>41</sub> Ce <sub>5</sub> < 635	<i>tI</i> 92 <i>I4/m</i> Mg <sub>41</sub> Ce <sub>5</sub>	$a = 1478$ $c = 1043$	[V-C2, 2002Gro]
Mg <sub>3</sub> Ce < 796	<i>cF</i> 16 <i>Fm</i> $\bar{3}m$ BiF <sub>3</sub>	$a = 744.3$	[V-C2, 2002Gro]
Mg <sub>2</sub> Ce < 750	<i>cF</i> 24 <i>Fd</i> $\bar{3}m$ Cu <sub>2</sub> Mg	$a = 873.3$	[V-C2, 2002Gro]
MgCe < 711	<i>cP</i> 2 <i>Pm</i> $\bar{3}m$ CsCl	$a = 391.2$	[V-C2, 2002Gro]

**Fig. 1: Ce-Mg-O.**

The quasibinary  
system MgO - CeO<sub>2</sub>

