Experimental Phase Diagram Determination and Thermodynamic Assessment of the CeO$_2$-Gd$_2$O$_3$-CoO System

Toni Ivas,† Erwin Povoden-Karadeniz,§ Nicholas Grundy,¶ Eva Jud-Sierra,‡ Jurgen Grässlin,‡‡ and Ludwig J. Gauckler††

†Department of Materials, ETH, Zurich, Switzerland
§Institut für Werkstoffwissenschaft und Werkstofftechnologie Christian Doppler Laboratory for Early Stages of Precipitation, TU Wien, Wien, Austria
¶Concast AG, Zurich, Switzerland
‡Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania 19104
‡‡Department of Materials, ETH, Zurich, Switzerland

New phase diagram data and a thermodynamic assessment of the CeO$_2$-Gd$_2$O$_3$-CoO system using the CALPHAD approach are presented. This information is needed to understand the surprisingly low sintering temperature (950°C–1050°C) of CeO$_2$-based materials doped with small amounts of transition metal oxide (e.g., CoO). Experimental phase equilibria between 1100°C and 1300°C are reported based on the analysis of annealed and molten samples. No isolated compound exists in the ternary. At 1300°C the Co solubility in the ternary compounds Ce$_{1-2x}$Gd$_x$Co$_{2x}$O$_{1+2y}$ (fluorite) is 2.7 mol% and is less than 1 mol% in the Gd$_{2-2x}$CeO$_{3+2y}$ (bixbyte). The Ce solubility in the perovskite GdCoO$_{3-6}$ was found to be 1 mol%. The lowest temperature eutectic melt in the ternary has a composition of 57.2 mol% Co and 41.1 mol% Gd melting at an onset temperature of 1303 ± 5°C, which is close to the binary eutectic in the Gd$_2$O$_3$-CoO system at 60 ± 2 mol% Co and 1348 ± 1°C.

I. Introduction

Cerium gadolinium oxide, CeO$_2$-Gd$_2$O$_3$ (CGO) is a promising oxygen ion conducting material showing higher conductivity at intermediate temperatures (500°C–800°C) compared to the state-of-the-art yttria-stabilized zirconia (YSZ). Therefore, solid oxide fuel cells with CGO electrolytes can be operated at lower temperatures than those with YSZ electrolytes. To ensure high efficiency and prolonged lifetime of the fuel cell, densely sintered CGO electrolytes are required. For pure, undoped CGO, this requires sintering temperatures >1300°C with the consequence that CeO$_2$ becomes reduced at sintering temperatures higher than 1200°C and reoxidizes upon cooling, which weakens the material. Therefore, it is desirable to lower the sintering temperature of CeO$_2$-based electrolytes. Doping the CGO with small amounts of transition metal oxides such as CoO drastically accelerates diffusion in CGO powder compacts and the rearrangement of particles. Such “liquid-like” sintering behavior of ceramic materials far below their melting temperature was termed “activated sintering” and has recently become a subject of vast interest. It was suggested that the reason for this “liquid-like” sintering might be due to a several nanometer thick film on the ceria particles enriched in CoO, that is observed in sintered Co-doped CGO. To elucidate whether this “liquid-like” sintering is caused by an equilibrium liquid phase in the system CeO$_2$-Gd$_2$O$_3$-CoO, the phase diagram and the composition with the lowest melting temperature need to be known. The subject of this study is to establish the thermodynamic description of the Ce-Gd-Co-O system.

The description of the quasi-binary system Gd$_2$O$_3$-CoO is taken from our previous work. It contains solid solutions of the endmembers and GdCoO$_{3-6}$ (P) with orthorhombic perovskite crystal structure decomposing at 1265°C and with the lowest melting point at 1348°C. The data for the simple eutectic system CeO$_2$-Gd$_2$O$_3$ for temperatures up to 1600°C are taken from the study by Zinkevich et al. that is expanded to include the reduction of Ce$_4^+$ to Ce$_3^+$ with the data from Bevan et al. The CeO$_2$-CoO system is reassessed in this study using experimental data from the literature and the present result is compared to the assessment of Kim. The three quasi-binary subsystems are finally combined to give a thermodynamic description of the complete quasi-ternary CeO$_2$-Gd$_2$O$_3$-CoO system. Experimental investigations were conducted on the ternary system to determine the solid solubility of Ce in the GdCo$_3$ perovskite and the temperature and composition of the ternary eutectic point. These experimental results were used to optimize the thermodynamic description of the ternary.

II. Literature Survey

(1) Quasibinary CeO$_2$-CoO System

Chen et al. investigated the phase equilibria in the CeO$_2$-CoO system at temperatures above 1500°C. They analyzed the microstructure and phase composition using scanning electron microscopy (SEM), energy dispersive X-ray (EDX), and wave dispersive X-ray (WDX). The eutectic concentration of 82 ± 2 mol% CoO and eutectic temperature of 1645 ± 5°C were determined. The solid solubility of CoO in CeO$_2$ was determined to be <5 mol% CoO at the eutectic temperature and ~3 mol% at 1580°C. There was no evidence of the formation of intermediate phases. An assessment of the experimental data and thermodynamic modeling of the CeO$_2$-CoO system were done by Kim. A simple regular solution model was used to describe the excess Gibbs energy for the solution phases. Kim also calculated the...
liquidus, solds, and solvens curves and estimated the thermodynamic lattice stabilities of the phases in the CeO₂-CoO system.

(2) Quasibinary CeO₂-Gd₂O₃ System
So far, most of the investigations on CGO systems were done on electrochemical properties of the material measuring electrical conductivity, oxygen ion permeability, oxygen exchange etc. Recently, Zinkevich et al.¹⁰ published experimental enthalpy of formation data and a thermodynamic assessment of the CeO₂-Gd₂O₃ system. They prepared Ce₁₋ₓR₂O₃₋ₓ/₂ with R = Sm, Gd, and Y in the complete composition range by the modified glycine-nitrate method. The enthalpy of formation of the solid solutions relative to the pure oxides, fluo- rite CeO₂, and C-type R₂O₃ was determined by oxide melt drop solution calorimetry. In addition, new measurement were published by Chen and Navrotsky,¹⁴ who performed similar experiments to determine the formation enthalpies of the solid solutions compared to the oxide end-members for the CeO₂-R₂O₃ (R = La, Gd, and Y) systems using high-temperature oxide melt droplet calorimetry. In contrast to Zinkevich et al.,¹⁰ they found slightly positive values for the enthalpies in these series of systems. This absence of the stabilization of the solid solutions in the CeO₂-Gd₂O₃ system was attributed to the large size of Ce⁴⁺, which does not have an affinity to the sevenfold coordination like the smaller Zr⁴⁺ and Hf⁴⁺ ions. The enthalpy of formation has a maximum at 10 mol% Gd. Above that concentration it drops rapidly to a constant value. These findings are in conflict with experimental data from Zinkevich et al.,¹⁰ who conclude that the enthalpy of formation of the fluorite-type solid solution is always negative and can be fitted to the substitutional solution model using a quadratic dependency of the enthalpy of formation in function of the Gd content. The discrepancy between the experimental results, Zinkevich et al. attributed to the fact that Chen and Navrotsky used commercial powders to measure the enthalpy of formation of the end-members CeO₂ and Gd₂O₃, whereas solid solutions of Zinkevich et al.¹⁰ have been prepared using modified glycine-nitrate method. Recently, Aizenshtein et al.¹⁵ measured the LaₓTh₁₋ₓO₂₋₀.₅ and YₓTh₁₋ₓO₂₋₀.₅ solid solutions with positive enthalpies of formation from fluorite ThO₂ and A-type La₂O₃ or C-type Y₂O₃. As suggested earlier by Avila-Paredes et al.¹⁶ the maxima in enthalpy of formation in these systems correlated with the maxima in ionic conductivity for ceria- and thoria-based oxide materials. One might extrapolate a similar behavior for the Ce₁₋ₓGdₓO₂₋ₓ/₂ solid solution in the CeO₂-Gd₂O₃ system. However, only further work will lead to a full understanding of these discrepancies in experimental data. Despite these discrepancies we relied in this work on the earlier data of Zinkevich et al.¹⁰

III. Experimental Procedure

(1) Experimental
Different samples of the CeO-Gd₂O₃-CoO were synthesized from oxide precursors using a standard solid-state reaction method. The compositions investigated are summarized in Table I. The oxide precursors used were as follows: CeO₂ (>99.9%; Alfa Aesar, Karlsruhe, Germany), Gd₂O₃ (99.99%; Alfa Aesar), and Co₃O₄ (puriss; Fluka, Buchs, Switzerland). After ballmilling for 24 h using Al₂O₃ balls the powders were uniaxially pressed with 45 MPa and then isostatically in a hydraulic press at 430 MPa. The disks were 10 mm in diameter, each weighing ∼1 g. The disks were then sintered for 2 h at 1100°C in air in a furnace (HT 10/18; Nabertherm, Lilienthal, Germany). The samples were quenched to room temperature by placing them on a massive copper plate. The quenching rate was estimated to be ∼200°C/s. The samples were reground and the resulting powders were processed as described above to obtain equilibrium.

The samples equilibrated at temperatures ranging from 1100°C to 1300°C were analyzed regarding chemical composition, phase content, microstructure, and the composition of the individual phases. The samples with different chemical compositions were annealed on their overall compositions using EDX and WDX spectroscopy analysis.

The phase assemblages of the samples were determined using powder X-Ray Diffraction using two different diffractometers, a XRD XPert Pro (PANanalytical B.V., Almelo, Netherlands) equipped with incident Soller slits, a theta compensating slit, and a CCD detector and a Siemens D-5000 XRD (Siemens AG, Munich, Germany) equipped with diffracted beam monochromator (graphite crystal CuKα) for elimination of the background radiation. The quantitative analysis of the diffractograms was done using Rietveld refinement¹⁷ by the freely available Maud (Materials Analysis Using Diffraction) program.¹⁸ To reduce the texture effects in the XRD samples, all samples were ground and subsequently sieved using a 0.25 μm sieve directly onto the zero-background graphite sample holder.

The GdCoO₃₋₀.₅ was prepared using a method developed by Liu et al.¹⁹: 25.830 g of ammonium bicarbonate was mixed with 20.0 g Gd(NO₃)₃·6H₂O (>99.9%; ABCR, Karlsruhe, Germany), and 12.1740 g Co(NO₃)₃·6H₂O (>99.9%; Fluka) in the agate mortar. To investigate the Ce-solubility in the GdCoO₃ perovskite, 1 mol% CeO₂ powder was added. Under constant stirring, a liquid precipitate was formed, which continually released CO₂ gas. This paste was heated in a Pt-crucible at 300°C for 1 h and then at 900°C for 2 h to burn out the organic residuals. The powder was then charac- terized using conventional XRD. To obtain a single-phase perovskite, the powder was calcined at 1000°C for 2 h with intermediate regrinding in an agate mortar.

To refine the crystal structure of the GdCoO₃ (P), a synchrotron powder XRD experiment was performed at room temperature with the high-resolution powder diffractometer at the Materials Sciences Beamline at the Swiss Light Source Synchrotron facility (SLS)²⁰ (Paul Scherrer Institute, Villigen, Switzerland). Several samples were investigated using a high-temperature XRD at 1000°C. The microstructures of the annealed samples were characterized using SEM (LEO Gemini Model 1530, Carl Zeiss AG, Jena, Germany and Hitachi SU-70, Hitachi High Technologies America Inc., Gaithersburg, MD). For the chemical analysis of the compositions of individual grains (single phase) also EDX and WDX were used.

The ternaryeutectic temperature in the CeO₂-CoO-Gd₂O₃ system was determined using differential thermal analysis

### Table I. Samples Prepared in the Present Study in the CeO₂-CoO-Gd₂O₃. The Fractions are Given in Molar Percents

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>CeO₂</th>
<th>CoO</th>
<th>Gd₂O₃</th>
</tr>
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<tbody>
<tr>
<td>CCG127</td>
<td>10</td>
<td>20</td>
<td>70</td>
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<td>CCG325</td>
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<td>50</td>
</tr>
<tr>
<td>CCG622</td>
<td>60</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>CCG145</td>
<td>10</td>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td>CCG343</td>
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<td>30</td>
</tr>
<tr>
<td>CCG163</td>
<td>10</td>
<td>60</td>
<td>30</td>
</tr>
<tr>
<td>CCG5342</td>
<td>2.5</td>
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<td>42.5</td>
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<td>CCG7522</td>
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<td>22.5</td>
</tr>
<tr>
<td>CCG5444</td>
<td>2.0</td>
<td>54</td>
<td>44</td>
</tr>
<tr>
<td>CCG5642</td>
<td>2.0</td>
<td>56</td>
<td>42</td>
</tr>
<tr>
<td>CCG5840</td>
<td>2.0</td>
<td>58</td>
<td>40</td>
</tr>
<tr>
<td>CCG5246</td>
<td>1.0</td>
<td>52.5</td>
<td>46.5</td>
</tr>
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<td>CCG424</td>
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<td>20</td>
<td>40</td>
</tr>
<tr>
<td>CCG442</td>
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<td>CCG154</td>
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<td>CCG523</td>
<td>50</td>
<td>20</td>
<td>30</td>
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<tr>
<td>CCG541</td>
<td>50</td>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>CCG5555</td>
<td>5.0</td>
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<td>45</td>
</tr>
<tr>
<td>CCG0155</td>
<td>1.0</td>
<td>50</td>
<td>49</td>
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</table>

The samples equilibrated at temperatures ranging from 1100°C to 1300°C were analyzed regarding chemical composition, phase content, microstructure, and the composition of the individual phases. The samples with different chemical compositions were annealed on their overall compositions using EDX and WDX spectroscopy analysis.
and differential scanning calorimetry (DTA, DSC STA 449 C Jupiter; Netzsch, Germany). All DTA/DSC experiments were carried out with a heating rate of 10°C/min up to 1400°C and subsequent cooling to room temperature with the same cooling rate. DTA experiments were done in 0.21 atm \( p_{O_2} \) using a mixture of argon (Argon 99.998% purity; PanGas AG, Dagmersellen, Switzerland) and oxygen (Oxygen 99.999% purity, PanGas AG). Melting points of samples were determined using the onset temperature of the melting peak of the DTA signal upon heating.

The eutectic composition was determined using EDX and WDX spectroscopy analysis in a Leo Gemini Model 1530/Hitachi SU-70 scanning electron microscope. The EDX/WDX measurements were done for both fine- and coarse-grained eutectic structures. The WDX analysis was performed using a Hitachi SU-70 scanning electron microscope equipped with Schottky Field Emission Gun with 20 kV accelerating voltage and 19–35 nA current. The standards used were \( \text{Gd}_2\text{O}_3 \) for \( \text{Gd} \) (L), metallic Co for Co (K\( _\alpha \)), and \( \text{CeO}_2 \) for Ce (K\( _\alpha \)). Overall compositions of the samples were checked with WDX to insure that all samples investigated did not contain any impurity phases exceeding 1 wt% of elements other than Ce, Gd, and Co. Several samples around the estimated eutectic composition were analyzed after being molten in the DTA experiment and cooled down at a cooling rate of 10°C/min. The eutectic structures in the images were analyzed for the relative phase contents using the ImageJ program.21

(2) Experimental Results and Discussion

For the isothermal sections the compositions of the samples annealed at 1100°C and 1300°C are listed in Table I. The sample name indicates the nominal composition: for example sample CCG325 has the composition Ce 30 mol% Co 20 mol% Gd 50 mol%, and sample CCG0155 has the composition Ce 1 mol% Co 50 mol% Gd 50 mol%.

To address the question whether equilibrium had been reached, all samples were annealed for 72 h at 1100°C, then quenched and reground, pelletized, and re-annealed for another 72 h at 1100°C. After the annealings, the samples were characterized for their phase compositions by XRD. In Fig. 1 we show exemplarily the XRD patterns of the sample CCG442 far away from the binary and ternary liquid. The patterns still change from the first to the second annealing, showing the phases: fluorite phase \( \text{CeO}_2 \) solid solution (F, strong), and cobalt oxide \( \text{CoO} \) (medium), and \( \text{GdCoO}_3 \) (P, weak). However, no substantial changes were observed after the third annealing in most of the samples.

(3) The Isothermal Section at 1100°C

All XRD phase analysis and EDX/WDX results for the 1100°C section are listed in Table II and the phase fields are shown in Fig. 2 together with the tie lines resulting from the CALPHAD assessment (see the modeling results and discussion later). The XRD phase compositions agree well with the phase fields from the CALPHAD assessment.

The bixbyte structure (B) is regarded as a superlattice of the fluorite structure with ordered oxygen vacancies and random distribution of cations.22,23 Thus, the three-phase region of bixbyte, fluorite, and perovskite is difficult to distinguish based on XRD data alone, due to the overlapping peaks of bixbyte and fluorite-type structures. The high temperature XRD of sample CCG424 at 1000°C shows the presence of fluorite solid solution (Fss) and \( \text{Gd}_{1-x}\text{CeO}_x\text{Co}_x \) (P) phase.

(4) The Isothermal Section at 1300°C

The results of the XRD phase analysis and phase compositions for the 1300°C isothermal section are listed in Table IV

![Fig. 1. Two XRD patterns of the CCG442 (Ce 40 mol% Co 40 mol% Gd 20 mol%) sample measured after 72 and 144 h annealing steps with an intermediate regrounding of the sample. The sample was annealed at 1100°C in air under normal atmospheric conditions.](image)
mental data (see next section for discussion). Only phase shown on Fig. 3(b) is based on our XRD and DTA experi-

The subsolidus isothermal section at 1264°C in air. CoO, cobalt-

The weight loss can be assigned to decomposition of the

We therefore conclude that CoO is the stable phase at temperatures

The second phase transformation is due to decomposition of the perovskite phase with the 1.8% weight loss in tempera-

The large uncertainty in decomposition temperature of the perovskite is due to overlap of melting and decomposition peak in DSC/TG experimental data. The third phase transformation at 1315°C–1316°C is assigned to the melting of the sample.

Upon cooling, we found two large exothermic peaks in the sample CCG154 at 1358°C and 1325°C, while the sample CCG555 has only two peaks found at 1332°C and 1303°C. We assign the latter as the lowest melt-

and shown together with the phase fields resulting from the experimental analysis in Fig. 3 (see modeling results and

and shown together with the phase fields resulting from the experimental analysis in Fig. 3 (see modeling results and discussions later). This section contains in the middle region a three-phase field with Gd-rich bixbyite (B), Ce-rich fluorite (F), and cobalt oxide (CoO). Adjacent are 2 two-phase regions, one of Gd-rich bixbyite containing ~30 cat% Ce and CoO, and the other of Ce-rich fluorite containing ~50 cat% Ce and CoO. The liquid phase (L) extends from the binary Gd2O3 (B) – CoO to a few percent (<2%) in the ternary. The subsolidus isothermal section at 1264°C shown on Fig. 3(b) is based on our XRD and DTA experimental data (see next section for discussion). Only phase composition of sample CCG523 is difficult to identify, due to the mixture of bixbyite and fluorite. The bixbyite structure is regarded as a superlattice of the fluorite structure with ordered oxygen vacancies and random distribution of cations. Thus, the three-phase region of bixbyite, fluorite, and CoO is difficult to distinguish based on XRD data alone, due to the overlapping peaks of bixbyite and fluorite-type structures.

(5) Melting Behavior

To find the composition with the lowest melting tempera-

The large uncertainty in decomposition temperature of the perovskite is due to overlap of melting and decomposition peak in DSC/TG experimental data. The third phase transformation at 1315°C–1316°C is assigned to the melting of the sample.

Upon cooling, we found two large exothermic peaks in the sample CCG154 at 1358°C and 1325°C, and a very small one at 1302°C, while the sample CCG555 has only two peaks found at 1332°C and 1303°C. We assign the latter as the lowest melting temperature in this system found in the specimen CCG0555 during heating. The micrograph of the specimen close to the eutectic concentration is shown in Fig. 5. From

![Fig. 2. Concentrations investigated in the CeO2-Gd2O3-CoO system. Experimental phase data at T = 1100°C in air. CoO, cobalt-

oxide; P, perovskite; F, fluorite; B, C-type Gd2O3. The calculated isostructural CeO2-Gd2O3-CoO system at 1100°C is shown with the solid lines.](image-url)
### Table III. Crystallographic Data and Structure Refinement

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tr>
<td>Space group</td>
<td>Pbnm (No. 62)</td>
</tr>
<tr>
<td>a, b, c (Å)</td>
<td>5.224(6), 5.392(0), 7.454(3)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>209.9499</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (X-ray) (g/cm³)</td>
<td>8.3598</td>
</tr>
<tr>
<td>Number of free parameters</td>
<td>12</td>
</tr>
<tr>
<td>Number of reflections</td>
<td>339</td>
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<tr>
<td>Profile</td>
<td>Pseudo-Voigt</td>
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### Atomic coordinates

<table>
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<th>Element</th>
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<th>y</th>
<th>z</th>
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</thead>
<tbody>
<tr>
<td>Gd</td>
<td>0.9880(5)</td>
<td>0.0920(3)</td>
<td>0.49883(3)</td>
</tr>
<tr>
<td>Co</td>
<td>0.0215(7)</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>O1</td>
<td>0.0920(3)</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>O2</td>
<td>0.6938(7)</td>
<td>0.2944(3)</td>
<td>0.0447(2)</td>
</tr>
</tbody>
</table>

- Numbers in parenthesis refer to standard deviation of the last significant digit.

### Thermodynamic Modeling

#### (1) Perovskite $Gd_{1-x}Ce_xCoO_3$-$\delta$

- The perovskite phase $Gd_{1-x}Ce_xCoO_3$-$\delta$ is modeled using the compound energy formalism (CEF) with three sublattices: Ce, Co, and O.

- The Gibbs molar energy of the $Gd_{1-x}Ce_xCoO_3$-$\delta$ perovskite is given as:

$$
\Delta G = \Delta G_{\text{cell}} + \Delta G_{\text{sub}} + \Delta G_{\text{ex}}
$$

#### (2) Fluorite $CeO_2$

- The Gibbs molar energy of the $CeO_2$ fluorite phase is given as:

$$
\Delta G_{\text{fluorite}} = \Delta H_{\text{fluorite}} + T\Delta S_{\text{fluorite}}
$$

where $y$ represents the site fraction of a particular species on the respective sublattice. The Gibbs energies of the end-members $\Delta G_{\text{CeO}_2}$ and $\Delta G_{\text{CoO}_2}$ are known from our previous study. While the remaining Gibbs energies are given as:

$$
\Delta G_{\text{CeO}_2} = \frac{1}{2} \Delta G_{\text{CeO}_2} + \frac{1}{2} \Delta G_{\text{CoO}_2}
$$

where the model parameters $\Delta G_{\text{CeO}_2}$ and $\Delta G_{\text{CoO}_2}$ are optimized using a least-square method by fitting experimental results of the solid solubility of Ce in $GdCoO_3$-$\delta$ perovskite.

### IV. Thermodynamic Modeling

- The Gibbs molar energy of Co-doped $CeO_2$ is expressed as:

$$
\Delta G_{\text{m}} = \frac{1}{2} \Delta G_{\text{CeO}_2} + \frac{1}{2} \Delta G_{\text{CoO}_2}
$$

where $y$ represents the site fraction of a particular species on the respective sublattice. The first six terms are Gibbs energies of the end-members of the Co-doped $CeO_2$ phase. The last two terms containing “RT” take into account the configurational entropies of mixing on the anion and cation sublattices. The last term takes into account the excess Gibbs energy of mixing.

Equation (6) can be easily visualized as corners of a compositional triangular prism representing six end-members of the fluorite phase, where each $G$ parameter in Eq. (6) represents one corner. Figure 6 shows that there is only one stoichiometric end-member representing the fluorite phase with the composition $CeO_2$, whereas all other end-members carry...
Table IV. Summary of the Results of XRD Measurements at 1300°C Showing the Crystal Data, Phase Assemblage, and Refinement Conditions for the Phase Compositions Studied in the CeO₂-CoO-Gd₂O₃ System

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Phases content by XRD (wt%)</th>
<th>Phase</th>
<th>Ce (mol%)</th>
<th>Gd (mol%)</th>
<th>Co (mol%)</th>
<th>O (mol%)</th>
<th>Lattice constants (Å)</th>
<th>Rp, Rwp, σ</th>
<th># points</th>
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<tbody>
<tr>
<td>CCG127</td>
<td>CoO + B</td>
<td>CoO</td>
<td>0</td>
<td>0.33 ± 0.16</td>
<td>0.38 ± 0.16</td>
<td>47.73 ± 0.86</td>
<td>51.88 ± 0.89</td>
<td>4.263 (3)</td>
<td>5.04, 6.37, 1.25</td>
</tr>
<tr>
<td>24/76</td>
<td>B</td>
<td>3.529 ± 0.57</td>
<td>31.963 ± 0.57</td>
<td>0.107 ± 0.12</td>
<td>64.403 ± 0.61</td>
<td>10.860 (2)</td>
<td>10</td>
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<td></td>
</tr>
<tr>
<td>CCG145</td>
<td>CoO + B</td>
<td>CoO</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>48.11 ± 0.26</td>
<td>51.56 ± 0.27</td>
<td>4.262 (0)</td>
<td>1.92, 2.82, 2.01</td>
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<tr>
<td>41/59</td>
<td>B</td>
<td>4.37 ± 0.24</td>
<td>0.53 ± 0.06</td>
<td>0.49 ± 0.37</td>
<td>66.19 ± 0.24</td>
<td>10.838 (7)</td>
<td>11</td>
<td></td>
<td></td>
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<tr>
<td>CCG325</td>
<td>CoO + B + F</td>
<td>CoO</td>
<td>0.32 ± 0.11</td>
<td>0.43 ± 0.16</td>
<td>0.50 ± 0.77</td>
<td>48.47 ± 0.58</td>
<td>4.261 (7)</td>
<td>5.52, 8.07, 1.9</td>
<td>11</td>
</tr>
<tr>
<td>13/66/21</td>
<td>B + F</td>
<td>10.10 ± 3.68</td>
<td>26.71 ± 1.89</td>
<td>0</td>
<td>62.56 ± 1.22</td>
<td>10.828 (9)</td>
<td>8</td>
<td></td>
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<tr>
<td>CCG343</td>
<td>CoO + B + F</td>
<td>CoO</td>
<td>0.83 ± 0.36</td>
<td>94.43 ± 0.36</td>
<td>49.38 ± 0.38</td>
<td>4.262 (8)</td>
<td>19.15, 23.99, 1.71</td>
<td>6</td>
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<tr>
<td>71.5/26.5/5</td>
<td>F</td>
<td>14.60 ± 1.98</td>
<td>1.29 ± 1.98</td>
<td>64.27 ± 1.98</td>
<td>10.828 (6)</td>
<td>6</td>
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<tr>
<td>CCG622</td>
<td>CoO + F</td>
<td>CoO</td>
<td>2.30 ± 1.40</td>
<td>1.10 ± 0.76</td>
<td>46.84 ± 3.00</td>
<td>49.77 ± 0.86</td>
<td>4.260 (8)</td>
<td>6.53, 8.31, 1.38</td>
<td>4</td>
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<tr>
<td>37/63</td>
<td>F</td>
<td>23.46 ± 0.94</td>
<td>11.43 ± 0.50</td>
<td>0.49 ± 0.37</td>
<td>64.62 ± 0.88</td>
<td>5.426 (4)</td>
<td>8</td>
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<td></td>
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<tr>
<td>CCG541</td>
<td>CoO + F</td>
<td>F</td>
<td>27.4 ± 0.67</td>
<td>3.65 ± 0.64</td>
<td>0.64 ± 0.15</td>
<td>68.33 ± 0.30</td>
<td>5.427 (3)</td>
<td>2.35, 3.48, 2.01</td>
<td>6</td>
</tr>
<tr>
<td>41/59</td>
<td>F</td>
<td>58.5 ± 0.30</td>
<td>0.08 ± 0.06</td>
<td>46.10 ± 1.22</td>
<td>53.24 ± 0.93</td>
<td>4.267 (4)</td>
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<tr>
<td>CCG523</td>
<td>CoO + B + F</td>
<td>CoO</td>
<td>1.19 ± 0.34</td>
<td>1.56 ± 0.66</td>
<td>39.82 ± 2.45</td>
<td>57.43 ± 1.50</td>
<td>4.263 (3)</td>
<td>11.66, 13.79, 3.2</td>
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<tr>
<td>7/43/50</td>
<td>B + F</td>
<td>13.97 ± 2.28</td>
<td>14.6 ± 2.28</td>
<td>0.96 ± 0.57</td>
<td>70.48 ± 0.97</td>
<td>10.865 (7)</td>
<td>4</td>
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</tr>
</tbody>
</table>

Fig. 3. Concentrations investigated in the CeO₂-Gd₂O₃-CoO system. (a) Experimental phase data at T = 1300°C in air. CoO, cobalt-oxide; P, perovskite; F, fluorite; B, C-type Gd₂O₃; L-ionic liquid. (b) The subsolidus isothermal section at 1264°C in air with experimental data from XRD and DTA analysis. The calculated isotherms of CeO₂-Gd₂O₃-CoO system at 1300°C (a) and 1264°C (b) are shown with the solid lines.

Table V. Summary of the Results of DTA Measurements Done in this Study Upon Heating

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>P1</th>
<th>P2</th>
<th>P3</th>
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<tr>
<td>CCG5542</td>
<td>910.5</td>
<td>1265.6</td>
<td>1344.9</td>
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<td>1308.6</td>
<td>1365.9</td>
</tr>
<tr>
<td>CCG145</td>
<td>907.3</td>
<td>1263.1</td>
<td>11</td>
</tr>
<tr>
<td>CCG325</td>
<td>–</td>
<td>1268.7</td>
<td>12</td>
</tr>
<tr>
<td>CCG127</td>
<td>–</td>
<td>1265.2</td>
<td>12</td>
</tr>
<tr>
<td>CCG622</td>
<td>904.4</td>
<td>–</td>
<td>12</td>
</tr>
</tbody>
</table>

P1, peak assigned to cobalt reduction; P2, peak from perovskite decomposition; P3, melting peak. All temperatures are given with precision ± 1°C determined from calibration runs with standard calibration sets (DIN 570001).³⁰

1. No data given due to the small grain size; Rp, Rwp, and σ: Rietveld refinement-factors.³⁰

An electrical charge and do not exist in nature. The charge-neutral plane represents the composition range of the solid solution of CoO in CeO₂, which is allowed by the electroneutrality requirement.

Equation (6) contains six unknowns G parameters. Six equations are required to solve Eq. (6). These are given as

\[ 2^\circ G_{\text{Fe}-\text{CoO}} = \frac{1}{2} G_{\text{Co}^{2+}}^{\circ} \cdot O^{2-} + \frac{1}{2} G_{\text{Co}^{4+}}^{\circ} \cdot V_a \]

\[ + 4RT \left( \frac{1}{2} \ln \frac{1}{2} + \frac{1}{2} \ln \frac{1}{2} \right) \]

\[ (7) \]

and

\[ 2^\circ G_{\text{Fe}-\text{CoO}} = \frac{3}{4} G_{\text{Co}^{3+}}^{\circ} \cdot O^{2-} + \frac{1}{4} G_{\text{Co}^{4+}}^{\circ} \cdot V_a \]

\[ + 4RT \left( \frac{3}{4} \ln \frac{3}{4} + \frac{1}{4} \ln \frac{1}{4} \right) \]

\[ (8) \]

The compounds in Eqs. (8) and (9) have the composition (Co²⁺)₂(O²⁻)₀.₅(Vₐ)₀.₅ and (Co³⁺)(O²⁻)₀.₇₅(Vₐ)₀.₂₅ and represent metastable CoO fluorite and CeO₂ fluorite. The last term is due to the ideal entropy of mixing on the anionic sublattice. The end-member with the highest charge Gⁿ of Ce³⁺:Vₐ is used as reference giving the equation

\[ 2G_{\text{Co}^{3+}}^{\circ} = 2^\circ G_{\text{CoO}} - 2^\circ G_{\text{O}_2} \]

(10)

Following Fig 6, the two reciprocal equations can be formed as given below:
\[ \Delta G_{r_1} = G_{\text{CeO}_2}^{F} + G_{\text{Co}_2O_4}^{F} - G_{\text{Co}_2O_3}^{F} - G_{\text{Co}_3O_4}^{F} \]
\[ \Delta G_{r_2} = G_{\text{CeO}_2}^{F} + G_{\text{Co}_2O_3}^{F} - G_{\text{Co}_2O_4}^{F} - G_{\text{Co}_3O_4}^{F} \]  

The values of the reciprocal reactions \( \Delta G_{r_1} \) and \( \Delta G_{r_2} \) are set to zero and the six Eqs. (7)–(12) can be solved for the six \( ^G \)  

\[ \Delta G_{r_1} = 2G_{\text{F} - \text{Co}_2O_3} \]  
\[ \Delta G_{r_2} = 2G_{\text{F} - \text{CeO}_2} - 2G_{\text{Gas}^{O_2}} \]  
\[ \Delta G_{r_3} = 2G_{\text{F} - \text{Ce}_2O_3} - 3G_{\text{Gas}^{O_2}} \]  
\[ \Delta G_{r_4} = 2G_{\text{F} - \text{Co}_2O_4} - 3G_{\text{Gas}^{O_2}} \]  
\[ \Delta G_{r_5} = 2G_{\text{F} - \text{Co}_3O_4} - 3G_{\text{Gas}^{O_2}} \]  
\[ \Delta G_{r_6} = 2G_{\text{F} - \text{Co}_4O_6} - 3G_{\text{Gas}^{O_2}} \]  

and the Gibbs energies \( G_{\text{F} - \text{Co}_2O_3}^{F}, G_{\text{F} - \text{Co}_2O_4}^{F}, G_{\text{F} - \text{Co}_3O_4}^{F}, G_{\text{F} - \text{Co}_4O_6}^{F}, G_{\text{F} - \text{Ce}_2O_3}^{F}, G_{\text{F} - \text{Ce}_2O_4}^{F}, G_{\text{F} - \text{Ce}_3O_4}^{F}, G_{\text{F} - \text{Ce}_4O_6}^{F} \) and \( G_{\text{Gas}^{O_2}}^{F} \) are unambiguously determined. The end-member in Eq. (15) has \( A_{\text{Gas}^{O_2}} \) and \( B_{\text{Gas}^{O_2}} \) parameters, which will be optimized by experimental data of the solid solubility.  

\[ \text{(B) Ionic Liquid (Binary Sub System CeO}_2\text{-CoO):} \]

The ionic liquid model\(^{27,28}\) is used to describe the liquid phase. Following Temkin,\(^{29}\) anions and cations in the liquid are assumed to occupy distinctive lattices and are allowed to mix freely on their respective sublattices. The liquid phase is modeled by combining the thermodynamic descriptions of the binary Co-O and Ce-O systems\(^{30,31}\) giving the extrapolation to the ternary Ce-Co-O system. The Ce-O system is modeled as \((\text{Ce}^{4+}, \text{Ce}^{3+}, \text{Co}^{2+})_p(\text{O}^{2-}, \text{Va}^{q-})_q\) and the Co-O system is modeled as \((\text{Co}^{3+}, \text{Co}^{2+})_p(\text{O}^{2-}, \text{Va}^{q-})_q\) therefore the ternary system is given as:  

\[ (\text{Ce}^{4+}, \text{Ce}^{3+}, \text{Co}^{2+})_p(\text{O}^{2-}, \text{Va}^{q-})_q \]  

The values of \( p \) and \( q \) are calculated as follows:  
\[ p = 2y_{\text{O}^{2-}} + qy_{\text{Va}} \]  
\[ q = 2y_{\text{Co}^{2+}} + 3y_{\text{Co}^{3+}} + 4y_{\text{Co}^{4+}} + 3y_{\text{Ce}^{4+}} \]  

The hypothetical vacancies have the induced charge \( -q \). The molar Gibbs energy of the liquid is given as follows:
\[ \delta G_m^{CL} = g \gamma_{Ce^{4+}} \gamma_{Va} \delta G^{CL}_{Ce^{4+}:Va} + g \gamma_{Ce^{3+}} \gamma_{Va} \delta G^{CL}_{Ce^{3+}:Va} + pRT(y_{Ce^{4+}} \ln y_{Ce^{4+}} + y_{Ce^{3+}} \ln y_{Ce^{3+}}) + \frac{1}{4} \delta G^{CL}_{Ce^{4+}:Va} \]

(20)

The excess Gibbs energy \( \delta G_m^{CL} \) is given as:

\[ \delta G_m^{CL} = \gamma_{Ce^{4+}} \gamma_{Ce^{4+}} \gamma_{O^2-} \gamma_{Va} \left( \gamma_{O^2-} - \gamma_{Va} \right)^2 \]

(21)

\( \delta G_m^{CL} \) is given by the Gibbs energy of pure CeO\(_2\), \( \gamma_{Ce^{3+}} \gamma_{Va} \gamma_{O^2-} \gamma_{Va} \gamma_{Va} \gamma_{Va} \), and \( \gamma_{Va} \gamma_{Va} \gamma_{Va} \gamma_{Va} \).

(22)

The Gibbs energy \( \delta G_m^{CL} \) of Ce-doped CeO\(_2\) is given by the equation:

\( \delta G_m^{CL} = \gamma_{Ce^{4+}} \gamma_{Ce^{4+}} \gamma_{O^2-} \gamma_{Va} \left( \gamma_{O^2-} - \gamma_{Va} \right)^2 \)

(23)

The meaning of the different terms in Eq. (23) is same as in Eq. (6). Similarly to the previous section, Eq. (23) can be visualized as corners of a compositional triangular prism representing six end-members of Ce\(_{1-x}\)Gd\(_x\)O\(_2\)-\(\gamma\) phase. Figure 7 shows only one stoichiometric end-member pure CeO\(_2\) phase, all other corner end-members are charged and do not exist in nature. The charge-neutral plane represents compositional range of the solid solution of GdO\(_2\) in CeO\(_2\), which is allowed by electroneutrality requirement. The Gibbs energy \( \delta G_m^{CL} \) is given by the Gibbs energy of pure CeO\(_2\), \( \delta G_m^{CL} = 2 \delta G_{Ce^{3+}}, \) and end-member with the highest charge \( \delta G_m^{CL} = 2 \delta G_{Ce^{3+}} \) is used as reference. The two neutral end-members \( \delta G_{Ce^{3+}} \) and \( \delta G_{Ce^{4+}} \) are given as:

\( \delta G_{Ce^{3+}} = \frac{3}{4} \delta G_{Ce^{4+}} - 1 \delta G_{Ce^{3+}} + \frac{1}{4} \delta G_{Ce^{4+}} \)

(24)

\[ \frac{1}{4} \delta G_{Ce^{4+}} = \gamma_{Ce^{4+}} \gamma_{Ce^{4+}} \gamma_{O^2-} \gamma_{Va} \left( \gamma_{O^2-} - \gamma_{Va} \right)^2 \]

(25)

Analogously to the previous description in CeO\(_2\)-CoO system, the two reciprocal equations are given by the following:

\( \delta G_m^{Co^{2+}} = \gamma_{Co^{2+}} \gamma_{Co^{2+}} \gamma_{O^2-} \gamma_{Va} \left( \gamma_{O^2-} - \gamma_{Va} \right)^2 \)

(26)

The meaning of the different terms in Eq. (26) is same as in Eq. (6). Similarly to the previous section, Eq. (26) can be visualized as corners of a compositional triangular prism representing six end-members of Ce\(_{1-x}\)Gd\(_x\)Co\(_{1-y}\)O\(_2\)-\(\gamma\) phase. Figure 7 shows only one stoichiometric end-member pure CeO\(_2\) phase, all other corner end-members are charged and do not exist in nature. The charge-neutral plane represents compositional range of the solid solution of GdO\(_2\) in CeO\(_2\), which is allowed by electroneutrality requirement. The Gibbs energy \( \delta G_m^{Co^{2+}} \) is given by the Gibbs energy of pure CeO\(_2\), \( \delta G_m^{Co^{2+}} = 2 \delta G_{Co^{2+}} \), and end-member with the highest charge \( \delta G_m^{Co^{2+}} = 2 \delta G_{Co^{2+}} \) is used as reference. The two neutral end-members \( \delta G_{Co^{2+}} \) and \( \delta G_{Co^{4+}} \) are given as:

\( \delta G_{Co^{2+}} = \frac{3}{4} \delta G_{Co^{4+}} - 1 \delta G_{Co^{2+}} + \frac{1}{4} \delta G_{Co^{4+}} \)

All end-members in Eq. (28) are known from previous models of the fluorite phase (Ce\(_{1-x}\), Ce\(_{1-x}\), Co\(_{1-x}\))\((O^2-, Va)\), and (Ce\(_{1-x}\), Ce\(_{1-x}\), Co\(_{1-x}\))\((O^2-, Va)\). The excess Gibbs energy of the ternary fluorite phase is given as:

\[ \delta G_{Ce^{4+}, Ce^{3+}, Co^{2+}} = \frac{3}{4} \delta G_{Ce^{4+}, Ce^{3+}, Co^{2+}} + \frac{1}{4} \delta G_{Ce^{4+}, Ce^{3+}, Co^{2+}} \]
where $0 L_{\text{Flour}}$ is excess interaction parameter independent of the constituents of the anion sublattice. The interaction parameters $0 L_{\text{Flour}}$, $L_{\text{Flour}}$, $0 G_{\text{Flour}}$, and $0 L_{\text{Flour}}$ are taken from the assessments of the quasibinary systems.

(E) Ionic Liquid: The two-sublattice ionic liquid model is used to describe liquid phase. The liquid phase exists at low oxygen and high oxygen composition relative to CoO. It is thus necessary to include $\text{Ce}^{4+}$, $\text{Ce}^{3+}$, $\text{Co}^{2+}$, and $\text{Co}^{3+}$ ions, and hypothetic vacancies on the anionic sublattice to maintain charge neutrality as the liquid becomes gradually more metallic.

$$\langle \text{Ce}^{4+}, \text{Ce}^{3+}, \text{Gd}^{3+}, \text{Ce}^{3+}, \text{Co}^{2+} \rangle_{p} (O^{2-}, \text{Va}^{3-})_q$$ (30)

The values of $p$ and $q$ are calculated as follows:

$$p = 2y_{\text{O}^2-} + q_{\text{Va}}$$

$$q = 3y_{\text{Ga}^{3+}} + 2y_{\text{Co}^{2+}} + 3y_{\text{Co}^{3+}} + 4y_{\text{Ce}^{4+}} + 3y_{\text{Ce}^{3+}}$$

The hypothetical vacancies have an induced charge $-q$. The molar Gibbs energy of the liquid is given by the equations:

$$G_m^{\text{Liq}} = y_{\text{Ce}^{4+}} v_{\text{Ce}^{4+}} G_{\text{Flour}} + y_{\text{Ce}^{3+}} v_{\text{Ce}^{3+}} G_{\text{Flour}}$$

$$+ y_{\text{Ga}^{3+}} v_{\text{Ga}^{3+}} G_{\text{Flour}} + y_{\text{Co}^{2+}} v_{\text{Co}^{2+}} G_{\text{Flour}} + y_{\text{Co}^{3+}} v_{\text{Co}^{3+}} G_{\text{Flour}}$$

$$+ y_{\text{Ga}^{3+}} v_{\text{Ga}^{3+}} G_{\text{Co}^{2+}} + y_{\text{Co}^{2+}} v_{\text{Co}^{2+}} G_{\text{Ga}^{3+}}$$

$$+ y_{\text{Ga}^{3+}} v_{\text{Ga}^{3+}} G_{\text{Co}^{3+}} + y_{\text{Co}^{3+}} v_{\text{Co}^{3+}} G_{\text{Ga}^{3+}}$$

$$+ y_{\text{Co}^{2+}} v_{\text{Co}^{2+}} G_{\text{Ga}^{3+}} + y_{\text{Ga}^{3+}} v_{\text{Ga}^{3+}} G_{\text{Co}^{3+}}$$

$$+ pRT(y_{\text{Ga}^{3+}} \ln y_{\text{Ga}^{3+}} + y_{\text{Ga}^{3+}} \ln y_{\text{Ga}^{3+}} + y_{\text{Co}^{2+}} \ln y_{\text{Co}^{2+}} + y_{\text{Co}^{3+}} \ln y_{\text{Co}^{3+}})$$

$$+ qRT(y_{\text{Ga}^{3+}} \ln y_{\text{Ga}^{3+}} + y_{\text{Ga}^{3+}} \ln y_{\text{Ga}^{3+}} + y_{\text{Co}^{2+}} \ln y_{\text{Co}^{2+}} + y_{\text{Co}^{3+}} \ln y_{\text{Co}^{3+}})$$

$$+ G_E^{\text{Liq}}$$

(31)

with the excess Gibbs energy $G_E^{\text{Liq}}$ being the following:

$$G_E^{\text{Liq}} = y_{\text{Co}^{2+}} v_{\text{Co}^{2+}} G_{\text{Liq}} + y_{\text{Ga}^{3+}} v_{\text{Ga}^{3+}} G_{\text{Liq}} + y_{\text{Co}^{3+}} v_{\text{Co}^{3+}} G_{\text{Liq}}$$

$$+ y_{\text{Co}^{2+}} v_{\text{Co}^{2+}} G_{\text{Ga}^{3+}} + y_{\text{Ga}^{3+}} v_{\text{Ga}^{3+}} G_{\text{Co}^{3+}}$$

$$+ y_{\text{Co}^{2+}} v_{\text{Co}^{2+}} G_{\text{Co}^{3+}} + y_{\text{Ga}^{3+}} v_{\text{Ga}^{3+}} G_{\text{Co}^{3+}}$$

$$+ y_{\text{Co}^{2+}} v_{\text{Co}^{2+}} G_{\text{Co}^{3+}} + y_{\text{Ga}^{3+}} v_{\text{Ga}^{3+}} G_{\text{Co}^{3+}}$$

$$+ y_{\text{Co}^{2+}} v_{\text{Co}^{2+}} G_{\text{Co}^{3+}} + y_{\text{Ga}^{3+}} v_{\text{Ga}^{3+}} G_{\text{Co}^{3+}}$$

$$+ G_E^{\text{Liq}}$$

(32)

To keep the description simple only two interaction parameters $0 L_{\text{Ga}^{3+}, \text{Ce}^{3+}, \text{O}^{2-}}$ and $0 L_{\text{Ga}^{3+}, \text{Co}^{2+}, \text{O}^{2-}}$ were required to reproduce the experimental data.

(F) Optimization of Model Parameters: The complete set of optimized thermodynamic parameters for the CeO$_2$-CoO, CeO$_2$-Gd$_2$O$_3$, and Gd$_2$O$_3$-CoO system used in this study is given in Tables VI and VII, respectively. The final set of parameters for the CeO$_2$-Gd$_2$O$_3$-CoO system is presented in Table VIII. The optimization was done using the PARROT module of the ThermoCalc program. The PARROT can take into account all thermodynamic and phase diagram data simultaneously and minimize the weighed sum of squared errors. The eutectic temperature and eutectic concentration in CeO$_2$-CoO system were optimized with $0 k_{\text{Co}^{2+}, \text{Ce}^{3+}, \text{O}^{2-}}$ and $0 k_{\text{Co}^{2+}, \text{Ce}^{3+}, \text{O}^{2-}}$ interaction parameters. The model parameters of the solid solubility of CoO in CeO$_2$, $A_{\text{Co0}}$ and $B_{\text{Co0}}$ in Eq. (15) were optimized using experimental data by Chen et al.

The experimentally determined eutectic temperature and compositions were used to optimize regular interaction parameters of the liquid phase. As it is assumed that interaction energies between cobalt and gadolinium ions have comparable values in the oxide melt, both regular interaction parameters were given the same value.

(2) Modeling Results and Discussion

(A) Binary Subsystem CeO$_2$-CoO: The binary CeO$_2$-CoO is a simple eutectic phase diagram with the small solid solubilities on both Ce and Co-rich side. To the best of our knowledge, the CALPHAD assessment of this system is not published, although critical assessment of the thermodynamic data was already given by Kim. Figure 8 summarizes the optimized phase diagram of CeO$_2$-CoO together with experimental data from the literature. As there is no available data on the lattice stability between the fluorite and halite phases, Kim used the method developed by Kaufmann et al. and estimated the metastable melting points. The extension of the solidus and liquidus trajectories from the two-phase fluorite liquid to the pure component CoO corresponds to the metastable melting point of the fluorite-type CoO. The metastable melting points of the fluorite-type CoO, $T_{\text{Fl}} = 233^\circ C$ and the halite-type CeO$_2$, $T_{\text{H}} = 850^\circ C$ were calculated by Kim. Due the small mutual solid solubility of CoO and CeO$_2$, it cannot be explained, as additional oxidizing of the samples in...
oxygen at 700°C for 12 h would oxidize any remaining Ce³⁺ in the samples, thus effectively reducing the lattice parameter due to the much smaller ionic radii of Ce⁴⁺ (0.97 Å) to Ce³⁺ (1.143 Å). All lattice constants data are simultaneously fitted using a weighted least-square method (Origin v.8.1), with smaller weighting given to the experimental data of Grover and Chen. A quadratic relationship for complete phase region is described as $a_r = 5.4105 + 8.09189 \times 10^{-4} T_{\text{Gd}} - 8.39562 \times 10^{-2} T_{\text{Gd}}^2$ ($T_{\text{Gd}}$ in K).

Raman spectroscopic studies in the complete range of ceria-gadolinia solid solutions were done by Banerji et al. All investigated CeₓGd_{1-x}O₂ samples in the range $x = 0$–1.0 were annealed up to 1400°C and slowly cooled down and subsequently analyzed using Raman spectra of a 632.8 nm He-Ne laser. These showed that up to 20 mol% Gd the Raman spectrum is completely representative of a fluorite-type CeO₂ structure. In the compositional range between 50 and 80 mol% Gd both phases coexist. Above 80 mol% Gd, only the bixbyte-type structure can be observed with the most intense Raman peak centered at ~370 cm⁻¹. As already discussed, it is difficult to infer the two-phase region of fluorite and bixbyte phase based on XRD data alone. The possible microdomains of C-type phase can coexist in the fluorite structure and go undetected by conventional XRD lab source as the peaks of both phases appear at the same angles. However, the Raman spectroscopy is more sensitive to the

### Table VI. Thermodynamic Parameters of the CeO₂-CoO System

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<tr>
<th>Liquid:</th>
<th>(Ce⁴⁺,Ce³⁺,Co²⁺,Co¹⁺)ₚ (O²⁻,Va)ₐ</th>
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<td>$G_{\text{Liq}}^{\text{CoO}}$</td>
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### Table VI. (Continued)

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<th>Co₂O₃:</th>
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<td>$G_{\text{Liq}}^{\text{Co}_2\text{O}_3}$</td>
</tr>
<tr>
<td>$G_{\text{Co}_2\text{O}_3}^{\text{Liq}}$</td>
<td>$G_{\text{Liq}}^{\text{Co}_2\text{O}_3}$</td>
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<td>$G_{\text{Co}_2\text{O}_3}^{\text{Liq}}$</td>
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</tbody>
</table>

$^1$All parameters are in SI units: J/mol, and K.
$^2$Magnetic contributions are added to the nonmagnetic part of the Gibbs energy, for more details see Chen et al. $^{30}$
Table VII. Thermodynamic Parameters of the CeO$_2$-Gd$_2$O$_3$ and Gd$_2$O$_3$-CoO Systems.\(^1\) Thermodynamic data are defined in Refs. 9, 10, 30, 32

<table>
<thead>
<tr>
<th>Phase</th>
<th>Parameters</th>
<th>( \Delta G ) (kJ mol(^{-1}))</th>
<th>( T ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-phase: ((\text{Ce}^{3+}, \text{Ce}^{4+}, \text{Gd}^{3+}) _2 (\text{O}^{2-})_2 (\text{O}^{2-}, \text{Va})_1)</td>
<td>( \Delta G^\text{A} _\text{Ce}^{3+} _\text{Ce}^{4+} _\text{Gd}^{3+} )</td>
<td>( 2 \text{G}_\text{Ce}^{\text{O}<em>2} + \frac{1}{2} \text{G}</em>\text{Ga}^{\text{O}_2} + 10000 )</td>
<td>-</td>
</tr>
<tr>
<td>B-phase: ((\text{Ce}^{3+}, \text{Ce}^{4+}, \text{Gd}^{3+}) _2 (\text{O}^{2-})_2 (\text{O}^{2-}, \text{Va})_1)</td>
<td>( \Delta G^\text{B} _\text{Ce}^{3+} _\text{Ce}^{4+} _\text{Gd}^{3+} )</td>
<td>( 2 \text{G}_\text{Ce}^{\text{O}<em>2} + \frac{1}{2} \text{G}</em>\text{Ga}^{\text{O}_2} + 1000 )</td>
<td>-</td>
</tr>
<tr>
<td>C-phase: ((\text{Ce}^{3+}, \text{Ce}^{4+}, \text{Gd}^{3+}) _2 (\text{O}^{2-})_2 (\text{O}^{2-}, \text{Va})_1)</td>
<td>( \Delta G^\text{C} _\text{Ce}^{3+} _\text{Ce}^{4+} _\text{Gd}^{3+} )</td>
<td>( 2 \text{G}_\text{Ce}^{\text{O}<em>2} + \frac{1}{2} \text{G}</em>\text{Ga}^{\text{O}_2} + 100 )</td>
<td>-</td>
</tr>
</tbody>
</table>

\( ^1 \)All parameters are in SI units: J, mol, and K.

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Table VII. (Continued)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Parameters</th>
<th>( \Delta G ) (kJ mol(^{-1}))</th>
<th>( T ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-phase: ((\text{Ce}^{3+}, \text{Ce}^{4+}, \text{Gd}^{3+}) _2 (\text{O}^{2-})_2 (\text{O}^{2-}, \text{Va})_1)</td>
<td>( \Delta G^\text{A} _\text{Ce}^{3+} _\text{Ce}^{4+} _\text{Gd}^{3+} )</td>
<td>( 2 \text{G}_\text{Ce}^{\text{O}<em>2} + \frac{1}{2} \text{G}</em>\text{Ga}^{\text{O}_2} + 10000 )</td>
<td>-</td>
</tr>
<tr>
<td>B-phase: ((\text{Ce}^{3+}, \text{Ce}^{4+}, \text{Gd}^{3+}) _2 (\text{O}^{2-})_2 (\text{O}^{2-}, \text{Va})_1)</td>
<td>( \Delta G^\text{B} _\text{Ce}^{3+} _\text{Ce}^{4+} _\text{Gd}^{3+} )</td>
<td>( 2 \text{G}_\text{Ce}^{\text{O}<em>2} + \frac{1}{2} \text{G}</em>\text{Ga}^{\text{O}_2} + 100 )</td>
<td>-</td>
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<td>C-phase: ((\text{Ce}^{3+}, \text{Ce}^{4+}, \text{Gd}^{3+}) _2 (\text{O}^{2-})_2 (\text{O}^{2-}, \text{Va})_1)</td>
<td>( \Delta G^\text{C} _\text{Ce}^{3+} _\text{Ce}^{4+} _\text{Gd}^{3+} )</td>
<td>( 2 \text{G}_\text{Ce}^{\text{O}<em>2} + \frac{1}{2} \text{G}</em>\text{Ga}^{\text{O}_2} + 100 )</td>
<td>-</td>
</tr>
</tbody>
</table>

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At high temperatures, the bixbyite solid solution region is extended, but shrinks to almost pure Gd$_2$O$_3$ at room temperature. Zinkevich et al.\(^{10}\) argued that the reason for this is a positive enthalpy of formation, which also causes a convex type phase boundary of the fluorite phase at the low temperatures.

\((C)\) Phase Diagram CeO$_2$-Gd$_2$O$_3$-CoO: Figures 2 and 3 show isothermal sections of the quasi-ternary phase diagram in the CeO$_2$-Gd$_2$O$_3$-CoO system at 1100°C and 1300°C.
Table VIII. Thermodynamic Parameters of the CeO$_2$-CoO-Gd$_2$O$_3$ System.$^4$ The Thermodynamic Properties of Solid Phases Gd$_2$O$_3$-CoO and Solid Phases in CeO$_2$-Gd$_2$O$_3$ System are Defined in Table VII.

C-phase: (Ce$^{3+}$,Ce$^{4+}$,Gd$^{3+}$,Co$^{3+}$)$_2$ (O$^{2-}$)$_3$ (O$^{2-}$,Va)$_1$

\[
\begin{align*}
G_{\text{C-phase}} & = g_{\text{CeO}_2} + 2g_{\text{CoO}} + 3g_{\text{O}_2} + 41000.2 + 28.4887T \\
0 & = g_{\text{CeO}_2} + 2g_{\text{CoO}} + 3g_{\text{O}_2} + 41000.2 + 28.4887T
\end{align*}
\]

Fluorite: (Ce$^{3+}$,Ce$^{4+}$,Gd$^{3+}$,Co$^{3+}$)$_2$ (O$^{2-}$)$_3$

\[
\begin{align*}
G_{\text{Fluorite}} & = g_{\text{CeO}_2} + 2g_{\text{CoO}} + 3g_{\text{O}_2} + 41000.2 + 28.4887T \\
0 & = g_{\text{CeO}_2} + 2g_{\text{CoO}} + 3g_{\text{O}_2} + 41000.2 + 28.4887T
\end{align*}
\]

Fluorite and liquid: (Ce$^{3+}$,Ce$^{4+}$,Gd$^{3+}$,Co$^{3+}$)$_2$ (O$^{2-}$,Va)$_1$

\[
\begin{align*}
G_{\text{Fluorite+Liquid}} & = g_{\text{CeO}_2} + 2g_{\text{CoO}} + 3g_{\text{O}_2} + 41000.2 + 28.4887T \\
0 & = g_{\text{CeO}_2} + 2g_{\text{CoO}} + 3g_{\text{O}_2} + 41000.2 + 28.4887T
\end{align*}
\]

Fluorite and CoO: (Ce$^{3+}$,Ce$^{4+}$,Gd$^{3+}$,Co$^{3+}$)$_2$ (O$^{2-}$,Va)$_1$

\[
\begin{align*}
G_{\text{Fluorite+CoO}} & = g_{\text{CeO}_2} + 2g_{\text{CoO}} + 3g_{\text{O}_2} + 41000.2 + 28.4887T \\
0 & = g_{\text{CeO}_2} + 2g_{\text{CoO}} + 3g_{\text{O}_2} + 41000.2 + 28.4887T
\end{align*}
\]

Fluid: (Ce$^{3+}$,Ce$^{4+}$,Gd$^{3+}$,Co$^{3+}$)$_2$ (O$^{2-}$,Va)$_1$

\[
\begin{align*}
G_{\text{Fluid}} & = g_{\text{CeO}_2} + 2g_{\text{CoO}} + 3g_{\text{O}_2} + 41000.2 + 28.4887T \\
0 & = g_{\text{CeO}_2} + 2g_{\text{CoO}} + 3g_{\text{O}_2} + 41000.2 + 28.4887T
\end{align*}
\]

\[\frac{1}{4}\ln T = 114250 \quad \text{Ce}^{3+} - \text{O}^{2-} - \text{Va}^{4+} = 270000 - 210T\]

\[\frac{1}{4}\ln T = 182675 - 30.5567T \quad \text{Co}^{3+} - \text{O}^{2-} - \text{Va}^{4+} = 54226 - 20T\]

\[\frac{1}{4}\ln T = -74000 \quad \text{Gas}^{2} - \text{O}^{2-} - \text{Va}^{4+} = -27499\]

\[\frac{1}{4}\ln T = 0 \quad \text{Gas}^{2} - \text{O}^{2-} - \text{Va}^{4+} = 0\]

\[\frac{1}{4}\ln T = -1360219 \quad \text{Ce}^{3+} - \text{O}^{2-} - \text{Va}^{4+} = -1360219\]

\[\frac{1}{4}\ln T = \text{All parameters are in SI units: J, mol, and K.}\]

Fig. 8. Optimized CeO$_2$-CoO phase diagram at atmospheric pressure, compared with experimental data from the literature. The literature data are taken from Chen et al.,$^{12}$ Dontsov et al.,$^{25}$ Pound,$^{37}$ and Hrovat et al.$^{43}$

together with experimental results obtained in this study. At 1100°C, the perovskite GdCoO$_{2-\delta}$ is stable under normal atmospheric conditions.$^{9,42}$ The three-phase region of the isothermal section is divided in the 2 three-phase regions, now also including gadolinium cobalt perovskite. The isothermal section of CeO$_2$-Gd$_2$O$_3$-CoO phase diagram at 1100°C is composed of the four regions: (1) two-phase region of bixbyite Gd$_2$O$_3$ and GdCoO$_{2-\delta}$ perovskite, (2) three-phase region of GdCoO$_{2-\delta}$ perovskite, bixbyite, and fluorite-type structure C$_{14}$-Gd$_2$O$_{3-x}$, (3) three-phase region CoO, fluorite, and perovskite, and (4) two-phase region of CoO and C$_{14}$-Gd$_2$O$_{3-x}$.

The decomposition temperature of gadolinium cobaltite in Gd$_2$O$_3$-CoO system has been determined in our previous study$^1 T = 1265 \pm 5°C.$ In quasi-ternary CeO$_2$-Gd$_2$O$_3$-CoO there is small solid solubility of CeO$_2$ (~1 mol%) in GdCoO$_3$. The stability of the perovskite increases slightly due to solid solution with Ce$^{3+}$. It could be speculated that this is a consequence of larger ionic radius of Ce$^{3+}$ compared to Gd$^{3+}$, which hinders the distortion of the perovskite structure at high temperatures.

At 1300°C, isothermal section contains a small amount of the liquid phase and gadolinium cobaltite. The liquid phase
and data acquired in the present study, the CALPHAD assessment is given. The DSC measurements were done to determine the eutectic temperature and composition. Eutectic composition was refined by measuring the eutectic volume fraction of samples in SEM images of different probes close to the eutectic concentration. Using this experimental data and selected literature data, the authors optimized the model parameters of the CeO$_2$-Gd$_2$O$_3$-CoO system and calculated the phase diagram. The XRD study of the quenched samples at 1100°C and 1300°C and in a complete compositional range refined by Rietveld method confirmed the calculated isothermal sections of the phase diagram. The only ternary phase GdCoO$_3$ was refined using Rietveld method and the resulting crystal structure is reported. The CoO octahedrons are tilted and the bond angle Co-O-Co is seen decreasing in the series of the rare earth ions from La to Gd.

The results of the phases in the subsolidus region of the phase diagram are in good agreement with the experimental data determined in this study. However, due to the lack of experimental data especially at high temperatures above 2000°C in CeO$_2$-Gd$_2$O$_3$ system, no data on liquidus stability and the eutectic point exist—the liquidus surface must be regarded as speculative. Once these basic experimental data are available, our description can be greatly improved.

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References


V. Conclusions

In this study, the phase diagram of CeO$_2$-Gd$_2$O$_3$-CoO is presented for the first time. Using the data from the literature