Phase Relation Studies in the CeO$_2$-Sm$_2$O$_3$ System at 1500 to 600 °C in Air

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Abstract

Materials based on CeO$_2$-Sm$_2$O$_3$ system are promising candidates for a wide range of applications, but the phase relationship has not been studied systematically previously. To address this challenge, the subsection of the phase diagram for 600, 1100 and 1500 °C has been elucidated. Samples of different compositions have been prepared from nitrate acid solutions using conventional ceramic techniques; evaporation, drying, and calcinations. The phase relations in the binary CeO$_2$-Sm$_2$O$_3$ system at 600-1500 °C in air were studied from the heat treated samples using X-ray diffraction analysis and in the overall concentration range. It was established that in the binary CeO$_2$-Sm$_2$O$_3$ system there exist fields of solid solutions based on monoclinic (B) modification of Sm$_2$O$_3$ cubic (C) modification of Sm$_2$O$_3$ and cubic modification of CeO$_2$ with fluorite-type structure (F). The systematic study that covered whole composition range excluded formation of new phases. The refined lattice parameters of the unit cells and the boundaries of the homogeneity fields for solid solutions were determined.

Keywords: Phase equilibria; Ceria; Samaria; Solid solutions; Lattice parameters

Introduction

For many years, CeO$_2$-based materials have been mainly used as catalysts and pigments in ceramics or glasses. Today ceria based materials are of great worldwide interest for many engineering applications such as catalysts, solid electrolytes, laser media, radio wave absorbers, components for electronics, and so on. Much attention is now focused on development of alternative power sources which are based on electrochemical devices, in particular on fuel cells. As solid electrolytes for fuel cells that operate at high temperatures (up to 1000 °C), materials on the basis of Y$_2$O$_3$ stabilized zirconia are used, whereas ceria based solid solutions are promising as electrolytes operating at moderate temperatures (to 600 °C) [1-10].

The right choice of an optimal electrolyte depends on reliability of data on solubility limits for REE oxides in the crystalline lattice of CeO$_2$, since high ion conductivity corresponds to maximal concentration of compensating oxygen vacancies. This, in its turn, requires good knowledge of phase equilibria in multicomponent oxide systems. Investigations of peculiarities of REE polymorphism, exsolution and formation of ordered phases as well as of the effect of electronic structure and relations between ion radii of lanthanides on the phase transformation, structure, and stability are also of keen scientific interest. Development of new materials and technologies based on CeO$_2$-Ln$_2$O$_3$ solid solutions needs phase equilibria studies and knowledge of properties of the phases formed in the systems. Phase equilibria in the CeO$_2$ based systems added with REE oxides and properties have been partially studied [11-17].

Phase reactions in CeO$_2$-Sm$_2$O$_3$ system were studied in [16]. They found stable solid solutions based on cubic modification of F-CeO$_2$ in concentrations range from pure CeO$_2$ to 40 mol % Sm$_2$O$_3$ and cubic modification of C-Sm$_2$O$_3$ in the range from 50 to 90 mol % Sm$_2$O$_3$ at 1400 °C. The lattice parameter of the unit cell of solid solutions varies from a=0.5411nm in pure CeO$_2$ to a=0.5452nm in the composition containing 40mol % Sm$_2$O$_3$ and from a=1.0914nm the composition containing 50mol % Sm$_2$O$_3$ to a=1.0928nm the two-phase composition (B+C) containing 90mol % Sm$_2$O$_3$. The two-phase region (F+C) in the system has not been determined correctly. The phase diagram has not been built [16].
Experimental

Cerium oxide nitrate, Ce(NO\(_3\))\(_2\)-6H\(_2\)O, samarium oxide, Sm\(_2\)O\(_3\) (all 99.99 % produced by Merck Corp.) and analytical-grade nitric acid were used as the starting materials. In totally 24 compositions in CeO\(_2\)-Sm\(_2\)O\(_3\) system were prepared in the present work for experimental analysis. The specimens were prepared in step 1-5mol % Sm\(_2\)O\(_3\) as follows: mixing the cerium and samarium nitrate solutions followed by their co-evaporation and calcination at 1000 °C for 2h until uniform mixtures of oxides formed. The as-prepared powders were pressed at 10MPa into pellets of 5mm in diameter and 4mm in height. To study phase relationships at 1500 °C thermal treatment of as-prepared samples was carried out in two stages: at 1100 °C (for 846h in air) and then at 1500 °C (for 150h in air) in the furnaces with heating elements based on Fecral (H23U5T) and Superkanthal (MoSi\(_2\)), respectively. The two-step annealing allows removing residuals of nitrogen oxides from the samples. At lower temperatures, ≤1250 °C, phase equilibria (which include processes of disordering/ordering) were reached rather slowly because of low velocity of diffusion processes in the cation sublattice, which requires long-term annealing of samples [18]. To study phase equilibria at 1100 °C and 600 °C, the heat treatment of the samples was carried out in air for 10813 hours and 33000 hours, respectively. The heating rate was 3.5 °C/min when switching off the power from the furnace. No phase composition changes were fixed at this rate or faster cooling. This technology of preparation doesn’t influence the valence of rare earth elements.

XRD analysis of samples was performed by powder procedure on a DRON-3 apparatus at ambient temperature under CuK\(_\alpha\) radiation. Scanning step was 0.05-0.1 ° in the range 2θ=15-90 °. Lattice parameters were calculated by the least square method using the LATTIC computer code with an error of not lower than 0.0001nm for the cubic phase. The phase composition was determined using the “Match” program, which utilizes PDF-2 database of standard X-ray data. Diffraction peaks parameters determined by approximating the peaks of experimental diffractograms using the Voigt function, were used for the phase identification and calculations of lattice parameters.

Results and discussion

The solid-phase reaction between CeO\(_2\) (fluorite-type, F, space group \(Fm\overline{3}m\)) and Sm\(_2\)O\(_3\) (monoclinic modification of rare-earth oxides, type B, space group C2/m) was studied at temperatures 600 °C, 1100 °C and 1500 °C. The x-ray analysis showed that three solid solutions of substitution type exist in the CeO\(_2\)-Sm\(_2\)O\(_3\) system in the given temperature interval. Two of them have cubic symmetry (fluorite F-CeO\(_2\) type and C-Sm\(_2\)O\(_3\) type) and the third one has monoclinic symmetry (B-Eu\(_2\)O\(_3\) type). The phases were separated by two-phase fields (C+F; B+C) as shown in Figure 1. Tables 1-3 contain data on the initial chemical and phase composition of samples annealed at 1500, 1100, and 600 °C as well as on lattice parameters for phases that are in equilibrium at the corresponding temperatures. Figure 2 demonstrate concentration dependences of solid solutions based on F-CeO\(_2\) and C-Sm\(_2\)O\(_3\) in the CeO\(_2\)-Sm\(_2\)O\(_3\) system after annealing at 1500, 1100, and 600 °C. The XRD patterns that characterize solid solution regions in the CeO\(_2\)-Sm\(_2\)O\(_3\) system at 1100 °C are shown in Figure 3, where the presence of two phases is distinctly seen at any percentage of components and phases, which made it possible to carry out an accurate phase analysis.
Figure 2: Concentration dependences of lattice parameters for solid solutions based on
a) F-CeO2 and
b) C-Sm2O3 in the system CeO2-Sm2O3 heat-treated at 1500 °C (●), 1100 °C (●) and 600 °C (▲).

Figure 3: XRD patterns from CeO2-Sm2O3 samples annealed at 1100 °C.
(a) 1 mol.% CeO2-99 mol.% Sm2O3, (C+B)
(b) 5 mol.% CeO2-95 mol.% Sm2O3, (C+B↓)
(c) 35 mol.% CeO2-65 mol.% Sm2O3 (C)
(d) 70 mol.% CeO2-30 mol.% Sm2O3 (C+F)
(e) 95 mol.% CeO2-5 mol.% Sm2O3 (F).
Table 1: Phase composition and lattice parameters of the phases in the CeO$_2$-Sm$_2$O$_3$ system, annealed at 1500 °C for 150h in air (XRD data).

| Chemical Composition (mol %) | Phase Composition | Lattice Parameters of the Phases $\pm 0.0002$ (nm) |
|-----------------------------|-------------------|-----------------------------------------------|
|                             | <F>               | <C>               | <B>               | a    | a    | a    | b    | c    | β    |
| CeO$_2$                     | 0                 | 100               | <B>               | -    | -    | -    | 1.3925 | 0.3632 | 0.868 | 90.4 |
| Sm$_2$O$_3$                 | 2                 | 98                | <B>               | -    | -    | -    | 1.3637 | 0.3615 | 0.8928 | 91.7 |
|                             | 5                 | 97                | <B> + <C>         | -    | -    | -    | 1.3655 | 0.3631 | 0.8922 | 91.9 |
|                             | 10                | 90                | <B> + <C>         | -    | 1.0922 | 1.3932 | 0.36 | 0.9157 | 91.6 |
|                             | 15                | 85                | <B> + <C>         | -    | 1.0921 | 1.5763 | 0.3607 | 0.909 | 94.5 |
|                             | 20                | 80                | <B> + <C>         | -    | 1.0922 | 1.6996 | 0.3705 | 0.8518 | 99.1 |
|                             | 25                | 75                | <B> + <C>         | -    | 1.0923 | -    | -    | -    | -    |
|                             | 30                | 70                | <B> + <C>         | -    | 1.0922 | -    | -    | -    | -    |
|                             | 35                | 65                | <C>               | -    | 1.0919 | -    | -    | -    | -    |
|                             | 40                | 60                | <C>               | -    | 1.0916 | -    | -    | -    | -    |
|                             | 45                | 55                | <C>               | -    | 1.0911 | -    | -    | -    | -    |
|                             | 50                | 50                | <C>               | -    | 1.0909 | -    | -    | -    | -    |
|                             | 55                | 45                | <C>               | -    | 1.0907 | -    | -    | -    | -    |
|                             | 60                | 40                | <C> + <F>         | -    | 0.5449 | 1.0904 | -    | -    | -    |
|                             | 65                | 35                | <C> + <F>         | -    | 0.5446 | 1.0904 | -    | -    | -    |
|                             | 70                | 30                | <C> + <F>         | -    | 0.5446 | 1.0903 | -    | -    | -    |
|                             | 75                | 25                | <F>               | -    | 0.5446 | -    | -    | -    | -    |
|                             | 80                | 20                | <F>               | -    | 0.544 | -    | -    | -    | -    |
|                             | 85                | 15                | <F>               | -    | 0.5434 | -    | -    | -    | -    |
|                             | 90                | 10                | <F>               | -    | 0.5426 | -    | -    | -    | -    |
|                             | 95                | 5                 | <F>               | -    | 0.5415 | -    | -    | -    | -    |
|                             | 100               | 0                 | <F>               | -    | 0.5409 | -    | -    | -    | -    |

Designation of phases: <B>-Solid solutions based on monoclinic modification of Sm$_2$O$_3$; <C>-Solid solutions based on cubic modification of Sm$_2$O$_3$; <F>-Solid solutions based on cubic modification with fluorite-type structure of CeO$_2$.

Table 2: Phase composition and lattice parameters of the phases in the CeO$_2$-Sm$_2$O$_3$ system, annealed at 1100 °C for 10813h in air (XRD data).

| Chemical Composition (mol %) | Phase Composition | Lattice Parameters of the Phases $\pm 0.0002$ (nm) |
|-----------------------------|-------------------|-----------------------------------------------|
|                             | <F>               | <C>               | <B>               | a    | a    | a    | b    | c    | β    |
| CeO$_2$                     | 0                 | 100               | <B>               | -    | -    | -    | 1.3925 | 0.3632 | 0.868 | 90.4 |
| Sm$_2$O$_3$                 | 1                 | 99                | <B> + <C>         | -    | 1.0918 | 1.3153 | 0.367 | 0.8666 | 91.7 |
|                             | 2                 | 98                | <B> + <C>         | -    | 1.092 | 1.4002 | 0.3653 | 0.8721 | 91.9 |
|                             | 3                 | 97                | <B> + <C>         | -    | 1.0918 | 1.6469 | 0.3679 | 0.8726 | 88.5 |
|                             | 4                 | 96                | <B> + <C>         | -    | 1.092 | 1.7067 | 0.3702 | 0.8719 | 91.6 |
|                             | 5                 | 95                | <B> + <C>         | -    | 1.0919 | 1.4041 | 0.3398 | 0.8718 | 96.9 |
|                             | 15                | 85                | <B> + <C>         | -    | 1.0925 | 1.6291 | 0.3667 | 0.8734 | 94.5 |
|                             | 20                | 80                | <B> + <C>         | -    | 1.0919 | 1.3113 | 0.3612 | 0.918 | 99.1 |
Table 3: Phase composition and lattice parameters of the phases in the CeO$_2$-Sm$_2$O$_3$ system, annealed at 600 °C for 33000h in air (XRD data).

| Chemical Composition (mol %) | Phase Composition | Lattice Parameters of the Phases $\pm 0.0002$ (nm) |
|-----------------------------|-------------------|-----------------------------------------------|
|                             |                   | $a$   | $b$   | $c$   | $\beta$ |
| CeO$_2$                    | Sm$_2$O$_3$       | $<F>$ | $<C>$ | $<B>$ |          |
| 0                          | 100               | -     | -     | 1.3925 | 0.3632 | 0.868  | 90.4  |
| 1                          | 99                | -     | -     | 1.0918 | 1.3153 | 0.367  | 0.8666 | 91.7  |
| 2                          | 98                | -     | -     | 1.0912 | 1.4002 | 0.3653 | 0.8721 | 91.9  |
| 3                          | 97                | -     | -     | 1.0916 | 1.6469 | 0.3679 | 0.8726 | 88.5  |
| 4                          | 96                | -     | -     | 1.0916 | 1.7067 | 0.3702 | 0.8719 | 91.6  |
| 5                          | 95                | -     | -     | 1.0916 | 1.5041 | 0.3398 | 0.8718 | 96.9  |
| 10                         | 90                | -     | -     | 1.0916 | 1.3514 | 0.366  | 0.5208 |
| 15                         | 85                | -     | -     | 1.0916 | 1.6291 | 0.3667 | 0.8734 | 94.5  |
| 20                         | 80                | -     | -     | 1.0916 | 1.3113 | 0.3612 | 0.918  | 99.1  |
| 25                         | 75                | -     | -     | 1.0916 | 1.0908 | -      | -      |
| 30                         | 70                | -     | -     | 1.0916 | 1.0908 | -      | -      |
| 35                         | 65                | -     | -     | 1.0916 | 1.0908 | -      | -      |
| 40                         | 60                | -     | -     | 1.0916 | 1.0908 | -      | -      |
| 45                         | 55                | -     | -     | 1.0916 | 1.0908 | -      | -      |
| 50                         | 50                | -     | -     | 1.0916 | 1.0908 | -      | -      |
| 55                         | 45                | -     | -     | 1.0916 | 1.0908 | -      | -      |
| 60                         | 40                | -     | -     | 1.0916 | 1.0908 | -      | -      |
| 65                         | 35                | -     | -     | 1.0916 | 1.0908 | -      | -      |
| 70                         | 30                | -     | -     | 1.0916 | 1.0908 | -      | -      |
| 75                         | 25                | -     | -     | 1.0916 | 1.0908 | -      | -      |
| 80                         | 20                | -     | -     | 1.0916 | 1.0908 | -      | -      |
| 85                         | 15                | -     | -     | 1.0916 | 1.0908 | -      | -      |
| 90                         | 10                | -     | -     | 1.0916 | 1.0908 | -      | -      |
| 95                         | 5                 | -     | -     | 1.0916 | 1.0908 | -      | -      |
| 100                        | 0                 | -     | -     | 1.0916 | 1.0908 | -      | -      |
Homogeneity region boundaries of F-CeO$_2$ based solid solutions correspond to the following compositions: 25-30 \% Sm$_2$O$_3$ at 1500 °C, 20-25 \% Sm$_2$O$_3$ at 1100 °C, and 10-15 \% Sm$_2$O$_3$ at 600 °C (Tables 1-3). The change in the lattice parameters in F-CeO$_2$ based solid solutions against the Sm$_2$O$_3$ concentration is shown in Figure 1. The results depicted in Figure 1 and 2 suggest that the solubility of Sm$_2$O$_3$ in F-modification of CeO$_2$ is about 15 mol \% for 600 °C and 20 mol \% for 1100 °C and 25 mol \% for 1500 °C. Lattice parameters increases from $a = 0.5409$nm for pure CeO$_2$ to $a = 0.5466$nm (1500 °C), 0.5456nm (1100 °C), and 0.5422nm (600 °C) for the limit solid solution compositions.

Dissolution of samaria in ceria during annealing in air proceeds by mutual diffusion and solid solution formation through different-valence substitution: Sm$^{3+}$ ions substitute for Ce$^{4+}$ ions in the F-type lattice sites. In order to preserve charge neutrality of the crystal, the difference in ion charge is compensated by the appearance of oxygen vacancies in sites of oxygen ions. There are however such solubility limit values which correspond to a critical concentration of vacancies, beyond of which the fluorite-type (Fm3m) lattice becomes unstable and transforms into another cubic lattice, namely IA$_c$ characteristic for solid solutions of the C-type on the basis of REE oxides. The solubility limit increases with temperature rising.

Homogeneity region boundaries of C-Sm$_2$O$_3$ based solid solutions correspond to the following compositions: 45-65 \% Sm$_2$O$_3$ at 1500 and 1100 °C, and 45-50 \% Sm$_2$O$_3$ at 600 °C (Tables 1-3). The parameter of the unit cell C-phase increases from $a = 1.0904$nm in the two-phase sample (F+C) containing 4mol \% Sm$_2$O$_3$ to $a = 1.0922$nm in the two-phase sample (B+C) containing 70mol \% Sm$_2$O$_3$ (at 1500 °C Table 1) and from $a = 1.0905$nm in the two-phase sample (F+C) containing 40mol \% Sm$_2$O$_3$ to $a = 1.0915$nm in the two-phase sample (B+C) containing 70mol \% Sm$_2$0$_3$ (at 1100 °C Table 2) and from $a = 1.0906$nm in the two-phase sample (F+C) containing 40mol \% Sm$_2$O$_3$ to $a = 1.0913$nm in the two-phase sample (B+C) containing 55mol \% Sm$_2$O$_3$ (at 600 °C Table 3).

The spread of the homogeneity field of the solid solution based on B-Sm$_2$O$_3$ at 600, 1100 °C remains negligible, less than 1 mol \% and 3 mol \% for 1500 °C. The substitution of ions Sm$^{3+}$ ($r = 0.100$nm) in the lattice of Sm$_2$O$_3$ by smaller ions Ce$^{4+}$ ($r = 0.090$nm) does not result in stabilization of the B-Sm$_2$O$_3$ neither at 600, nor at 1100 °C. Lattice parameters increases from $a = 1.3925$nm, $b = 0.3632$nm, $c = 0.8680$nm, $\beta = 90.4$° for pure Sm$_2$O$_3$ to $a = 1.3018$nm, $b = 0.3578$nm, $c = 0.9433$nm, $\beta = 88.5$° in the two-phase sample (B+C) containing 97mol \% Sm$_2$O$_3$ (1500 °C) and to $a = 1.3153$nm, $b = 0.3670$nm, $c = 0.8666$nm, $\beta = 91.7$° in the two-phase sample (B+C) containing 99mol \% Sm$_2$O$_3$ (1100 and 600 °C). XRD patterns acquired from in the CeO$_2$-Sm$_2$O$_3$ system at 1100 °C are presented in Figure 3a. As seen, at 1100 °C, the sample 1mol \% CeO$_2$,99mol \% Sm$_2$O$_3$ in addition to the basic B-phase, exhibits distinct peaks which are characteristic for the cubic C-phase.

The results obtained may be interpreted on the basis of literature data [19,14], which will permit one to forecast phase interaction and properties of solid solutions in other systems of the CeO$_2$-Ln$_2$O$_3$ series. The 25mol \% Eu$_2$O$_3$ doped CeO$_2$ preserves the initial F-type of the CeO$_2$ lattice (1500 °C). Thus, a decrease in the lanthanide ion radius makes the homogeneity region of F-CeO$_2$ based solid solutions narrower: from 49mol \% for La$^{3+}$ (0.104nm) [19,14] to 25mol \% for Sm$^{3+}$ (0.100nm) (this work) at 1500 °C and from 49mol \% for La$^{3+}$ (0.104nm) [19] to 20mol \% for Sm$^{3+}$ (0.100nm) (this work) at 1100 °C.

**Conclusion**

The phase equilibria in the CeO$_2$-Sm$_2$O$_3$ system at 600, 1100 and 1500 °C were studied in the whole concentration range. The subsection of the phase diagram has been developed. The solid solutions of monclinic (B) modification of Sm$_2$O$_3$ and cubic (C) modification of Sm$_2$O$_3$ with C-type structure of rare-earth oxides, as well as solid solution with cubic modification of CeO$_2$ with fluorite-type structure (F) were found that had limited solubility. The refined solubility of Sm$_2$O$_3$ in cubic F-ceria decreases from 25 to ~15mol \% with decreasing temperature at 1500 and 600 °C, respectively. The width of the homogeneity field of the solid solutions based on B-Sm$_2$O$_3$ is less than 1mol \% at 600-1100 °C and 3 mol \% for 1500 °C. In this temperature range, ordering of intermediate phases was not confirmed.

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