



The interaction between cerium dioxide, lanthanum and europium oxides at 1500 °C

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Abstract

Materials based on CeO_2 - La_2O_3 - Eu_2O_3 and La_2O_3 - Eu_2O_3 systems are promising candidates for a wide range of applications, but the phase relationship has not been studied systematically previously. The phase relations in the CeO_2 - La_2O_3 - Eu_2O_3 ternary system at 1500 °C and binary La_2O_3 - Eu_2O_3 system at 1600–1500 °C were studied in air by X-ray diffraction (XRD) investigation in the overall concentration range. The isothermal section of the phase diagram for the CeO_2 - La_2O_3 - Eu_2O_3 system has been constructed. It was established that in the ternary CeO_2 - La_2O_3 - Eu_2O_3 system there exist fields of solid solutions based on hexagonal (A) modification of La_2O_3 , cubic modification of CeO_2 with fluorite-type structure (F), cubic (C) and monoclinic (B) modification Eu_2O_3 . It was established that in the binary La_2O_3 - Eu_2O_3 system there exist fields of solid solutions based on hexagonal (A) modification of La_2O_3 and monoclinic (B) modification Eu_2O_3 . The phases were separated by two-phase fields (A+B). The refined lattice parameters of the unit cells for solid solutions and microstructures of the definite field of compositions for the systems were determined.

Keywords: CeO_2 , phase diagrams, X-ray diffraction (XRD), solid solutions

I. Introduction

Stabilization of the particular phase of a solid solution possessing optimal thermal, mechanical, or electrical properties is a challenge relevant to a wide variety of materials ranging from ion conductors to ferroelectrics [1]. The CeO_2 - Ln_2O_3 solid solutions are the subject of numerous structural studies motivated by the fact that Ln-doped ceria is one of the most important oxygen ion conductors for solid oxide fuel cells (SOFC). Structural modification of ceria-based solutions by co-doping is one possible way to increase the ionic oxide conductivity of ceria-based electrolytes at an intermediate temperature range (500–700 °C) [1–10]. Materials co-stabilized with Gd_2O_3 or Eu_2O_3 and other trivalent cations such as La^{3+} , Nd^{3+} , Y^{3+} , Bi^{3+} or divalent

cations Ca^{2+} , Mg^{2+} , Sr^{2+} , depending on chemical composition, have generally improved ionic conductivities, although in some cases a deterioration in ionic conductivity or increased electronic conductivity have been observed [6]. The incorporation of co-doped ceria electrolytes into IT-SOFC produced higher power and current densities from this cell compared with the same SOFC utilised with an oxide membrane single-doped ceria $Ce_{1-x}M_xO_{1.9}$ ($M = Gd, Sm, Y$ and $0.1 < x < 0.3$) [6]. The right choice of an optimal electrolyte depends on the 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 turn, requires good knowledge of the 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

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on the phase transformation, structure, and stability are also of keen scientific interest [10].

The phase relations at the boundary of binary CeO_2 - Ln_2O_3 , La_2O_3 - Ln_2O_3 systems have been studied [5,6,10–27]. Phase equilibrium in the binary CeO_2 - Ln_2O_3 systems studied in the past were characterized by the formation of limited solid solutions based on different polymorphs of initial components [5,6,10–27]. The phase equilibria in the CeO_2 - Eu_2O_3 system at 600, 1100 and 1500 °C were studied in the whole concentration range [17–20]. The X-ray analysis showed that three solid solutions of substitution type exist in the CeO_2 - Eu_2O_3 system in the given temperature interval. Two of them have cubic symmetry (fluorite F- CeO_2 type and C- Eu_2O_3 type) and the third one has monoclinic symmetry (B- Eu_2O_3 type). The phases were separated by two-phase fields (C + F; B + C). The number of phase fields decreases with the temperature decrease to 600 °C, because the monoclinic B- Eu_2O_3 exists only above 1000 °C [20]. The boundaries of the homogeneity fields at 1500 °C for F- CeO_2 , C- Eu_2O_3 and B- Eu_2O_3 solid solutions were determined from the samples containing 20–25 mol%, 80–85 mol% and 95–99 mol% of Eu_2O_3 , respectively. Similarly, to determine boundaries of the homogeneity fields for F- CeO_2 and C- Eu_2O_3 solid solutions, samples containing 20–25 mol% and 90–99 mol% of Eu_2O_3 , respectively, were used for heat treatment at 1100 °C. By reducing the temperature to 600 °C, the homogeneity field of solid solutions based on the F- CeO_2 and C- Eu_2O_3 were significantly narrowed. The boundaries of this field were defined by the samples containing 10–15 mol% and 97–98 mol% of Eu_2O_3 , respectively [20].

The solubility of CeO_2 in hexagonal A-lanthanum oxide attain 25 mol% at 1500 °C. The A- La_2O_3 solid solutions of CeO_2 - La_2O_3 remain stable at 1500 °C. In contrary, La_2O_3 on the surface is exposed to water-containing environment and forms lanthanum hydroxide instead of hexagonal phase of La_2O_3 for the samples containing from 100 to 70 mol% La_2O_3 . Increasing of ceria content coincides with the appearance of A-modification of La_2O_3 , as determined by X-ray diffraction (XRD) patterns [23,24].

Albeit its great prospects for technological applications [1–5], the phase relationship of the ternary CeO_2 - La_2O_3 - Eu_2O_3 and binary La_2O_3 - Eu_2O_3 systems has not been investigated. In this paper, we present the phase equilibrium in the CeO_2 - La_2O_3 - Eu_2O_3 ternary and La_2O_3 - Eu_2O_3 binary systems in the whole range of compositions at temperature 1500 °C.

II. Experimental

The starting materials were La_2O_3 of LaO-1 grade, Eu_2O_3 (content of the main components reaches 99.99%) and cerium nitrate $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ of grade “ch” (above 98%). Before being weighed, the oxides were dried in a muffle chamber at 1200 °C (2 h). The

samples were prepared with a concentration step of 1–5 mol%. Weighed oxide portions were dissolved in HNO_3 (1:1). $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was added into a mixture after the oxides were completely dissolved. A homogeneous solution of nitrates was evaporated to remove nitric acid and calcined at 800 °C for 2 h. The powders were subjected to single-action pressing in a steel die without a binder at 10–30 MPa to make pellets 5 mm in diameter and 4 mm in height. Annealing at 1500 °C was conducted via two stages: first in a furnace with H23U5T (federal) heaters at 1250 °C for 600 h, then in a furnace with molybdenum disilicide heaters at 1500 °C for 80 h in air. The two-step annealing allows removing residuals of nitrogen oxides from the samples. At lower temperatures, ≤ 1250 °C, phase equilibriums (which include processes of exsolution and ordering) were reached rather slowly because of low velocity of diffusion processes in the cation sublattice, which requires long-term annealing of samples [28]. The synthesis completeness was regularly controlled. Then the samples were pressed and annealed again. Upon annealing for 80 h (1500 °C) no change in the phase composition of the samples was observed. Cooling was conducted inside the furnace. The chemical analysis of the powders was done prior to heat treatment and after it selectively. No changes of the chemical composition were revealed. The prepared samples with different compositions have following notation C $_x$ -L $_y$ -E $_z$, where x , y and z denote mol% of CeO_2 , La_2O_3 and Eu_2O_3 , respectively.

XRD analysis of the samples was performed by powder procedure on a DRON-3 apparatus at ambient temperature under $\text{CuK}\alpha$ radiation. Scanning step was 0.05–0.1°, exposition 4 s and 2θ angle interval 10 to 90°. Lattice parameters were calculated by the least square method using the LATTIC program with an error of not lower than 0.0001 nm for the cubic phase. Phase com-

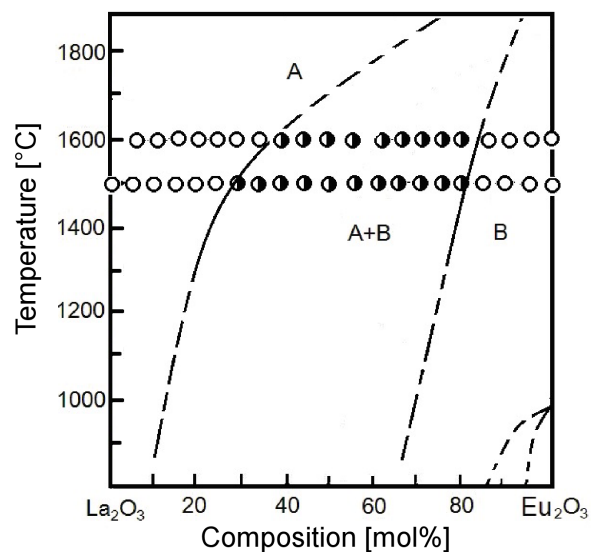


Figure 1. Phase equilibria in the La_2O_3 - Eu_2O_3 system at 1600–1500 °C (○ - single-phase samples, ● - two-phase samples)

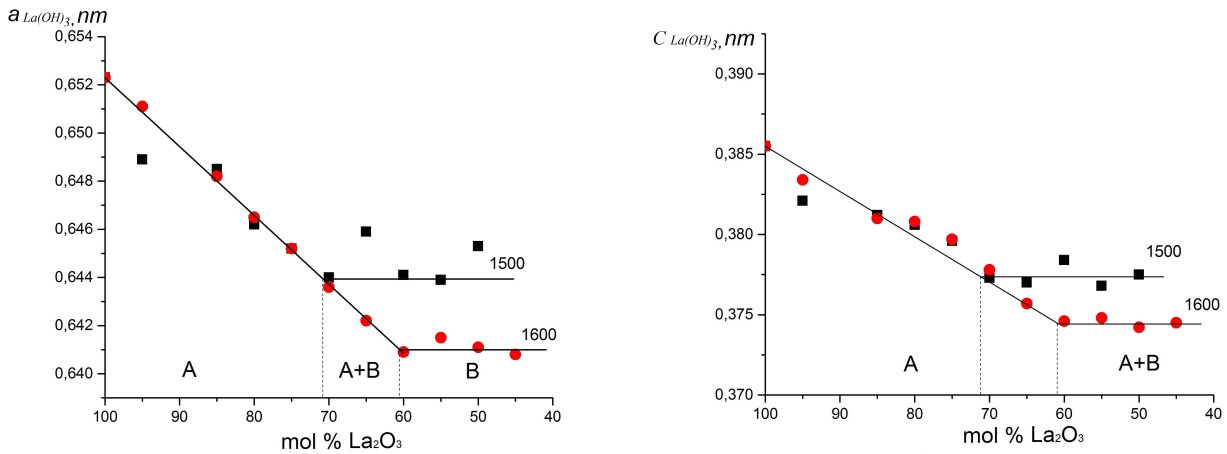


Figure 2. Concentration dependences of the lattice parameters a (a) and c (b) of $\text{La}(\text{OH})_3$ based solid solutions in the La_2O_3 -system upon annealing at 1500 and 1600 °C

position was identified using the base of JSPDS (International Center for Diffraction Data 1999).

III. Results and discussion

3.1. Phase relation in La_2O_3 - Eu_2O_3 system

The study of solid phase interaction of La_2O_3 (hexagonal modification of rare-earth oxide, type A, space group $P63/m$) with Eu_2O_3 (monoclinic modification of rare-earth oxide, type B, space group $C2/m$) in the temperature range of 1600–1500 °C revealed that in the La_2O_3 - Eu_2O_3 system two types of solid solutions are formed which have a hexagonal A- La_2O_3 and monoclinic B- Eu_2O_3 structure. The phases were separated by two-phase fields (A+B) as shown in Fig. 1. It is important to underline that in accordance with the XRD phase analysis, in the samples containing from 20 to 100 mol% of La_2O_3 , instead of the hexagonal modification of A- La_2O_3 , the hexagonal lanthanum hydroxide A- $\text{La}(\text{OH})_3$ was observed because the samples absorb water from wet air and transform into hydroxide after annealing and cooling. The input chemical and phase compositions of the samples, annealed at 1600 and 1500 °C, and the lat-

tice parameters of the corresponding equilibrium phases at given temperatures are presented in the Supporting Information (Tables 1 and 2). The change in the lattice parameters in A- $\text{La}(\text{OH})_3$ and B- Eu_2O_3 based solid solutions against the Eu_2O_3 concentration is shown in Figs. 2 and 3.

The solubility of Eu_2O_3 in A- La_2O_3 is 28 mol% at 1500 °C and 38 mol% at 1600 °C (Fig. 1). Data given in Fig. 2 reveal that the lattice parameters decrease from $a = 0.6523$ nm, $c = 0.3855$ nm for the pure $\text{La}(\text{OH})_3$ to $a = 0.6440$ nm, $c = 0.3773$ nm for the two-phase (A+B) sample L70-E30 at 1500 °C and to $a = 0.6409$ nm, $c = 0.3746$ nm for the two-phase (A+B) sample L60-E40 at 1600 °C.

The solubility of La_2O_3 in the monoclinic B- Eu_2O_3 modification is ~19 mol% at 1500 °C and 16 mol% at 1600 °C (Fig. 1). The lattice parameters (Fig. 3) of B- Eu_2O_3 solid solution decrease from $a = 1.4882$ nm, $c = 0.3562$ nm, $b = 0.8960$ nm, $\beta = 90.26$ for the pure Eu_2O_3 to $a = 1.3086$ nm, $c = 0.3646$ nm, $b = 0.8875$ nm, $\beta = 96.45$ for the L20E80 sample at 1500 °C and to $a = 1.3505$ nm, $c = 0.3646$ nm, $b = 0.8885$ nm, $\beta = 96.45$ for the L20E80 sample at 1600 °C.

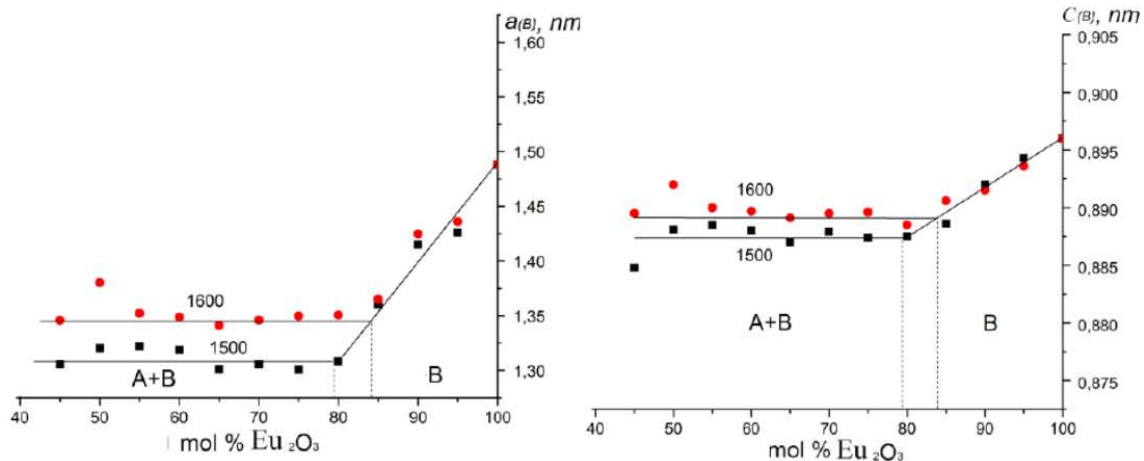


Figure 3. Concentration dependences of the lattice parameters a (a) and c (b) of B- Eu_2O_3 based solid solutions in the La_2O_3 - Eu_2O_3 system upon annealing at 1500 and 1600 °C

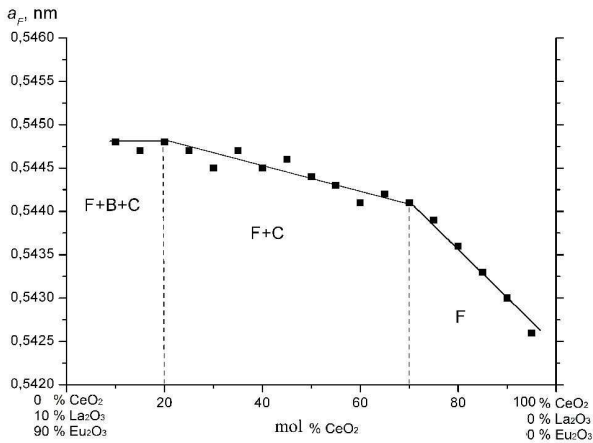


Figure 6. Concentration dependence of lattice parameters for solid solutions on the basis of F-CeO₂ on the section CeO₂ - (10 mol% La₂O₃ - 90 mol% Eu₂O₃) in the CeO₂-La₂O₃-Eu₂O₃ system after annealing of samples at 1500 °C

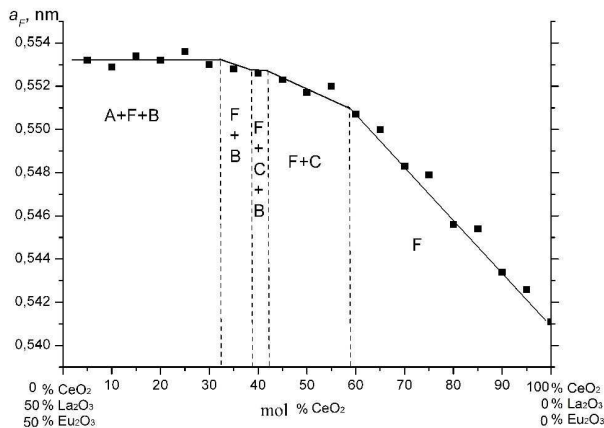


Figure 7. Concentration dependence of lattice parameters for solid solutions on the basis of F-CeO₂ on the section CeO₂ - (50 mol% La₂O₃ - 50 mol% Eu₂O₃) in the CeO₂-La₂O₃-Eu₂O₃ system after annealing of samples at 1500 °C

parameters and comparison of the identified phases determined by X-ray and petrography techniques are summarized in the Supporting Information (Table 3). The concentration dependences of lattice parameters for F- and C-phases for the binary subsection of CeO₂-La₂O₃-Eu₂O₃ system are presented in Figs. 6-11. The lattice parameters shown in Figs. 6-11 were used to determine the boundaries of the phase fields and the phase compositions.

F-solid solution

The cubic ceria-based solid solution has a fluorite-type structure and homogeneity field shows the maximum extension. The boundary of the homogeneity field of F-phase is curved from the center of triangle towards the CeO₂ corner and passes through appropriate points in the binary CeO₂-Eu₂O₃ (80 mol% CeO₂) and CeO₂-La₂O₃ (51 mol% CeO₂) systems (Fig. 4). The ex-

tent of the F-phase (Fig. 4) is defined by the single-phase compositions (C60-L20-E20 and C70-L3-E27) and two-phase F+C composition (C65-L3.5-E31.5 and C55-L22.5-Eu 22.5).

The lattice parameters also vary from $a = 0.5409$ nm in the pure CeO₂ to $a = 0.5442$ nm in the two-phase F+C sample C65-L3.5-E31.5 and to $a = 0.5448$ nm in the three-phase F+B+C sample C20-L8-E72 along the section CeO₂ - (10 mol% La₂O₃ - 90 mol% Eu₂O₃) (Fig. 6). Along the section CeO₂ - (50 mol% La₂O₃ - 50 mol% Eu₂O₃), the lattice parameters vary from $a = 0.5409$ nm in the pure CeO₂ to $a = 0.5520$ nm in the two-phase F+C sample C55-L22.5-E22.5 and to $a = 0.5526$ nm in the three-phase F+B+C sample C40-L30-E30 and to $a = 0.5528$ nm in the two-phase F+B sample C35-L32.5-E32.5 and to $a = 0.5530$ nm in three-phase A+F+B sample C30-L35-E35 (Fig. 7). Along the section Eu₂O₃ - (50 mol% CeO₂ - 50 mol%

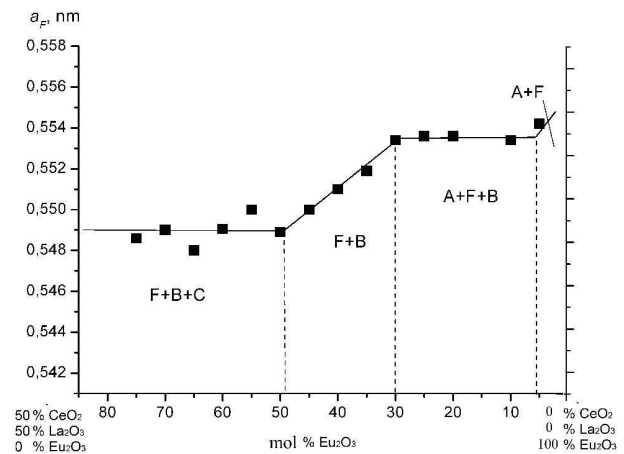


Figure 8. Concentration dependence of lattice parameters for solid solutions on the basis of F-CeO₂ on the section Eu₂O₃ - (50 mol% La₂O₃ - 50 mol% CeO₂) in the CeO₂-La₂O₃-Eu₂O₃ system after annealing of samples at 1500 °C

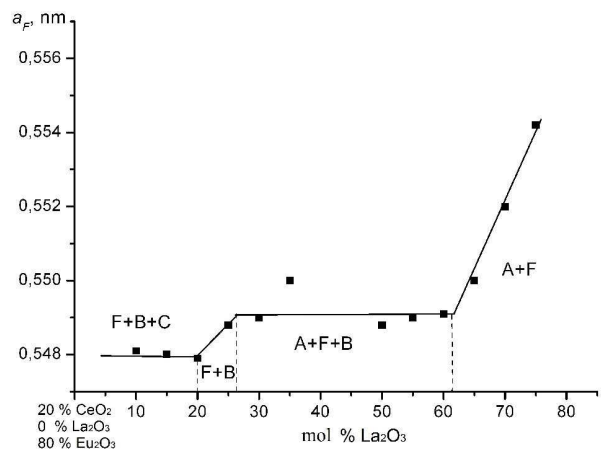


Figure 9. Concentration dependence of lattice parameters for solid solutions on the basis of F-CeO₂ along isoconcentrate 20 mol% CeO₂ in the CeO₂-La₂O₃-Eu₂O₃ system after annealing of samples at 1500 °C

La₂O₃) the lattice parameters of F-CeO₂ vary from $a = 0.5542$ nm in the two-phase F+A sample C47.5-L47.5-E5 to $a = 0.5534$ nm in the three-phase A+F+B sample C45-L45-E10 and to $a = 0.5519$ nm in the two-phase F+B sample C32.5-L32.5-E35 and to $a = 0.5489$ nm in the three-phase F+B+C sample C25-L25-E50 (Fig. 8). Finally, along the isoconcentrate 20 mol% CeO₂ line changes of the lattice parameter of F-CeO₂ faze are shown in Fig. 9.

Dissolution of Ln³⁺ in ceria during annealing in air proceeds by mutual diffusion and solid solution formation through different-valence substitution: Ln³⁺ ions substitute for Ce⁴⁺ 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 which the fluorite-type (*Fm3m*) lattice becomes unstable and transforms into another cubic lattice, namely *Ia3*, characteristic for solid solutions of the C-type on the basis of REE oxides.

B-solid solution

In the europium-rich corner, the solid solutions based on the monoclinic modification of Eu₂O₃ are formed. The phase field B-Eu₂O₃ is narrow and elongated (0–19 mol% CeO₂) along the La₂O₃-Eu₂O₃ side of the binary system (Fig. 4). The solubility of CeO₂ in the B-Eu₂O₃ is low and amounts to ~0.5 mol%, as evidenced by XRD analysis results.

The lattice parameters for B-phase vary from $a = 0.1412$ nm, $b = 0.3609$ nm, $c = 0.8819$ nm, $\beta = 99.98$ in the two-phase B+C sample C0.5-L0.5-E99 to $a = 0.1422$ nm, $b = 0.3631$ nm, $c = 0.8879$ nm, $\beta = 100.47$ in the three-phase F+B+C sample C10-L10-E80 and to $a = 0.1422$ nm, $b = 0.3657$ nm, $c = 0.8950$ nm, $\beta = 100.16$ in the two-phase F+B sample along the section Eu₂O₃ - (50 mol% La₂O₃ - 50 mol% CeO₂) (data are presented in the Supporting Information Table 3). The solid solution based on B-Eu₂O₃ is in equilibrium with all phases existing in the ternary CeO₂-La₂O₃-Eu₂O₃ system at 1500 °C.

The difference between B and F solid solutions is in the charge compensation mechanisms. In the fluorite-type solid solutions, the oxygen vacancies compensate the charge difference between Ce⁴⁺ and Ln³⁺. The fluorite-type lattice allows high concentration of oxygen vacancies and, therefore, the solubility of europia and lanthanum in ceria is high. In opposite, the charge compensation in the ceria substituted Ln³⁺ is defined by the concentration of electrons or oxygen interstitial atoms, which is smaller as compared with concentration of oxygen vacancies in the fluorite-type solid solution.

C-solid solution

The phase field C-Eu₂O₃ is narrow and elongated (14–26 mol% CeO₂) along the CeO₂-Eu₂O₃ side of the binary system (Fig. 4). The solubility of La₂O₃ in the

C-Eu₂O₃ is up to 6 mol%, along the isoconcentrate 20 mol% CeO₂ line (Fig. 4), as evidenced by XRD analysis results.

The lattice parameters for C-phase vary from $a = 1.0864$ nm in the single-phase sample C20-L1-E79 to $a = 1.0907$ nm in three-phase C+F+B sample C20-L10-E70 along the isoconcentrate 20 mol% CeO₂ line (data are presented in the Supporting Information Table 3). Along the section CeO₂ - (10 mol% La₂O₃ - 90 mol% Eu₂O₃) the lattice parameters for C-phase vary from $a = 1.0899$ nm in the two-phase C+B sample C2-L9.8-E88.2 to $a = 1.0892$ nm in the three-phase F+B+C sample C10-L9-E81 and to $a = 1.0890$ nm in the two-phase F+C sample C25-L7.5-E67.5 (Fig. 10). Along the section Eu₂O₃ - (50 mol% CeO₂ - 50 mol% La₂O₃) the lattice parameters for C-phase vary from $a = 1.0835$ nm in the two-phase B+C sample C0.5-L0.5-E99 to $a =$

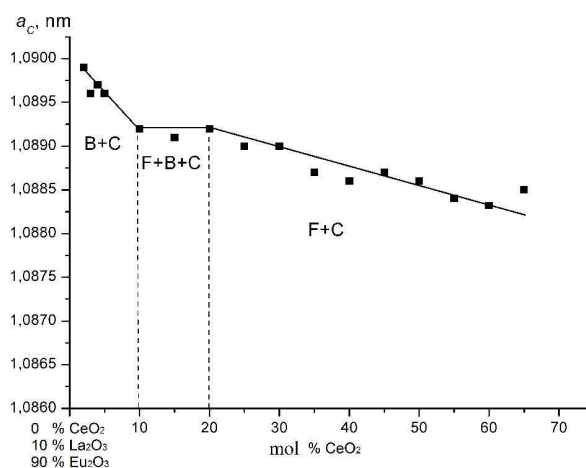


Figure 10. Concentration dependence of lattice parameters for solid solutions on the basis of C-Eu₂O₃ on the section CeO₂ - (10 mol% La₂O₃ - 90 mol% Eu₂O₃) in the CeO₂-La₂O₃-Eu₂O₃ system after annealing of samples at 1500 °C

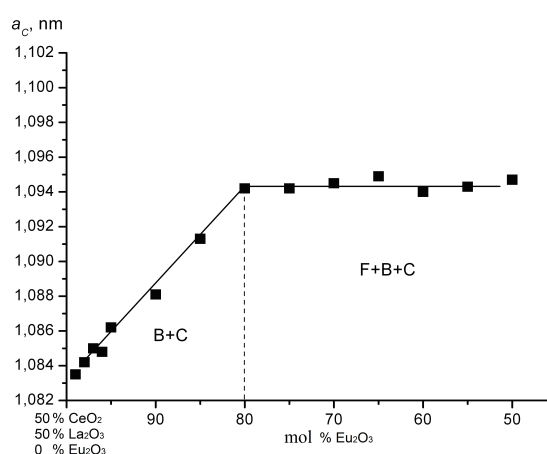


Figure 11. Concentration dependence of lattice parameters for solid solutions on the basis of C-Eu₂O₃ on the section Eu₂O₃ - (50 mol% La₂O₃ - 50 mol% CeO₂) in the CeO₂-La₂O₃-Eu₂O₃ system after annealing of samples at 1500 °C

1.0942 nm in the three-phase F+B+C sample C10-L10-E80 (Fig. 11).

A-solid solution

The homogeneity field of solid solution based on A-La₂O₃ extends to 25 mol% CeO₂ and 28 mol% Eu₂O₃ in the corresponding binary systems (Fig. 4). It should be noted that the samples with higher lanthanum oxide content after annealing and cooling rapidly absorb water in humid air and become hydrated. Hence, according to XRD, the hexagonal A-La(OH)₃ modification is formed instead of the hexagonal A-La₂O₃ phase.

IV. Conclusions

The phase equilibria in the La₂O₃-Eu₂O₃ system were studied at 1500 and 1600 °C in the whole concentration range using XRD. The system was characterized by formation of solid solutions with a hexagonal (A-La₂O₃) and monoclinic (B-Eu₂O₃) structures separated with a wide heterogeneous region A+B. Homogeneous boundary regions of A-La₂O₃ based solid solutions correspond to the following compositions: 100–72 mol% La₂O₃ at 1500 °C, 100–62 mol% La₂O₃ at 1600 °C. As temperature reduces from 1600 to 1500 °C, the homogeneity regions of solid solutions based on the monoclinic modification B-Eu₂O₃ narrow from 84 to 81 mol% La₂O₃. In accordance with Vegard's law the lattice parameter linearly decreases. The 1500 °C phase equilibria in the ternary CeO₂-La₂O₃-Eu₂O₃ system were studied for the first time over the entire triangle composition, and the 1500 °C section of the CeO₂-La₂O₃-Eu₂O₃ phase diagram was constructed. The solid solutions of limited solubility based on all components in their different polymorphic modifications were found and characterized. The ceria-based fluorite solid solutions are represented by the largest homogeneity field originating from the sizes of F-fields in the two boundary binary systems CeO₂-La₂O₃ and CeO₂-Eu₂O₃. It was revealed that in the CeO₂-La₂O₃-Eu₂O₃ system the phases of cubic symmetry predominate such as: F - *Fm3m*, C - *Ia3*. The isothermal section of the CeO₂-La₂O₃-Eu₂O₃ system at 1500 °C contains two three-phase regions (A+F+B, F+B+C) and five two-phase regions (F+A, A+B, B+F, F+C, C+B).

§ Supporting Information can be downloaded using following link: <https://bit.ly/3diC9r7>

References

1. B. Wang, B. Zhu, S. Yun, W. Zhang, C. Xia, M. Afza, Y. Cai, Y. Liu, Y. Wang, H. Wang, "Fast ionic conduction in semiconductor CeO_{2-δ} electrolyte fuel cells", *NPG Asia Mater.*, **51** (2019) 1–12.
2. C.X. Hua, "Lithium storage mechanism and catalytic behavior of CeO₂", *Electrochem. Commun.*, **25** (2012) 66–69.
3. T. Hong, Y.X. Zhang, K. Brinkman, "Enhanced oxygen electrocatalysis in heterostructured ceria electrolytes for intermediate-temperature solid oxide fuel cells", *ACS Omega*, **3** (2018) 13559–13566.
4. L. Ping, Ch. Xiaoyin, L. Yongdan, S.W. Johannes, "A review on oxygen storage capacity of CeO₂-based materials: Influence factors, measurement techniques, and applications in reactions related to catalytic automotive emissions control", *Catal. Today*, **327** (2018) 90–115.
5. E.R. Andrievskaya, O.A. Kornienko, O.I. Bykov, A.V. Sameljuk, Z.D. Bohatyriova, "Interaction of ceria and ytterbia in air within temperature range 1500–600 °C", *J. Eur. Ceram. Soc.*, **39** (2019) 2930–2935.
6. O.A. Kornienko, A.V. Sameljuk, O.I. Bykov, Yu.V. Yurchenko, A.K. Barshchevskaya, "Phase relation studies in the CeO₂-La₂O₃-Er₂O₃ system at 1500 °C", *J. Eur. Ceram. Soc.*, **40** (2020) 4184–4190.
7. J. Gulicovski, S. Nenadović, L. Kljajević, M. Mirković, M. Nišavić, M. Kragović, M. Stojmenović, "Geopolymer/CeO₂ as Solid Electrolyte for IT-SOFC", *Polymers*, **248** (2020) 2–19.
8. S.I. Ahmad, "Nanostructured cerium oxide (ceria): electrolyte for IT-SOFC", *Int. J. Nano Res.*, **1** (2018) 11–13.
9. S. Li, X. Lu, S. Shi, L. Chen, Z. Wang, Y. Zhao, "Europium-doped ceria nanowires as anode for solid oxide fuel cells", *Frontiers Chem.*, **8** (2020) 1–10.
10. O. Kornienko, O. Bykov, A. Sameliuk, Y. Yurchenko, "Phase relation studies in the CeO₂-La₂O₃-Eu₂O₃ system at 1250 °C", *Ukrainian Chem. J.*, **86**, (2020) 37–45.
11. B.P. Mandal, V. Grover, A.K. Tyagi, "Phase relations, lattice thermal expansions in Ce_{1-x}Sm_xO_{2-x/2} systems and stabilization of cubic RE₂O₃ (RE: Eu, Sm)", *Mater. Sci. Eng. A*, **430** (2006) 120–124.
12. V. Grover, A. Banerji, P. Sengupta, A.K. Tyagi, "Raman, XRD and microscopic investigations on CeO₂-Lu₂O₃ and CeO₂-Sc₂O₃ systems: A sub-solidus phase evolution study", *J. Solid State Chem.*, **181** (2008) 1930–1935.
13. O.R. Andrievskaya, O.A. Kornienko, O.I. Bykov, A.V. Sameliuk, Z.D. Bohatyriova, "Interaction of ceria and erbia in air within temperature range 1500–600 °C", *J. Eur. Ceram. Soc.*, **40** (2020) 3098–3103.
14. M. Stopyra, I. Saenko, M. Ilatovskaia, G. Savinykh, O. Fabrichnaya, "Phase relations in the ZrO₂-La₂O₃-Gd₂O₃ system: experimental studies and phase modeling", *J. Am. Ceram. Soc.*, **102** (2019) 7628–7644.
15. E.R. Andrievskaya, O.A. Kornienko, A.I. Bykov, A.V. Sameljuk, "Phase relation studies in the ZrO₂-La₂O₃-Gd₂O₃ system at 1600 °C", *Pow. Metall. Met. Ceram.*, **58** (2020) 714–724.
16. M. Ilatovskaia, S. Sun, I. Saenko, G. Savinykh, O. Fabrichnaya, "Experimental investigation of phase relations in the ZrO₂-La₂O₃-Yb₂O₃ system", *J. Phase Equilib. Diffus.*, **41** (2020) 311–328.
17. J.P. Traverse, *Contribution au developpement de methodes d' experimentation a temperature elevee: application a l' etude du polymorphisme des sesquioxides de terres rares et des changements de phases dans les systems zircone-chaux et zircone-oxyde de strontium*, Thèse L'Université Scientifique et Medicale de Grenoble, Grenoble, 1971.
18. H. Yamamura, H. Nishino, K. Kakinuma, "AC conductivity for Eu₂Zr₂O₇ and La₂Ce₂O₇ with pyrochlore-type composition", *J. Ceram. Soc. Jpn.*, **111** (2003) 907–911.
19. S.A. Toropov, *Phase Diagrams of the Refractory Oxide Systems, Binary Systems*, Chapter 3, Leningrad, Nauka, 1987.

20. B.A. Kumar, V. Sankaranarayanan, “Ionic transport properties in nanocrystalline $Ce_{0.8}A_{0.2}O_{2-\delta}$ (with A = Eu, Gd, Dy, and Ho) materials”, *Nanoscale Res. Lett.*, **5** (2010) 637–643.
21. N.M. Masaki, A. Nakamura, F. Furuuchi, Y. Hinatsu, “ ^{151}Eu -Mössbauer spectroscopic and X-ray diffraction study of the $\text{Eu}_2(\text{Ce}_{1-x}\text{Zr}_x)_2\text{O}_7$ and $\text{LnEuZr}_2\text{O}_7$ (Ln = lanthanide) systems”, *J. Phys. Chem. Solids*, **66** (2005) 312–317.
22. E.R. Andrievska, O.A. Kornienko, A.V. Sameliuk, A. Sair, “Phase relation studies in the CeO_2 - Eu_2O_3 system at 1500 to 600 °C in air”, *J. Eur. Ceram. Soc.*, **40** (2020) 751–758.
23. E.R. Andrievskaya, O.A. Kornienko, A.V. Sameljuk, A. Sayir, “Phase relation studies in the CeO_2 - La_2O_3 system at 1100–1500 °C”, *J. Eur. Ceram. Soc.*, **31** (2011) 1277–1283.
24. E.R. Andrievskaya, O.A. Kornienko, A. Sayir, O.O. Vasylyuk, S. Yoshio, “Phase relation studies in the ZrO_2 - CeO_2 - La_2O_3 system at 1500 °C”, *J. Am. Ceram. Soc.*, **94** (2011) 1911–1919.
25. B.C. Morris, W.R. Flavell, W.C. Mackrodt, M.A. Morris, “Lattice parameter changes in the mixed oxide system $\text{La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ - A combined experimental and theoretical study”, *J. Mater. Chem.*, **3** [10] (1993) 1007–1013.
26. F. Sibieude, G. Schiffmacher, P. Caro, “Étude au microscope électronique de structures modulées dans les régions système La_2O_3 - CeO_2 riches en La_2O_3 ”, *J. Solid State Chem.*, **23** (1968) 361–367.
27. N. Minkova, S. Aslanian, “Isomorphic substitutions in the CeO_2 - La_2O_3 system at 850 °C”, *Cryst. Res. Technol.*, **24** (1984) 351–354.
28. E.R. Andrievskaya, *Phase Equilibria in the Systems of Hafnia, Yttria with Rare-Earth Oxides*, Scientific book Project, Kiev, Naukova Dumka, 2010, 470 p.