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Sub-solidus phase equilibria in CeO_2–SrO system

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Abstract

In this communication, we report on the synthesis and characterization of a series of compounds with the general composition $Ce_{1-x}Sr_xO_{2-x}$ ($0.0 \leq x \leq 1.0$), to establish a detailed phase relation in the CeO_2–SrO system. The X-ray diffraction (XRD) pattern of the each product was refined to determine the solid solubility and the homogeneity range. The solid solubility limit of SrO in CeO_2 lattice, under the slow cooled conditions, is represented as $Ce_{0.91}Sr_{0.09}O_{1.91}$ (i.e. 9 mol% of SrO). A careful delineation of the phase boundary revealed that the stoichiometric $SrCeO_3$, in fact, contains a little amount of CeO_2 also. The mono-phasic compound could be obtained at the nominal composition $Sr_{0.55}Ce_{0.45}O_{1.45}$. The nominal composition Sr_2CeO_4, under the heat treatment used in the present investigation, was a bi-phasic mixture of $SrCeO_3$ and SrO. No new ordered phases were obtained in this system.

Keywords: Oxides; X-ray diffraction; Phase equilibria

1. Introduction

Doped ceria is an important material in view of its potential applications as solid electrolyte for its use in oxygen concentration cells and in the solid oxide fuel cells. The high ionic conductivity, coupled with the low activation energy for ionic conduction, makes the doped CeO_2 an attractive material for use at temperatures below 800 °C [1]. The doped ceria is also a candidate material for applications in controlling the air-to-fuel ratio in automobile exhaust [2]. A number of reports appeared in literature during the last few decades on alkaline- and rare-earth oxide doping in CeO_2, e.g. MgO [3], CaO and SrO [4], Sc_2O_3 [5], Y_2O_3, Gd_2O_3, La_2O_3, Nd_2O_3, Yb_2O_3, etc. [6], La_2O_3 [7] and Eu_2O_3 [8]. In these investigations, the solubility of the guest ions in ceria has been reported at about 1400–1600 °C and, e.g. the solubility of MgO, CaO, SrO in CeO_2 was found to be ~2, 15 and 9 mol%, respectively at 1600 °C. Sorokina et al. [9] used X-ray analysis and electrochemical methods to determine the solubility of SrO in CeO_2 at 1200–1400 K to be 8 mol%. However, most of these reports are confined to only a few compositions in the CeO_2 rich region of CeO_2–SrO system. Also, there are no reports of the solubility of CeO_2 in alkaline- or rare-earth oxides.

In the recent time, the research on various aspects of doped ceria systems suddenly witnessed a tremendous upsurge [10–12]. An emphasis is also laid on preparing doped ceria by soft chemical routes [13]. The CeO_2–SrO in an important system for a number of other reasons also, e.g. apart from solid solutions, this system exhibits the presence of a ternary compound $SrCeO_3$, which is a high temperature protonic conductor [14]. The $SrCeO_3$ is reported to crystallize on an orthorhombic space group *Pbnm* [15] whereas the yttrium doped $SrCeO_3$ was shown to crystallize in an orthorhombic space group *Pnma* [16], which is a

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different setting of the earlier space group. Another ternary compound in this system, i.e. Sr_2CeO_4, has been shown to act as an efficient blue phosphor, after an appropriate doping of Eu^{3+} [17]. CeO_2 is a very important material for yet another fascinating reason. Since CeO_2 and PuO_2 have quite a similar physico-chemical properties, viz. ionic size in octahedral and cubic coordinations, melting points, standard enthalpies of formation and specific heats, etc. the plutonium chemistry can be well simulated using CeO_2 in place of highly active PuO_2 [18,19]. Recently, we used CeO_2 as a surrogate material to simulate thermal expansion behavior of $Th_{1-x}Pu_xO_2$ in the complete homogeneity range [20]. In this manuscript, the detailed phase relation in CeO_2–SrO system under slow cooled conditions will be discussed. Contrary to most of the available reports, where mainly the cubic solid solution region is investigated, the entire composition range in this system was covered in the present studies. The Sr^{2+} has been chosen as a guest ion because it is one of the major fission products [21] in the nuclear fuels and it is desired to know its chemical state as the burn-up of a the nuclear fuel proceeds.

2. Experimental

$SrCO_3$ (AR grade) and CeO_2 (99.9%, obtained from Indian rare-earths) were first dried by heating at 700 and 900 °C, respectively for overnight. Appropriate mixtures to give the nominal composition $Ce_{1-x}Sr_xO_{2-x}$ ($0.0 \leq x \leq 1.0$) were prepared by an intimate mixing of the starting materials and pressed into 8 mm pellets. A preheat-treatment at 900 °C for 24 h was given to each pellet. In order to ensure completion of the reaction, after the preheat-treatment, each pellet was ground and once again mixed thoroughly, pelletized and heated at 1400 °C for 36 h in static air, followed by slow cooling to the room temperature at the rate of 1 °C/min. The X-ray diffraction (XRD) patterns were recorded on a Philips X-ray diffractometer (Model PW 1710) with Ni-filtered Cu Kα radiation using silicon as an external standard. The XRD patterns were well analyzed by comparing with the reported ones, which confirmed the phase purity of the products. In order to determine the solubility limits, the lattice parameters were refined by a least squares method.

3. Results and discussion

The phase identification and the lattice parameters are given in Table 1. No additional peaks appeared in the XRD pattern up to the composition $Ce_{0.91}Sr_{0.09}O_{1.91}$. However, the cubic lattice parameter increases up to the nominal composition $Ce_{0.91}Sr_{0.09}O_{1.91}$ and thereby indicating that 9 mol% of SrO can be incorporated into the lattice of CeO_2 even under the slow cooled conditions. The earlier reports [4,9] had shown solubility of SrO in CeO_2 as 9 and 8 mol%, at the higher temperatures. The present results are not only in good agreement with the earlier reports, but also indicate that the solubility limits under quenched or slow cooled conditions are more or less the same. This observation is contrary to our phase relation investigations [22] on MF_2–YF_3 systems (M: alkaline-earths), in which a considerable difference in solubility limits of YF_3 in MF_2 was observed depending upon the heat treatment. This is not surprising as both SrO and CeO_2 are high melting solids and probably the lattice expansion at 1400 °C is not sufficient enough so as to accommodate significantly higher amount of SrO compared to the slow cooled product. The XRD pattern of the products beyond the nominal composition $Ce_{0.91}Sr_{0.09}O_{1.91}$ started showing new peaks due to an additional phase, which could be identified as $SrCeO_3$. This observation indicates that the CeO_2 lattice is not able to accommodate more than 9 mol% of SrO. Therefore, at and beyond the nominal composition $Ce_{0.90}Sr_{0.10}O_{1.90}$ there is a phase separation into Sr^{2+} doped ceria and $SrCeO_3$ type phase. A mono-phasic product was not obtained even after quenching the nominal composition $Ce_{0.90}Sr_{0.10}O_{1.90}$ from 1300 °C to liquid nitrogen. The intensity of the peaks, due to the additional phase, increases with a concomitant reduction in the intensity of the fluorite type peaks. It was surprising to note that a slight amount of CeO_2 was present even at the nominal composition $Ce_{0.5}Sr_{0.5}O_{1.50}$ also. However, the majority phase was $SrCeO_3$. The single phasic product was obtained at the nominal composition $Ce_{0.45}Sr_{0.55}O_{1.45}$ which could be indexed on an orthorhombic unit cell with parameters 8.584(2), 6.009(1) and 6.148(1) Å. It may be noted that the cell volume of this phase is 317.0(2) $Å^3$ as against 316.4(3) $Å^3$ for the orthorhombic phase obtained at the nominal composition $Ce_{0.5}Sr_{0.5}O_{1.50}$. The next nominal composition, i.e.

Table 1
Nominal compositions and the corresponding phases in $Ce_{1-x}Sr_xO_{2-x}$

Number	Nominal composition	SrO (mol%)	Phase(s) present	a (Å)	b (Å)	c (Å)	V (Å^3)
1	$Ce_{1.00}Sr_{0.00}O_2$	0.00	C	5.402(3)			157.6(1)
2	$Ce_{0.95}Sr_{0.05}O_{1.95}$	5.00	C	5.416(1)			158.8(1)
3	$Ce_{0.925}Sr_{0.075}O_{1.925}$	7.50	C	5.422(1)			159.4(4)
4	$Ce_{0.91}Sr_{0.09}O_{1.91}$	9.0	C	5.427(2)			159.8(1)
5	$Ce_{0.90}Sr_{0.10}O_{1.90}$	10.0	C, O[a]	5.429(1)			160.0(1)
6.	$Ce_{0.85}Sr_{0.15}O_{1.85}$	15.00	C, O[a]	5.432(1)			160.2(1)
7	$Ce_{0.80}Sr_{0.20}O_{1.80}$	20.00	C, O[a]	5.431(1)			160.2(1)
8	$Ce_{0.75}Sr_{0.25}O_{1.75}$	25.00	C, O[a]	5.428(1)			160.0(1)
9	$Ce_{0.70}Sr_{0.30}O_{1.70}$	30.00	C	5.430(1)			160.1(1)
			O	8.584(8)	6.008(4)	6.121(7)	315.6(5)
10	$Ce_{0.65}Sr_{0.35}O_{1.65}$	35.00	C	5.423(1)			158.5(1)
			O	8.857(9)	6.009(4)	6.128(6)	315.8(5)
11	$Ce_{0.60}Sr_{0.40}O_{1.60}$	40.00	C	5.430(2)			160.1(1)
			O	8.574(6)	6.007(2)	6.134(4)	315.9(3)
12	$Ce_{0.55}Sr_{0.45}O_{1.55}$	45.00	C	5.429(1)			160.0(1)
			O	8.577(7)	6.006(3)	6.128(4)	315.7(3)
13	$Ce_{0.50}Sr_{0.50}O_{1.50}$	50.00	C	5.432(3)			160.3(2)
			O	8.577(4)	6.008(2)	6.139(2)	316.4(2)
14	$Ce_{0.45}Sr_{0.55}O_{1.45}$	55.00	O	8.584(2)	6.009(1)	6.148(1)	317.0(1)
15	$Ce_{0.40}Sr_{0.60}O_{1.40}$	60.00	O	8.572(4)	6.009(2)	6.144(2)	316.4(2)
16	$Ce_{0.33}Sr_{0.66}O_{1.33}$	66.00	O	8.585(3)	6.009(1)	6.147(1)	317.1(2)
			S[a]				
17	$Ce_{0.30}Sr_{0.70}O_{1.30}$	70.00	O	8.576(9)	6.022(4)	6.148(5)	317.5(5)
			S[a]				
18	$Ce_{0.25}Sr_{0.75}O_{1.25}$	75.00	[b]				
19	$Ce_{0.20}Sr_{0.80}O_{1.20}$	80.00	[b]				
20	$Ce_{0.15}Sr_{0.85}O_{1.15}$	85.00	[b]				
21	$Ce_{0.10}Sr_{0.90}O_{1.10}$	90.00	[b]				
22	$Ce_{0.05}Sr_{0.95}O_{1.05}$	95.00	[b]				
23	$Ce_{0.00}Sr_{1.00}O_{1.00}$	100.00	[b]				

C: cubic (fluorite) type; O: orthorhombic $SrCeO_3$ type phases; S: SrO.
[a] Corresponding phases were not refined due to very insignificant intensities of reflections.
[b] Could not be characterized as they reacted very fast with atmospheric gases.

$Ce_{0.4}Sr_{0.6}O_{1.40}$ was also found to be single phasic with a cell volume of 316.4(2) Å^3. It may be noted that the cell volume of $SrCeO_3$ type phase, obtained at the nominal composition $Ce_{0.55}Sr_{0.45}O_{1.45}$, is 315.7(3) Å^3. Unlike the isovalent ion substitution in a host lattice, the variation of cell volume, in case of aliovalent substitution, as a function of dopant ion concentration is not a simple function of ionic size difference alone, as it is always accompanied by introduction of the corresponding defects, e.g. anion vacancy in the present case. Always there are competing effects namely variation of lattice parameter due to relative ionic radii consideration and the interaction among the defects, which sometime can mask the effect of relative ionic radii [22]. The subsequent compositions after $Ce_{0.4}Sr_{0.6}O_{1.40}$ were bi-phasic as the peaks due to SrO also started to appear (Fig. 1). Therefore, it indicates that the orthorhombic phase $SrCeO_3$ ($Ce_{0.5}Sr_{0.5}O_{1.50}$) probably exists in a very narrow homogeneity range. The highly Sr^{2+} rich compositions like $Ce_{0.25}Sr_{0.75}O_{1.25}$, $Ce_{0.2}Sr_{0.8}O_{1.20}$, $Ce_{0.1}Sr_{0.9}O_{1.10}$, etc. were difficult to characterize as they tend to react with

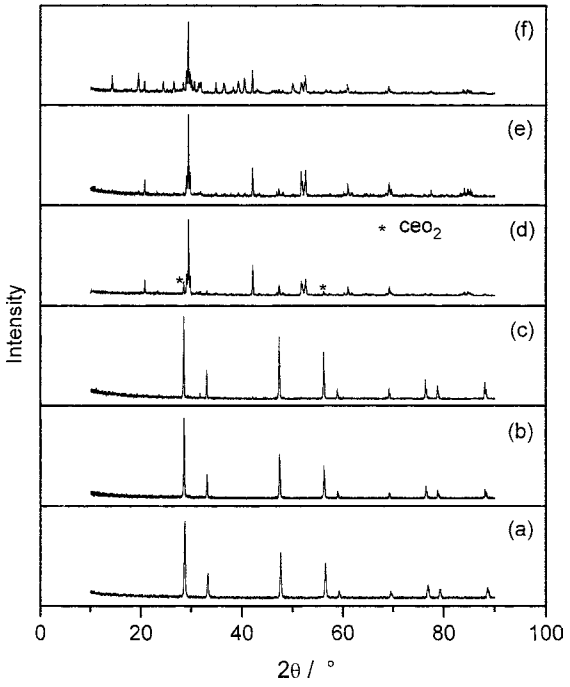

Fig. 1. (a) CeO_2, (b) $Ce_{0.91}Sr_{0.09}O_{1.91}$, (c) $Ce_{0.90}Sr_{0.10}O_{1.90}$, (d) $Ce_{0.50}Sr_{0.50}O_{1.50}$, (e) $Ce_{0.40}Sr_{0.60}O_{1.40}$, (f) $Ce_{0.20}Sr_{0.80}O_{1.20}$.

atmospheric gases very fast. Another important observation was that the Sr_2CeO_4 could not be obtained under the heat treatment used in the present investigations. It could be prepared by heating the reactants in an appropriate ratio at 1050 °C for 60 h with three intermittent grindings, as reported in [17].

4. Conclusions

A complete low temperature phase relation in CeO_2–SrO system has been investigated. The detailed XRD analysis of the phases was used to delineate the phase boundary in this system. $SrCeO_3$ appears to exist in a very narrow homogeneity range, under the present experimental conditions. No ordered phases could be obtained in this system. Another important conclusion drawn from this work is that about 9 mol% Sr^{2+} can be dissolved into the lattice of CeO_2, and in turn that of PuO_2. This observation would be useful in knowing the chemical state of Sr^{2+} in PuO_2-based nuclear fuels at different burn-ups.

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