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Phase studies in the Cs–Sr–U–O system

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Abstract

The phase diagram in Cs–Sr–U–O quaternary system was analyzed at 900 °C in air atmosphere. A novel quaternary phase, $Cs_2Sr_2U_4O_{15}$, was identified in the system. It was obtained by heating the respective oxides at 900 °C in air. X-ray diffraction data of the compound was indexed in a monoclinic system with cell parameters, $a = 0.9627(6)$ nm, $b = 1.3742(8)$ nm, $c = 0.7681(5)$ nm and $\beta = 107.72(5)°$, and was found to be isostructural with $Rb_2Sr_2U_4O_{15}$. A pseudo-ternary phase diagram of Cs_2O–SrO–UO_3 was drawn using a new quaternary compound and various phase fields were established by XRD analysis.

1. Introduction

For understanding the behavior of nuclear fuel during the operation of a reactor, the knowledge of interaction of fuel and fission products is important. In fast breeder reactor with mixed oxide as fuel, alkali metals such as cesium and rubidium and alkaline earth metals such as strontium and barium have high fission yields. During the burn up of the oxide fuel, fission product ^{137}Cs (half life ≈30 yr) has been observed to migrate axially with high concentration and may form low density ternary Cs–U–O compounds [1]. These compounds may cause deformation and breaching of the fuel pins and also can change stoichiometry of fuel oxide and thus affect the fuel behavior. The formation of mono, di- or poly-uranates of cesium depend on metal/uranium ratio, oxygen potential and temperature of the reaction and thus the knowledge of conditions required for their formation, phase equilibria, thermal stability and other thermodynamic properties is necessary for the advancement of the technology of nuclear energy production.

The phase equilibria of alkali metal oxides and their interaction with other oxides relevant to nuclear fuels, fission products and structural materials have been considered in detail in a review by Lindemer et al. [2]. The high temperature reactions of uranium oxides in molten salts and in the solid state, to form alkali metal uranates and their composition and properties have been reviewed by Griffiths and Volkovich [3]. A phase diagram of Na–U–O system at 1000 K was discussed by Kleykamp [4], describing a series of sodium uranates in the system. Several uranates of potassium and rubidium are reported in the literature [5]. Studies of the cesium–uranium–oxygen in air have led to the determination of various cesium hexavalent

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uranates, which were investigated using X-ray diffraction, thermal analysis and other techniques [1,6]. The crystalline structure of hexavalent cesium uranates was investigated by Van Egmond [7]. Solid state chemistry of ternary uranium oxides with alkaline earth metal oxides is reported by Yamashita [8]. In the Sr–U–O system, quasi-bianary SrO–UO_2 phase diagram obtained in air is discussed by Brisi et al. [9] reporting several strontium uranates.

However, very less work on the quaternary mixed oxide system involving both alkali metal and alkaline earth metal ions with uranium is reported in the literature. The phase studies on the quaternary mixed oxide system Rb–Sr–U–O equilibrated in air at 900 °C, was carried out by us [10], where the preparation and characterization of two novel quaternary phases; $Rb_2Sr_2U_4O_{15}$ and $Rb_8Sr_2U_6O_{24}$ in the system was reported. The preparation and structure analysis of $K_8A_2U_6O_{24}$ compounds (A = Ca, Sr and Ba) have been reported earlier [11].

In continuation of earlier work, the present study is carried out on Cs–Sr–U–O system to establish the phase relationship in the system as a prelude to investigations of a series of alkali metal–alkaline earth metal–uranium–oxygen system. The investigations were carried out by preparing various phases of different compositions in the Cs–Sr–U–O system by solid state reaction route and characterizing them by the X-ray powder diffraction (XRD) method.

2. Experimental

2.1. Preparation of samples

UO_3, Cs_2CO_3 (Merck, 99.99%) and $SrCO_3$ (Merck, 99.99%) were used as the starting materials. UO_3 was prepared by precipitating a uranyl nitrate (nuclear pure) solution as ammonium diuranate (ADU) with ammonia and decomposing it at 350 °C. The formation of β-UO_3 was confirmed by comparing the XRD data with those reported in the literature [12]. Cs_2CO_3 and $SrCO_3$ were dried at 200 °C for 12–14 h before weighing. As Cs_2CO_3 is very hygroscopic, it was weighed in a dry box with weighing error of 1–2%. Stock solutions of the three reactants were prepared by dissolving UO_3, Cs_2CO_3 and $SrCO_3$ salts in 1–2 M HNO_3 to get the molarity of around 0.5 M. The three solutions were then mixed in different molar ratios of UO_3, Cs_2O and SrO for making twenty equilibrium mixtures listed in Table 1. The solutions were evaporated to dryness after adding a few drops of glycerol, to get homogenized amorphous powder [13]. The powdered mixtures were heated in platinum boats, in air at 900 °C, for 30 h with intermittent grinding and mixing and the products were air quenched.

2.2. Instrumental analysis

XRD patterns of all the heated products were recorded using monochromatized Cu $K\alpha_1$ radiation ($\lambda = 0.15406$ nm) on a STOE X-ray diffractometer at the rate of 1° (2θ) per minute in the range of 6–60° (2θ), to analyze the formation of various phases. The phases identified in the samples are listed in Table 1 along with their composition.

3. Results and discussion

3.1. X-ray studies

The XRD data of novel quaternary phase, $Cs_2Sr_2U_4O_{15}$, was indexed on the monoclinic system with $a = 0.9627(6)$ nm, $b = 1.3742(8)$ nm, $c = 0.7681(5)$ nm and $\beta = 107.72(5)°$ with $\rho_{(obs)} = 5.4$ g/cm^3 and $Z = 2$. Indexed XRD data of the compound is given in Table 2. The similarity in cell parameters of $Cs_2Sr_2U_4O_{15}$ and $Rb_2Sr_2U_4O_{15}$, reported earlier [10], suggests the compounds are isostructural. Many attempts were made to prepare another pseudo-ternary compound, $Cs_8Sr_2U_6O_{24}$, similar to the one reported in Rb_2O–SrO–UO_3 system. But the samples prepared of that composition were always found to be a mixture of $Cs_2Sr_2U_4O_{15}$, $Cs_2U_2O_7$ and Cs_2O.

3.2. Phase diagram studies

The three pseudo-binary systems, Cs_2O–UO_3, SrO–UO_3 and Cs_2O–SrO were used for establishing the pseudo-ternary phase diagram in Cs_2O–SrO–UO_3 system. The Cs–U–O phase diagram and its application to uranium–plutonium oxide have been discussed by Fee et al. [1]. No ternary compounds are reported in Cs_2O–SrO system, whereas, in Cs_2O–UO_3 and SrO–UO_3 systems many ternary compounds prepared by high temperature reactions between the uranium oxides and various salts under oxidising and non oxidising conditions have been reviewed critically by Griffiths and Volkovich [3] and Sali [14].

Table 1
Phase identification of various compounds in the Cs_2O–SrO–UO_3

Mixture number	Mole fraction of the oxides			Phase identified by XRD		
	Cs_2O	SrO	UO_3			
A	0.14	0.28	0.58	$Cs_2Sr_2U_4O_{15}$[a]		
M1	0.15	0.23	0.62	A	$Cs_4U_5O_{17}$	SrU_4O_{13}
M2	0.33	0.17	0.5	A	$Cs_2U_2O_7$	Cs_2O
M3	0.4	0.1	0.5	A	$Cs_2U_2O_7$	Cs_2O
M4	0.38	0.15	0.47	A	$Cs_2U_2O_7$	Cs_2O
M5	0.05	0.16	0.79	$Cs_4U_5O_{17}$	SrU_4O_{13}	$Cs_2U_4O_{13}$
M6	0.08	0.49	0.43	A	Sr_2UO_5	$Sr_3U_2O_9$
M7	0.12	0.34	0.54	A	Sr_2UO_5	$Sr_3U_2O_9$
M8	0.05	0.35	0.6	A	SrU_4O_{13}	$SrUO_4$
M9	0.08	0.4	0.52	A	$Sr_3U_2O_9$	$SrUO_4$
M10	0.2	0.07	0.73	A	$Cs_4U_5O_{17}$	SrU_4O_{13}
M11	0.25	0.5	0.25	A	Cs_2O	Sr_2UO_5
M12	0.11	0.72	0.17	Sr_3UO_6	Cs_2O	SrO
M13	0.1	0.64	0.26	Sr_2UO_5	Sr_3UO_6	Cs_2O
M14	0.2	0.4	0.4	A	Sr_2UO_5	Cs_2O
M15	0.03	0.56	0.41	A	Sr_2UO_5	$Sr_3U_2O_9$
M16	0.27	0.06	0.67	A	$Cs_2U_2O_7$	$Cs_4U_5O_{17}$
M17	0.18	0.05	0.77	$Cs_4U_5O_{17}$	SrU_4O_{13}	$Cs_2U_4O_{13}$
M18	0.07	0.06	0.87	$Cs_2U_4O_{13}$	SrU_4O_{13}	UO_3
M19	0.1	0.15	0.75	A	$Cs_4U_5O_{17}$	SrU_4O_{13}

[a] The new phase = A.

Table 2
X-ray diffraction data of $Cs_2Sr_2U_4O_{15}$ ($\lambda = 0.15406$ nm) $a = 0.9627(6)$ nm, $b = 1.3742(8)$ nm, $c = 0.7681(5)$ nm and $\beta = 107.72(5)°$

h	k	l	$d_{(obs)}$ (nm)	$d_{(cal)}$ (nm)	I/I_0
0	1	0	1.3710	1.3742	20
0	2	0	0.6855	0.6871	100
0	3	0	0.4579	0.4581	60
0	4	0	0.3437	0.3436	80
2	3	0	0.3239	0.3241	20
1	0	2	0.3093	0.3090	32
−1	3	2	0.2931	0.2935	15
1	4	1	0.2840	0.2836	08
2	4	0	0.2750	0.2749	30
−3	2	2	0.2597	0.2595	05
2	4	2	0.2027	0.2027	08
1	3	3	0.1980	0.1981	05
−1	6	2	0.1964	0.1965	25
−5	1	3	0.1729	0.1729	06
5	3	0	0.1702	0.1703	05

In Cs_2O–UO_3 pseudo-binary system several hexavalent uranium compounds, reported in the literature are, $Cs_2U_{16}O_{49}$, $Cs_2U_{15}O_{46}$, $Cs_2U_7O_{22,}$, $Cs_2U_5O_{16}$, $Cs_4U_5O_{17}$, $Cs_2U_4O_{13}$, $Cs_2U_2O_7$ and Cs_2UO_4, which contain Cs_2O and UO_3 in the ratios: $(Cs_2O)(UO_3)_{16}$, $(Cs_2O)(UO_3)_{15}$, $(Cs_2O)(UO_3)_7$, $(Cs_2O)(UO_3)_5$, $(Cs_2O)_2(UO_3)_5$, $(Cs_2O)(UO_3)_4$, $(Cs_2O)(UO_3)_2$ and $(Cs_2O)(UO_3)$, respectively. However, much of the literature data on cesium uranates are conflicting and no comprehensive phase diagram of the Cs–U–O system has been published. Fee et al. [15] have extensively studied the phase equilibrium in the Cs–U–O system in the temperature range from 873 to 1273 K. Cordfunke et al. [6] prepared $Cs_2U_{16}O_{49}$, $Cs_2U_7O_{22}$, $Cs_2U_5O_{16}$, $Cs_4U_5O_{17}$, $Cs_2U_4O_{13}$, $Cs_2U_2O_7$ and Cs_2UO_4 by heating amorphous UO_3 and caesium carbonate in golden boat in air at 600 °C over a period of one week. The formation of cesium uranate phases by solid state reactions was reported to be very slow, especially for compounds with low Cs/U ratios. However, $Cs_2U_7O_{22}$ could not be obtained in pure form [6], even after heating the mixture for several weeks and it was reported $Cs_2U_7O_{22}$ coexisted with $Cs_2U_{16}O_{49}$ and $Cs_2U_5O_{16}$. Similarly, coexistence of $Cs_2U_7O_{22}$ and U_3O_8 with $Cs_2U_{16}O_{49}$ was reported by Cordfunke et al. [6]. They have reported that the structure of $Cs_2U_{16}O_{49}$ is closely related to that of $Cs_2U_7O_{22}$ and its X-ray pattern always contains the lines of U_3O_8 and $Cs_2U_7O_{22}$. Similarly, XRD pattern of $Cs_2U_5O_{16}$ is also always contaminated with the lines of $Cs_2U_7O_{22}$ and $Cs_2U_4O_{13}$ and below 700 °C, the compound does not crystallize properly [6]. This may be due to kinetic hindrance to the formation of these uranium rich $(Cs_2O)_x(UO_3)_y$

compounds from their respective mixtures. On the other hand, cesium rich compound, Cs_2UO_4 can be prepared in the pure form, but the compound is very hygroscopic and therefore very difficult to record XRD pattern in air and the thus needed to be handled in a dry box [16]. In the absence of this precaution, XRD lines of Cs_2UO_4 could not be observed. It is also reported that caesium monouranates when heated at 650 °C, lose not only Cs_2O but also oxygen, producing $Cs_2U_2O_7$ and $Cs_4U_5O_{17}$. The latter in turn decomposes above 1000 °C to form $Cs_2U_4O_{73}$ [16]. For these reasons, $Cs_2U_{16}O_{49}$, $Cs_2U_{15}O_{46}$, $Cs_2U_7O_{22}$, $Cs_2U_5O_{16}$, and Cs_2UO_4, were not included in the present work for drawing phase diagram. Berghe et al. [17] also prepared and identified Cs–U–O compounds and the Cs_2O-UO_3 compounds reported by them are $Cs_4U_5O_{17}$, $Cs_2U_4O_{13}$, and $Cs_2U_2O_7$. Thus, during the present phase diagram study, only well characterized phases existing at 900 °C in Cs–U–O system, i.e., $Cs_4U_5O_{17}$, $Cs_2U_4O_{13}$, and α and β phases of $Cs_2U_2O_7$ are considered. The *d*-values of the 10 strongest lines in the decreasing order of intensity of the above mentioned ternary compounds in the Cs_2O–UO_3 systems, used for the identification of the phases are given in Table 3.

The limiting pseudo-binary SrO–UO_3 system has seven hexavalent compounds reported by different workers [9,18,19], Sr_3UO_6, Sr_2UO_5, $Sr_3U_2O_9$, $SrUO_4$, $Sr_3U_{11}O_{36}$, SrU_4O_{13}, and $Sr_5U_3O_{11}$ which are made up of SrO and UO_3 in the ratios, $(SrO)_3(UO_3)$, $(SrO)_2(UO_3)$, $(SrO)_3(UO_3)_2$, $(SrO)(UO_3)$, $(SrO)_3(UO_3)_{11}$, $(SrO)(UO_3)_4$, and $(SrO)_5(UO_3)_3$, respectively. Some SrO–UO_3 compounds, such as SrU_2O_7 and $Sr_2U_3O_{11}$ are reported in the literature [8,14], but they are not well characterized and hence not included in the present work for drawing the phase diagram. Moreover the compounds, $Sr_3U_{11}O_{36}$ and SrU_4O_{13} are very closely placed in the phase diagram and have very similar XRD lines. Similarly, XRD lines of $Sr_5U_3O_{11}$ are same as that of Sr_2UO_5 and $Sr_3U_2O_9$ and therefore, the compounds $Sr_3U_{11}O_{36}$ and $Sr_5U_3O_{11}$ were also excluded from present phase diagram analysis. The remaining compounds, Sr_3UO_6, Sr_2UO_5, $Sr_3U_2O_9$, $SrUO_4$, and SrU_4O_{13}, were used for the identification of various phases prepared in the present work. The *d*-values of the 10 strongest lines in the decreasing order of intensity of the above mentioned ternary compounds in the SrO–UO_3 systems are also included in Table 3.

In the literature, there is no reported solubility of Cs_2O, SrO and UO_3 in each other or in the compounds formed from them.

The pseudo-ternary phase diagram of Cs_2O–SrO–UO_3 system, shown in Fig. 1, was drawn on the basis of phase analysis of the samples listed in Table 1, the knowledge of reported phases in Cs_2O–UO_3 and SrO–UO_3, discussed above and a new phase $Cs_2Sr_2U_4O_{15}$, identified during the present work. In the phase diagram, the compositions investigated by XRD to establish the coexisting phases, listed in Table 1, are shown as triangles. In the figure, the new phase, $Cs_2Sr_2U_4O_{15}$, is shown as an open hexagon and the ternary compounds considered in present work are shown as squares. The stable phase boundaries are drawn on the basis of the analyzed samples, considering the reported ternary compounds and the new quaternary compound.

Table 3
'*d*' values of the compounds in Cs_2O–UO_3 and SrO–UO_3 systems, used in this work

Compound	*d* values[a] (nm)										Refs.
$Cs_4U_5O_{17}$	0.748_{10}	0.367_9	0.332_8	0.303_6	0.374_4	0.347_4	0.344_3	0.320_3	0.696_3	0.342_3	[7]
$Cs_2U_4O_{13}$	0.775_{10}	0.387_5	0.312_5	0.337_4	0.309_4	0.341_2	0.302_2	0.339_2	0.256_2	0.432_2	[7]
$Cs_2U_2O_7$(α)	0.334_{10}	0.315_9	0.350_7	0.362_6	0.700_5	0.308_5	0.174_3	0.216_3	0.184_3	0.134_3	[7]
$Cs_2U_2O_7$(β)	0.332_{10}	0.317_8	0.370_6	0.683_5	0.342_5	0.308_5	0.216_3	0.215_2	0.241_2	0.203_2	[7]
Sr_3UO_6	0.303_{10}	0.298_3	0.502_2	0.428_2	0.309_2	0.214_2	0.177_2	0.173_2	0.256_2	0.214_2	[9]
Sr_2UO_5	0.329_{10}	0.313_{10}	0.564_8	0.505_8	0.283_8	0.202_8	0.198_8	0.196_8	0.383_8	0.379_8	[9]
$Sr_3U_2O_9$	0.322_{10}	0.197_4	0.280_4	0.169_4	0.552_3	0.396_3	0.207_3	0.643_2	0.276_2	0.168_2	[9]
$SrUO_4$	0.327_{10}	0.323_{10}	0.285_8	0.198_7	0.550_6	0.399_5	0.270_5	0.407_4	0.253_4	0.203_3	[9]
SrU_4O_{13}	0.349_{10}	0.420_9	0.268_7	0.337_4	0.180_4	0.178_4	0.263_4	0.210_3	0.197_2	0.161_1	[20]
Cs_2O	0.344_{10}	0.291_7	0.213_3	0.317_2	0.177_2	0.200_2	0.181_1	0.169_1	0.633_1	0.134_1	[21]
SrO	0.258_{10}	0.298_9	0.183_8	0.156_5	0.115_3	0.149_3	0.118_2	0.105_2	–	–	[6]
UO_3	0.303_{10}	0.307_9	0.358_7	0.340_6	0.194_4	0.478_3	0.250_3	0.247_3	0.192_3	0.190_3	[12]

[a] Ten strong lines in descending order of intensity (given as subscripts).

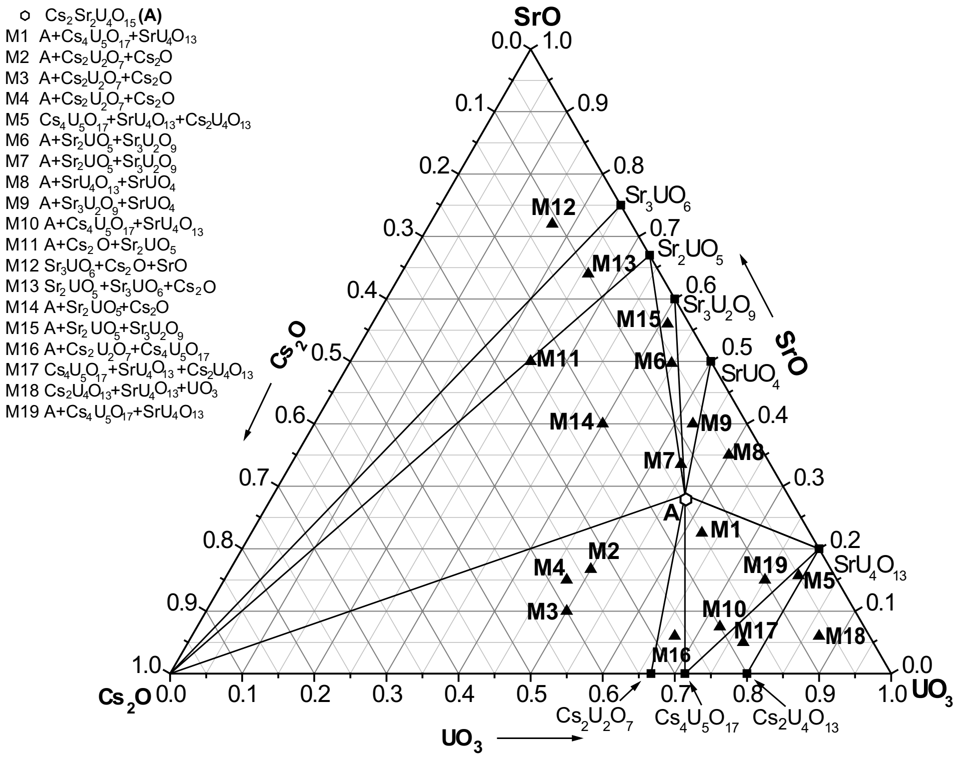

Fig. 1. Isothermal section of the pseudo-ternary phase diagram of the Cs_2O–SrO–UO_3 system at 900 °C.

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