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Thermodynamic properties of the ternary oxides in the system Sm–Ru–O

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Abstract

The Gibbs free energies of formation of Sm_3RuO_7(s), Sm_2RuO_5(s) and $Sm_2Ru_2O_7$(s) have been determined using solid-state electrochemical cell employing oxide ion conducting electrolyte. The electromotive force (e.m.f.) of the following solid-state electrochemical cells have been measured:

- Cell (I): (−)Pt/{Sm_3RuO_7(s) + Sm_2O_3(s) + Ru(s)}‖CSZ‖O_2($p(O_2)$ = 21.21 kPa)/Pt(+)
- Cell (II): (−)Pt/{Sm_3RuO_7(s) + Sm_2RuO_5(s) + Ru(s)}‖CSZ‖($p(O_2)$ = 21.21 kPa)/Pt(+)
- Cell (III): (−)Pt/{Sm_2RuO_5(s) + $Sm_2Ru_2O_7$(s) + Ru(s)}‖CSZ‖O_2($p(O_2)$ = 21.21 kPa)/Pt(+)

The Gibbs free energies of formation of Sm_3RuO_7(s), Sm_2RuO_5(s) and $Sm_2Ru_2O_7$(s) from elements in their standard state, calculated by the least squares regression analysis of the data obtained in the present study can be given respectively by:

$$\{\Delta_f G^0(Sm_3RuO_7, s)/(kJ\,mol^{-1}) \pm 3.1\} = -3161.5 + 0.6528\,(T/K); \quad (969 \leq T/K \leq 1222.8),$$

$$\{\Delta_f G^0(Sm_2RuO_5, s)/(kJ\,mol^{-1}) \pm 2.6\} = -2151.0 + 0.4544\,(T/K); \quad (917.1 \leq T/K \leq 1240.8),$$

$$\{\Delta_f G^0(Sm_2Ru_2O_7, s)/(kJ\,mol^{-1}) \pm 3.1\} = -2506.7 + 0.6345\,(T/K); \quad (1034.7 \leq T/K \leq 1221.1).$$

The uncertainty estimates for $\Delta_f G^0(T)$ include the standard deviation in e.m.f. and uncertainty in the data taken from the literature.
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Keywords: System Sm–Ru–O; Samarium ruthenates; Solid-state electrochemical technique; Gibbs free energy of formation

1. Introduction

A plethora of research has been initiated in recent years towards understanding the physical properties of 4d and 5d transition metal oxides, which show a variety of magnetic and transport transitions indicative of highly correlated electronic interactions and strong spin charge coupling [1]. However, studies of oxides with 4d transition metals and rare earth have been largely limited to pyrochlore systems such as $Ln_2Ru_2O_7$(s).

The Sm–Ru–O system, investigated in this study, comprises of the following binary oxides: Sm_3RuO_7(s), Sm_2RuO_5(s) and $Sm_2Ru_2O_7$(s). Sm_3RuO_7(s) was indexed on an orthorhombic unit cell (space group *Cmcm*) [2]. Physical properties such as, magnetization, electrical resistivity and heat capacity of the ternary oxide were investigated. It was found to have nonmetallic electrical resistivity. Temperature dependence of magnetic susceptibility was measured by Harada and Hinatsu [3]. Specific heat measurements show first order transition peak at T = 190 K. The results indicate

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that the transition is a structural phase transition. Sm_2RuO_5(s) has a complex orthorhombic structure (space group *Pnma*) [4] possessing chains of RuO_5, five oxygen coordinated square pyramids which are corner sharing and two inequivalent seven coordinated L sites which are edge sharing. Magnetization, electrical resistivity and heat capacity of Sm_2RuO_5(s) were investigated by Cao et al. [5].

In the pyrochlore oxide, $A_2^{3+}B_2^{4+}O_7^{2-}$ when both the A and B sites are occupied by magnetic ions, these compounds show very interesting magnetic features, caused by the coupled magnetic interactions between the 4f electrons of rare-earths, those between the d and g electrons [6,7]. The ruthenium pyrochlore has been studied for their novel conductivity [8,9] and catalytic activity [10,11]. The pyrochlore $Sm_2Ru_2O_7$(s) can be considered as an ordered defective fluorite (space group *Fd3m*) [12]. Magnetic properties for $Sm_2Ru_2O_7$(s) were measured by Taira et al. [13]. The magnetic properties should be attributable to the Ru^{4+} ion and also rare earth ion Sm^{3+} that is paramagnetic. $Sm_2Ru_2O_7$(s) shows magnetic transition at $T = 135$ K. Specific heat and susceptibility studies on $Sm_2Ru_2O_7$(s) were also carried out by Taira et al. [14].

Crystal structure, magnetic and electrical properties of the oxides have been thoroughly investigated by many researchers. However thermodynamic properties of these oxides need investigation. Quantitative information on the thermodynamic properties of these compounds is useful for assessing the interaction of platinum group metals with ceramic compounds containing rare-earth oxides under different environments. The information is also important for the design of processes for the recovery of rare-earth and precious metals from scrap. In this study, based on the phase relations between the oxides, solid-state cells were designed to measure the Gibbs free energies of formation of the ternary oxides. The Gibbs free energies of formation of Sm_3RuO_7(s), Sm_2RuO_5(s) and $Sm_2Ru_2O_7$(s) were determined by an oxide electrochemical cell using 0.15 mole fraction calcia stabilized zirconia (CSZ) solid electrolyte, in the temperature range from 963.6 to 1222.8, 917.1 to 1240.8 and 1034.7 to 1221.1 K, respectively.

2. Experimental

2.1. Materials

Sm_3RuO_7(s) was synthesized from stoichiometric proportions of preheated Sm_2O_3(s) (0.9985 mass fraction, Leico Industries Inc.) and RuO_2(s) (0.997 mass fraction, Prabhat Chemicals, India) powders. The powders were intimately ground and the mixture was then pelletized. The pellets were subjected to a pressure of 50 MPa and then fired in air at $T = 1273$ K for several hours with repeated grindings. The pellets were reground and repelletized and heated in air several times to ensure homogeneity. Sm_2RuO_5(s) was prepared from stoichiometric proportions of the respective oxides, mixed homogeneously, pelletized and heated to a temperature of 1473 K for several hours. A few firings at the same temperature with intermediate grindings were necessary to ensure homogeneity. $Sm_2Ru_2O_7$(s) was prepared similarly by mixing stoichiometric proportions of the respective oxides. The homogeneous mixture was pelletized and sealed in an evacuated ampoule. The ampoule was then heated to $T = 1423$ K. The values of the interplanar d spacing obtained for Sm_3RuO_7(s), Sm_2RuO_5(s) and $Sm_2Ru_2O_7$(s) recorded on powder diffractometer using Cu Kα radiation is in good agreement with those reported in JCPDS file number #39–1027 [2], #44–1035 [4] and #28–997 [12], respectively.

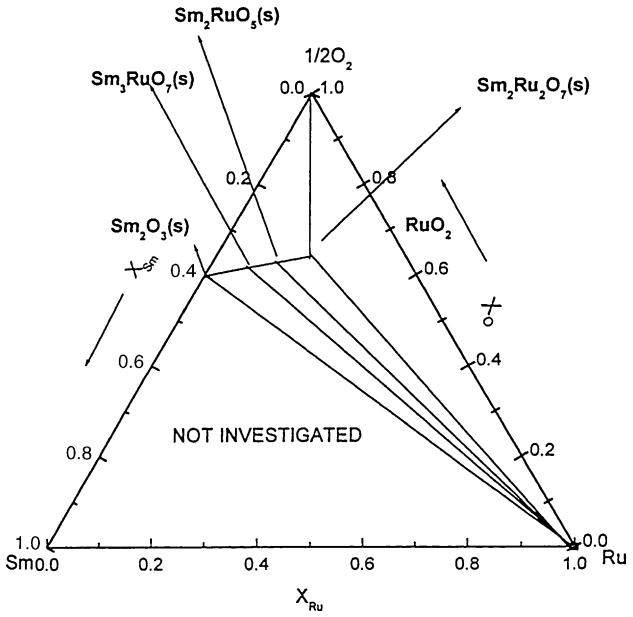

Fig. 1. Isothermal section of the phase diagram for the system Sm–Ru–O at $T = 1150$ K.

An isothermal section of the phase diagram for the Sm–Ru–O system at $T = 1150$ K is shown in Fig. 1. All the compounds in the phase diagram were prepared separately characterized by X-ray diffraction and then mixed in stoichiometric ratios of the individual oxides to obtain the respective phase fields. The following phase mixtures were prepared: $\{Sm_3RuO_7(s) + Sm_2O_3(s) + Ru(s)\}$, $\{Sm_3RuO_7(s) + Sm_2RuO_5(s) + Ru(s)\}$ and $\{Sm_2RuO_5(s) + Sm_2Ru_2O_7(s) + Ru(s)\}$ by mixing the individual compounds in the appropriate molar ratios and then pelletized into pellets of dimension 7 mm diameter and 3 mm thickness using a tungsten carbide die at a pressure of 100 MPa. The pellets were sintered in purified argon gas atmosphere at $T = 1000$ K for several hours. The sintered pellets were re-examined by X-ray diffraction and the phase compositions were found to be unchanged after sintering. These pellets were then used for e.m.f. measurements.

2.2. The oxide cell assembly

A double compartment cell assembly, with 0.15 mole fraction calcia stabilized zirconia (CSZ) solid electrolyte tube

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