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Phase Equilibria in Europium(III) Oxide–Titanium(IV) Oxide System at Temperatures from 900 to 1400 °C

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The phase equilibria in the Eu_2O_3–TiO_2 system has been established at temperatures from 900 to 1400 °C in air using coprecipitated gels as starting materials. In this system, Eu_2O_3, TiO_2, Eu_2TiO_5, and $Eu_2Ti_2O_7$ are stable. The stoichiometric $Eu_2Ti_2O_7$ has a cubic pyrochlore type structure with $a = 1.0210(3)$ nm, and forms a solid solution with TiO_2. The TiO_2 contents and the lattice constants of these solid solutions equilibrated with TiO_2 at different temperatures were [given as mol %, a/nm, θ/°C]: 70.4(5), 1.0187(1), 1409(9); 69.5(5), 1.0193(1), 1292(8); 68.9(5), 1.0197(1), 1191(9); 68.4(5), 1.0200(1), 1099(2); 68.1(5), 1.0202(1), 996(4); and 68.0(5), 1.0203(1), 898(3). Numbers in parentheses are errors in the last digits.

Europium(II) titanium(IV) trioxide (perovskite type), $EuTiO_3$, is an interesting compound in field of inorganic chemistry and geochemistry, because it forms an extensive solid solution with respect to oxygen.[1] It may be used as an oxygen barometer, according to the principle that it is formed from dieuropium(III) dititanium(IV) heptaoxide, $Eu_2Ti_2O_7$, at a given temperature and oxygen fugacity.[2] In order to furnish thermodynamic data on the $EuTiO_3$ solid solution at high temperatures, a phase diagram for the system europium(III) oxide[3]–titanium(IV) oxide[4] is required. This binary system has not been systematically studied, while the europium–titanium–oxygen system at 1400 °C including this binary system has been reported McCarthy *et al.*[1] On the other hand, dieuropium(III) titanium(IV) pentaoxide, Eu_2TiO_5,[5] and $Eu_2Ti_2O_7$[6] have been observed in this binary system.

The purposes of this study are to establish the phase relations in this binary system in the temperature range between 900 and 1400 °C in air, to determine the solubility of titanium(IV) oxide in $Eu_2Ti_2O_7$, and to obtain the phase diagram of this binary system.

Experimental

Materials. The samples prepared by the coprecipitation method were used as starting materials. Both the stock solutions of europium and titanium were prepared separately as follows: (i) the freshly ignited Eu_2O_3 having a purity of 99.9% was dissolved in conc. hydrochloric acid; (ii) Guaranteed reagent-grade $TiCl_4$ was dissolved in 3 mol/dm^3 hydrochloric acid solution at a temperature below 65 °C.[7] Both the metals in the 1 mol/dm^3 hydrochloric acid solution prepared by mixing the stock solutions in the desired ratios were coprecipitated with aqueous ammonia. After being washed thoroughly with water, these coprecipitates were dried at about 100 °C for 12 h, heated at about 400 °C for 12 h, and finely ground by an agate mortar.

Furnaces and Temperature Control. Vertical tube quench furnaces with a 60%Pt-40%Rh winding were used for the equilibration runs.

Furnace temperatures were kept constant within the temperature range given in Table 1 by means of an electric controller activated by a Pt-(87%Pt-13%Rh) thermocouple inserted close to the hot spot of the furnace. The actual temperatures within the furnace were measured with the other thermocouple which was calibrated within ±0.5 °C against the melting points of diopside, 1394 °C, and gold, 1064 °C.

General Procedure. About 0.1-g powdered starting material was placed in a 60%Pt-40%Rh foil envelope, about 0.05 mm in thickness and 10×10 mm in area, and heated in air at the temperatures listed in Table 1. After heated during the reaction time given in Table 1, the samples were quenched rapidly to the temperature of ice by burning away the thin Pt wire with an electric current. In a single run, 10 or 12 charges were heated together by suspending these envelopes over the hooks of a 60%Pt-40%Rh wire netting.

Identification of Phases and Determination of Lattice Constants. The phases present in the starting materials and the quenched samples were identified by X-ray powder diffraction method using a scintillation counter diffractometer with Ni-filtered Cu $K\alpha$ radiation.

Lattice constants were determined by the same method with a scanning rate of 1/4° or 1/8° per min and with an internal standard of high-purity silicon.

Chemical Analysis. The titanium content in the titanium stock solution was determined by precipitating as titanium(IV) oxide hydrate in the presence of acetic acid, and igniting the precipitates to titanium(IV) oxide.

After the freshly ignited starting materials and the quenched samples were fused with potassium disulfate, the cold melt obtained was dissolved in sulfuric acid solution. The europium content in the sulfuric acid solution was determined by precipitating as europium(III) oxalate and igniting the precipitates to europium(III) oxide, while the titanium content in the solution was determined photometrically by the hydrogen peroxide method.[8]

Table 1. Temperature and reaction time

A group[a]		B group	
θ/°C	t/d	θ/°C	t/d
901±1	32.8	898±3	29.9
998±2	30.8	996±4	26.8
1100±1	19.8	1099±2	23.8
1209±10	14.9	1191±9	14.9
1295±6	9.9	1292±8	9.8
1406±6	7.9	1409±9	6.9

a) The samples with different chemical compositions were divided into two groups, according to the period when the samples were prepared. One group is composed of 10 or 12 samples heated together at constant temperature.

Table 2. Results of equilibration runs in the temp range between 900 and 1400 °C

No.[a)]	Materials		Phase[b)]
	TiO_2(mol %)	Eu_2O_3(mol %)	
B-1[c)]	15.4	84.6	E + Y
B-2	30.6	69.4	E + Y
A-1	35.9	64.1	E + Y
B-3	49.8	50.2	Y
A-2	55.8	44.2	Y + P
A-3	57.8	42.2	Y + P
A-4	62.6	37.4	Y + P
B-4	67.4	32.6	Ps
A-5	72.4	27.6	Ps + R
A-6	74.2	25.8	Ps + R
A-7	77.1	22.9	Ps + R
A-8	81.4	18.6	Ps + R

a) The samples labeled as A and B, respectively, belong to A group and B group in Table 1. For example, the sample of A-1 was heated at the temperatures and for the reaction times given as A group in Table 1. b) E = Eu_2O_3, Y = Eu_2TiO_5, P = $Eu_2Ti_2O_7$, Ps = $Eu_2Ti_2O_7$ solid solution, R = TiO_2. c) Only one of the most intense reflections of Eu_2TiO_5 in addition to reflections of Eu_2O_3 was detected in the sample heated at 898 °C.

Results and Discussion

Reaction Time for Equilibration. According to preliminary experiments, in which, Eu_2TiO_5, the poorest crystalline substance in this system, was synthesized from oxide mixtures, trace amounts of $Eu_2Ti_2O_7$ and europium(III) oxide in addition to Eu_2TiO_5 were detected in the sample heated at 1200 °C for 13.6 d, and further heat treatment was necessary to obtain Eu_2TiO_5 as a single phase. Therefore, the samples prepared by the coprecipitation method were selected as starting materials in order to shorten the time of equilibration.

More than both phases were not detected in all the quenched samples obtained in this study (Table 2). Furthermore, Eu_2TiO_5 was definitely identified in all the quenched samples expected to contain this phase, except in the sample B-1 heated at 900 °C. Each reaction time listed in Table 1 is thought to be sufficient as the reaction time needed for equilibrium.

Chemical Composition. The ratios of europium to titanium in the starting materials were in agreement with those in the quenched samples within the limit of analytical errors. The chemical compositions of the samples listed in Table 2 are based on chemical analyses.

Phases in Starting Materials. Most of the starting materials indicated an amorphous condition. Small amounts of europium(III) chloride oxide, EuClO,[9)] were identified in a few of the starting materials, *e.g.* B-3. The occurrence of this compound may be attributed to the thermal decomposition of europium(III) chloride dihydroxide, $EuCl(OH)_2$, precipitated from the mixtures of both the stock solutions. Trace amounts of $Eu_2Ti_2O_7$ were detected in few of them, *e.g.* B-7.

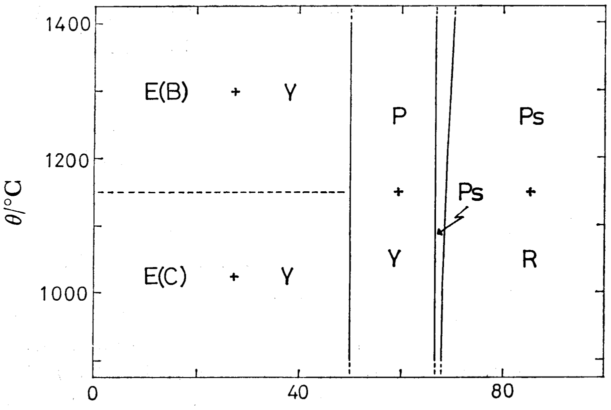

Fig. 1. Phase diagram for Eu_2O_3–TiO_2 system. Abbreviations are the same as those in Table 2 except for the followings: E(B) = Eu_2O_3(B-form), E(C) = Eu_2O_3 (C-form).

TiO₂ mol %

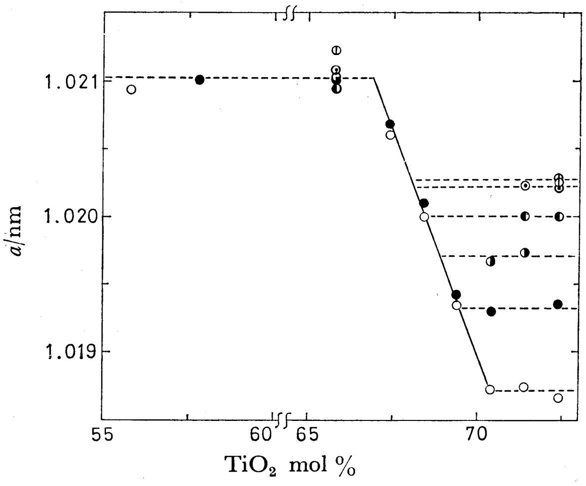

Fig. 2. Lattice constant, *a*, of $Eu_2Ti_2O_7$ solid solution *vs.* chemical composition.
○: 1409 °C, ●: 1292 °C, ◑: 1191 °C, ◐: 1099 °C, ⊙: 996 °C, ⦶: 898 °C, ◔: 1409 and 1191 °C.

Phases and Phase Relations. The equilibrium data obtained at temperatures ranging from 900 to 1400 °C are summarized in Table 2, and illustrated graphically in Fig. 1 together with the addtiona data shown in Fig. 2.

In the present system, four compounds were stable: Eu_2O_3, TiO_2, Eu_2TiO_5, and $Eu_2Ti_2O_7$.

Europium(III) Oxide: This oxide[3)] found in this study occurred in a cubic C-type form below 1100 °C, and crystallized in a monoclinic B-type structure above 1200 °C. Warshaw and Roy[10)] have reported that trace amounts of the C-form were converted to the B-form after 30 h at 1105 °C. The present findings are compatible with their observations.

Titanium(IV) Oxide: The tetragonal rutile type structure of this oxide,[4)] which is believed to be thermodynamically stable,[11)] was observed under the present experimental conditions.

Dieuropium(III) Titanium(IV) Pentaoxide: This compound[5)] found in this study had an orthorhombic

TiY_2O_5 type structure. The lattice constants were a=1.054(1)* nm, b=1.133(1) nm, c=0.376(1) nm, and V=0.449 nm^3, which is in good agreement with those reported by McCarthy *et al.*[5] (a=1.054 nm, b=1.132 nm, c=0.378 nm, and V=0.451 nm^3.)

The lattice constants of this compounds equilibrated with europium(III) oxide and with $Eu_2Ti_2O_7$ were identical with each other, irrespective of temperature. Therefore, there is the possibility that this compound is stoichiometric.

Dieuropium(III) Dititanium(IV) Heptaoxide: This compound[6] with a cubic pyrochlore type structure was stable in this study, and formed a solid solution with titanium(IV) oxide.

Figure 2 shows the relationship between the titanium(IV) oxide contents in the samples and the lattice constants of this solid solution. The lattice constants of this solid solution within the region for the coexistence of both $Eu_2Ti_2O_7$ and Eu_2TiO_5 phases were identical with each another within the limit of experimental errors, regardless of temperature. The datum was a= 1.0210(3) nm, while this compound has been reported to have a lattice constants of a=1.0193 nm.[6] The data within the $Eu_2Ti_2O_7$-stable region showed such a straight line as represented by the equation

$$a = 1.0648 - 0.0654X(\mathrm{TiO_2}), \qquad (1)$$

where a and $X(\mathrm{TiO_2})$, respectively, represent the lattice constant and the titanium(IV) oxide content given in mol% of $Eu_2Ti_2O_7$. The data on $Eu_2Ti_2O_7$ within the region for the coexistence of both $Eu_2Ti_2O_7$ and titanium(IV) oxide phases were identical with each other at constant temperature, and decreased with an increase in temperature.

The chemical composition of this solid solution equilibrated with Eu_2TiO_5 was calculated to be 66.9 mol%TiO_2, by substituting the a-value given above in Eq. 1, indicating good agreement with the stoichiometric value, 66.7 mol % TiO_2. The chemical compositions of these solid solutions equilibrated with titanium(IV) oxide at each temperature have been calculated according to the same treatment reported above, and illustrated in Fig. 1.

Solubility of Titanium(IV) Oxide in Dieuropium(III) Dititanium(IV) Heptaoxide. The equation for the solution of rutile in the pyrochlore phase may be written as

$$\mathrm{TiO_2(rutile)} = \mathrm{TiO_2(in\ pyrochlore)}, \qquad (2)$$

for which the equilibrium constant is

$$K = \frac{a(\mathrm{TiO_2})^{\mathrm{p}}}{a(\mathrm{TiO_2})^{\mathrm{r}}}, \qquad (3)$$

where $a(\mathrm{TiO_2})^{\mathrm{p}}$ and $a(\mathrm{TiO_2})^{\mathrm{r}}$, respectively, indicates the activity of titanium(IV) oxide in the pyrochlore phase and in the rutile phase. As the rutile is considered to be pure, the activity of rutile may be taken as unity; also the solubility of rutile is low as given below, and the activity of titanium(IV) oxide in the pyrochlore phase may be assumed to be proportional to the mole fraction, if Henry's law is applicable.

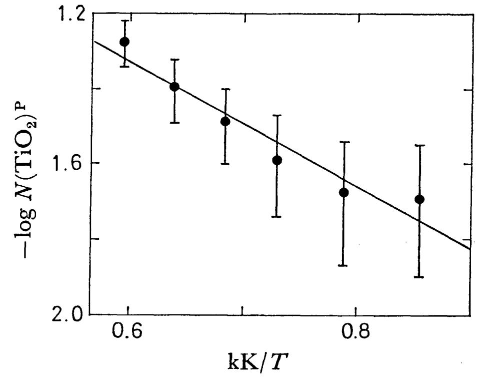

Fig. 3. Change of the solubility of TiO_2 in $Eu_2Ti_2O_7$ with temperature.

Hence,

$$K = kN(\mathrm{TiO_2})^{\mathrm{p}}, \qquad (4)$$

where k is the Henry's constant, and $N(\mathrm{TiO_2})^{\mathrm{p}}$ denoted the mole fraction of titanium(IV) oxide in the pyrochlore phase.

The solubility of rutile in $Eu_2Ti_2O_7$, calculated from such chemical compositions of these solid solutions equilibrated with rutile as obtained above, are given as $N(\mathrm{TiO_2})^{\mathrm{p}}$, θ/°C: 0.020(8), 898; 0.021(8), 996; 0.026(8), 1099; 0.033(8), 1191; 0.040(8), 1292; and 0.053(8), 1409. Figure 3 shows the relationship between temperature and the solubility of rutile in $Eu_2Ti_2O_7$. It may be seen from Fig. 3 that the amount of rutile increases with an increase in temperature, while a linear relationship exists between them, as predicted from the equation

$$\left[\frac{\partial \ln K}{\partial(1/T)}\right]_P = -\frac{\Delta H}{R}, \qquad (5)$$

where T is the absolute temperature, P is the pressure, ΔH indicates the enthalpy change of Eq. 2, which corresponds to the relative partial enthalpy of solution,[12] and R is the gas constant. This line may be represented by the equation

$$\log N(\mathrm{TiO_2})^{\mathrm{p}} = -\frac{1700}{T} - 0.33, \qquad (6)$$

corresponding to ΔH=33(2) kJ.

The Phase Diagram. The present results obtained are shown as a phase diagram in Fig. 1. A comparison of this phase diagram with those of the systems M_2O_3-TiO_2 (M=La,[13] Gd,[13] Dy,[15] Yb[16]) shows that the present phase diagram is the most similar to that for the Gd_2O_3-TiO_2 system among them. The similarity in phase diagrams may be due to the similarity in ionic radii.

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