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Experimental study and thermodynamic calculation of Lu_2O_3-SiO_2 binary system

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Abstract: As a binary system of BaO-Lu_2O_3-SiO_2 ternary system, Lu_2O_3-SiO_2 system was optimized and calculated by CALPHAD approach based on available phase diagram and relevant thermodynamic data of RE_2O_3-SiO_2 (RE=Lu,Yb,Y) binary systems as well as our experimental data of Lu_2O_3-SiO_2 system obtained by quenching experiment. The Gibbs free energy of high temperature solution was described by an ionic two-sublattice model as $(Lu^{3+})_P(O^{2-}, SiO_2^0)_Q$. The calculated phase diagram below 1873 K was in good agreement with experimental data at 1573, 1773 and 1873 K. The calculated Gibbs energies of two intermediate phases Lu_2SiO_5 and $Lu_2Si_2O_7$, the activity of Lu_2O_3 and SiO_2 and specific heat capacities of intermediate phases agreed well with experimental results of Y_2O_3-SiO_2 system. This tentative study will offer help for the research of single-phase phosphor and related metallurgical slags, refractories, high-temperature superconductivity material systems.

Keywords: phase diagram; Lu_2O_3-SiO_2; thermodynamics; ionic two-sublattice model; CALPHAD; rare earths

As a binary system of BaO-Lu_2O_3-SiO_2 ternary system, the Lu_2O_3-SiO_2 system is of great interest because of the potential application of the intermediate compounds in phosphors[1–3] and inorganic scintillators[4,5]. However, the information of phase relationship and thermodynamics of Lu_2O_3-SiO_2 system is insufficient for design and optimization of luminescent materials. Actually, it is very difficult to achieve the real phase equilibria in Lu_2O_3-SiO_2 system due to the slow diffusion rate in solid phases at low temperatures and measure liquidus at very high temperatures. Fortunately, with the help of the CALPHAD approach based on experimental phase diagram and relevant thermodynamic data, it is possible to obtain consistent thermodynamic description of such system from limited experimental information.

On the basis of X-ray phase analysis and measurements of melting points of a series of powdered compositions, a part of Lu_2O_3-SiO_2 phase diagram (Fig. 1) was constructed by Zagumennyi et al.[6] to improve the performance of Lu_2SiO_5:Ce^{3+} optical ceramic scintillator. In this diagram, the solid and broken lines indicated experimental data and predictions, respectively. The region of phase "S"(solid solution) was surrounded by the fields of two-phase equilibria L+S, Lu_2O_3+S and S+$Lu_2Si_2O_7$. The maximum temperature of melting point of "S" was 2263 K corresponding to the composition of 51.9 mol.% Lu_2O_3-48.1 mol.% SiO_2.

Except for phase diagram, the crystal chemistry of the rare-earth silicates have been summarized by Felsche[7] in 1973. In the Lu_2O_3-SiO_2 binary system, intermediate compounds are known of composition 1:1 (Lu_2SiO_5), 2:3 ($Lu_4Si_3O_{12}$), and 1:2 ($Lu_2Si_2O_7$) at high temperature[7]. There are five different crystal structures for $Lu_2Si_2O_7$ compound, in which only C monoclinic form is the thermodynamic stable state[8]. The melting points of cerium-doped Lu_2SiO_5 and $Lu_2Si_2O_7$ scintillators have been

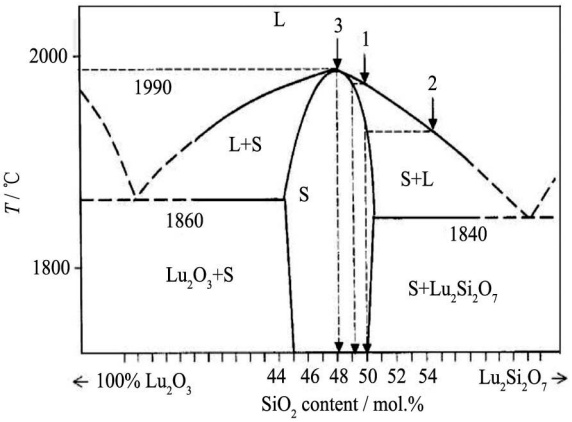

Fig. 1 Partial phase diagram of Lu_2O_3-SiO_2 system[6]

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measured to be 2373 and 2173 K, respectively[4]. The phase diagrams for the RE_2O_3-SiO_2 (RE=Lu, Yb, Y) systems are very similar due to the analogous existence of intermediate compounds of disilicate and monosilicate at high temperature[9] and similarity of physical and chemical properties of rare earth elements Lu, Yb and Y. Owing to the lack of information of the Lu_2O_3-SiO_2 system, some phase diagram and thermodynamic data were chosen from the analogous RE_2O_3-SiO_2 (RE=Yb,Y) binary systems as reference data. For Yb_2O_3-SiO_2 system, the experimental phase diagram including three intermediate phases Yb_2SiO_5, $Yb_2Si_2O_7$, $Yb_4Si_3O_{12}$ has been reported by Toropov et al.[9]. For Y_2O_3-SiO_2 system, three intermediate phases Y_2SiO_5, $Y_2Si_2O_7$, $Y_4Si_3O_{12}$ were first presented by Toropov and Bondar[10]. There is a miscibility gap in the liquid phase on the SiO_2-rich side[10]. However, $Y_4Si_3O_{12}$ with apatite structure was not confirmed by following studies[11–13]. Drummond et al.[13] reported a corrected phase diagram of Y_2O_3-SiO_2 system excluding the apatite phase ($Y_4Si_3O_{12}$). Calculation results showed that Y_2SiO_5 melts congruently at 2232 K and $Y_2Si_2O_7$ melts incongruently at 2060 K[14]. Based on measurements of enthalpy of formation and heat capacity for the solid phases, Fabrichnaya et al.[15] gave a thermodynamic assessment of the Y_2O_3-SiO_2 system and the obtained phase diagram was in good agreement with experimental data.

In our previous work, the BaO-SiO_2 system[16] and BaO-Lu_2O_3 system[17] have been thermodynamically assessed. As a part of the series of studies, the Lu_2O_3–SiO_2 system was optimized and calculated in the present work by CALPHAD approach based on the available phase diagram and relevant thermodynamic data of RE_2O_3-SiO_2 (RE=Lu, Yb, Y) binary systems as well as our experimental data of Lu_2O_3-SiO_2 system. The study of the Lu_2O_3-SiO_2 binary system may offer help for the research of single-phase phosphor and related metallurgical slags, refractories, high-temperature superconductivity material systems.

1 Experimental

1.1 Procedure

The samples were synthesized by solid-state reaction in air with high purity raw powders. Lu_2O_3 (99.99%) and SiO_2 (99.99%) were weighed in an appropriate stoichiometric ratio. After thoroughly mixing and grinding in an agate mortar for 2 h, the powders were pressed with 1 MPa to form pellets and fired at 1573, 1773, 1873 K for 10 h. After sintering step, the samples were took out immediately from a heat shock furnace at high temperature and cooled quickly to room temperature in air. All the samples can be removed directly from heat shock furnace under high temperature and cooled quickly to room temperature in air. The identification of the phases was analyzed by using a PANalytical X-ray diffractometer (Cu Kα radiation, λ=0.154187 nm) after grinding samples mentioned above into fine powders.

1.2 Results and discussion

Fig. 2 shows X-ray diffraction patterns of the samples sintered at 1573, 1773 and 1873 K with SiO_2 contents of 45 mol.%, 50 mol.%, 55 mol.%, 60 mol.%, 67 mol.% and 70 mol.%. The phases for all samples constituted with the same ratio did not change from 1573 to 1873 K. Except SiO_2, Lu_2O_3, Lu_2SiO_5 and $Lu_2Si_2O_7$, no traces from impurity phases were observed. The Lu_2O_3 was found in the composition of 45 mol.% SiO_2-55 mol.% Lu_2O_3 (a) samples and SiO_2 were found in the 70 mol.% SiO_2-30 mol.% Lu_2O_3 (f) samples at all experimental temperatures. Two intermediate compounds Lu_2SiO_5 and $Lu_2Si_2O_7$ were proved to exist at 1573, 1773 and 1873 K with SiO_2 contents at 55 mol.% (c), 60 mol.% (d). Lu_2SiO_5 and $Lu_2Si_2O_7$ exhibited pure phases when the contents of SiO_2 are 50 mol.% (b) and 67 mol.% (e), respectively. The experimental results of the phase diagram of Lu_2O_3-SiO_2 system are similar to those of the Yb_2O_3-SiO_2 system reported by Toropov et al.[7] and the Y_2O_3-SiO_2 system of Fabrichnaya et al.[13]. The existent Lu_2SiO_5 solid solution in the composition range of 45 mol.%–51 mol.% SiO_2[4] was not conformed with our experimental data (Fig. 2(a)). Consequently, Lu_2SiO_5 was treated as the stoichiometric compound instead of solid solution in the present study.

2 Model

2.1 Reference state

As reference states for the Lu_2O_3-SiO_2 binary system, all of the Gibbs energies are given relative to the enthalpy of selected reference states for the elements at 298.15 K and 1.013×10^5 Pa (stable element ${}^0\Delta G_i^{\varphi}(T)$ reference, SER)

$$ {}^0\Delta G_i^{\varphi}(T)=a+bT+cT\ln T+dT^2+eT^{-1}+fT^3+gT^7+hT^{-9} \quad (1) $$

${}^0\Delta G_i^{\varphi}(T)$ is the standard molar Gibbs energy of compound i in phase φ (solid state or liquid state) at the absolute temperature T(K). In different temperature ranges, different sets of the coefficients a to h can be used. The last two terms in Eq. (1) are used only outside the ranges of stability, the term gT^7 is relative to the liquid below the melting point and hT^{-9} to the solid phases above the melting point[18]. In the present work, the Gibbs energy functions of pure Lu_2O_3 and SiO_2 were taken from SSUB5 substance database in the Thermo-Calc Software.

2.2 Intermediate phases

Three intermediate phases, Lu_2SiO_5, $Lu_2Si_2O_7$ and