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Experimental determination of phase equilibria in the $\text{REM}_2\text{O}_3\text{--SiO}_2$ (REM = Y/Yb/La) systems at elevated temperatures

Longgong Xia^{1,3}; Dmitry Sukhomlinov^{2,3}; Fengchun Ye^{1,4}; Zhihong Liu^{1,5,#}; Pekka Taskinen³

longgong.xia@csu.edu.cn; dmitry.sukhomlinov@ntnu.no; yefengchun@nerin.com;
zhliu@csu.edu.cn; pekka.taskinen@aalto.fi

1, Refractory Material Processing and Slag Chemistry Research Group, School of Metallurgy and Environment, Central South University, Changsha 410083, PR China

2, Department of Material Science and Engineering, Norwegian University of Science and Technology, Trondheim N-7491, Norway

3, Metallurgical Thermodynamics and Modelling Research Group, School of Chemical Technology, Aalto University, Espoo 02150, Finland

4, Jiangxi Huagan Nerin Rare & Precious Metal Technology Co., Ltd., Fengcheng 331100, PR China

5, National Engineering Laboratory of High Efficiency Recovery of Refractory Nonferrous Metals, Central South University, Changsha 410083, PR China

#, Corresponding author, zhliu@csu.edu.cn

Abstract

Phase relations in the $\text{REM}_2\text{O}_3\text{--SiO}_2$ (REM=Y/Yb/La) system have been studied with the equilibration/quenching/SEM-EPMA technique. The solvus and liquidus between 1400°C and 1650°C have been determined. Results obtained in this study show that Yb_2O_3 can dissolve maximumly 0.57 wt.% in SiO_2 phases, and the maximum solubility of La_2O_3 and Y_2O_3 in SiO_2 phase were 0.22 wt.% and 0.07 wt.% respectively. Correspondingly, SiO_2 has a low solubility in $\text{La}_2\text{Si}_2\text{O}_7$, and nearly doesn't dissolve in $\text{Y}_2\text{Si}_2\text{O}_7$ or $\text{Yb}_2\text{Si}_2\text{O}_7$. No liquid phase was detected in the $\text{Y}_2\text{O}_3\text{--SiO}_2$ system or the $\text{Yb}_2\text{O}_3\text{--SiO}_2$ system in the temperature range of interest. One oxide liquid phase composing of 39.27 wt.% SiO_2 and 59.07 wt.% La_2O_3 was found in the $\text{La}_2\text{O}_3\text{--SiO}_2$ system sample equilibrated at 1653°C, revealing that the eutectic point temperature between $\text{La}_2\text{Si}_2\text{O}_7$ and SiO_2 locates between 1600 °C and 1653 °C. Results from this study were compared with previous observations, and differences were significant.

Keywords: EBCs, Rare Earth Oxide, CALPHAD, Molten oxide, Slag

Introduction

Rare earth metals (REM) are not available in good concentrations for economic mining, but they are generally abundant in the earth's crust, even more abundant than many metals with lower values [1-3]. But REM containing materials have crucial applications in many important industries due to their unique properties [4,5]. For example, compounds of the $\text{REM}_2\text{O}_3\text{-SiO}_2$ systems, in particular, yttrium, ytterbium and lanthanum silicates, have proved to be promising materials for high temperature structural applications and rare earth (RE) silicates have been recognized as the third generation of EBC materials for silicon-based ceramics [6-9]. A remarkable progress has been achieved in the bonding, thermal treatment and doping of rare-earth silicates in order to improve their performance [5-9]. But the understanding and control of these material preparation processes may still be improved. As the most intuitive thermodynamic tool, phase diagrams are commonly used in guiding the synthesis of compounds, predicting compositions of phases, and controlling the crystalline structures, and for improving the material properties [10,11]. However, very limited phase equilibria data concerning the $\text{REM}_2\text{O}_3\text{-SiO}_2$ ($\text{REM}=\text{Y/Yb/La}$) systems are available in the literature [12-22].

In the $\text{REM}_2\text{O}_3\text{-SiO}_2$ ($\text{REM}=\text{Y/Yb/La}$) system, there are three compounds, REM_2SiO_5 , $\text{REM}_3\text{Si}_2\text{O}_{12}$ and $\text{REM}_2\text{Si}_2\text{O}_7$. REM_2SiO_5 and $\text{REM}_2\text{Si}_2\text{O}_7$ have been reported to be stable from room temperature to their respective melting point, but $\text{REM}_3\text{Si}_2\text{O}_{12}$ is only stable at elevated temperature and within a narrow temperature range [12,13]. The phase diagram of $\text{Y}_2\text{O}_3\text{-SiO}_2$ was experimentally studied by several researchers [12-17]. Toropov and Bondar [12-14] firstly presented phase diagram of the $\text{Y}_2\text{O}_3\text{-SiO}_2$ system, and reported that there was a miscibility gap in the liquid phase on the SiO_2 -rich side, which was later confirmed by Hageman and Oonk [16]. Melting temperatures of Y_2SiO_5 and $\text{Y}_2\text{Si}_2\text{O}_7$ were measured in the previous studies [12-14,16], and they reported congruent melting character of Y_2SiO_5 and incongruent melting of $\text{Y}_2\text{Si}_2\text{O}_7$. However, the reported apatite structured compound ($\text{Y}_4\text{Si}_3\text{O}_{12}$) was not found in the latter studies [17-19], and Drummond [19] presented a corrected phase diagram excluding the apatite structured phase.

The silica activity in the $\text{Yb}_2\text{O}_3\text{-SiO}_2$ system has been measured using a Knudsen effusion mass spectrometer (KEMS) technique by Costa and Jacobson [8], and the enthalpy of formation of Yb_2SiO_5 was $2774 \pm 11 \text{ kJ mol}^{-1}$. In the $\text{Yb}_2\text{O}_3\text{-SiO}_2$ system, Yb_2SiO_5 and $\text{Yb}_2\text{Si}_2\text{O}_7$ phases were reported to be stable from room temperature to their respective melting points, while $\text{Yb}_4\text{Si}_3\text{O}_{12}$ was found to be stable only at 1675–1920 °C [12,13]. In the constructed binary phase diagram of the $\text{La}_2\text{O}_3\text{-SiO}_2$ system by Toropov, La_2SiO_5 , $\text{La}_2\text{Si}_2\text{O}_7$, and $\text{La}_4\text{Si}_3\text{O}_{12}$ have been found [12,13]. Bondar [21] then corrected the stoichiometric ratio of $\text{La}_4\text{Si}_3\text{O}_{12}$ to $\text{La}_{4.67}\text{Si}_3\text{O}_{13}$. The phase equilibrium relations in the ternary $\text{CaO-SiO}_2\text{-La}_2\text{O}_3$ system at 1100–1600 °C were experimentally studied by Liu and Qiu [22] and the primary crystal fields of SiO_2 , $\text{La}_2\text{O}_3 \cdot 2\text{SiO}_2$, $\text{CaO} \cdot 3\text{SiO}_2 \cdot 2\text{La}_2\text{O}_3$, and $2\text{CaO} \cdot \text{SiO}_2$ have been identified.

The present study aims at providing solvus and liquidus information of the $\text{REM}_2\text{O}_3\text{-SiO}_2$ ($\text{REM} = \text{Y/Yb/La}$) systems at SiO_2 saturation within the temperature

range of 1400-1650 °C. The experimental part includes sintering synthesis of $\text{REM}_2\text{Si}_2\text{O}_7$, equilibration of SiO_2 and $\text{REM}_2\text{Si}_2\text{O}_7$ mixtures at the target temperatures, and rapid quenching of the equilibrated samples with subsequent analysis of the chemical compositions of the equilibrium phases by using electron probe X-ray microanalysis (EPMA). The “equilibration-quenching technique” employed in the present work has been proven to be a reliable and efficient method in acquiring high temperature phase equilibrium information in geochemical [23] and metallurgical [24] systems. The acquired phase equilibrium data are useful for the related material preparation and essential for the subsequent thermodynamic modeling and assessment of the investigated oxide systems.

2. Materials and methods

2.1 Raw materials

Granulate (0.2-0.7 mm) SiO_2 (purity, 99.99 wt%) supplied by Umicore (Belgium) was ground into fine powder (particle size smaller than 75 μm , by passing a 200-mesh sieve) in an agate mortar. Powders of Y_2O_3 , Yb_2O_3 , and $\text{La}(\text{OH})_3$ were utilized as starting materials, and their individual chemical purity was 99.95 wt%.

2.2 REM-orthosilicates (REM = Y/Yb/La) sintering

SiO_2 powder was thoroughly mixed with REM_2O_3 (REM = Y/Yb) in a molar ratio of 2:1, aiming the stoichiometric $\text{REM}_2\text{Si}_2\text{O}_7$. In case of La, one molar unit of $\text{La}(\text{OH})_3$ was mixed with two molar units of SiO_2 . These mixtures were pressed into pellets (8 ton/3 cm^2 or ≈ 0.27 GPa) and subjected to heat-treatment in a Lenton (UK) chamber furnace (UAF 16/10 type) in three cycles with intermediate grinding and pelletizing. The first two cycles were at 1400 and 1500 °C and the sintering time was set as 48 and 24 hours, respectively. The third cycle had a stepwise-increasing temperature profile: 1500, 1550, and 1600 °C and 4 hours dwelling time at each step. The purity of the samples was maintained in such a way that the primary pellets were placed on sacrificial pellets with the same composition, while the sacrificial pellets were placed on a Pt substrate.

2.3 Sample equilibration and quenching

In the equilibrium experiments, SiO_2 and sintered REM-orthosilicates were weighed in the weight ratio of 1:2, mixed thoroughly in an agate mortar, and pelletized to 0.2 GPa in a 5 mm-diameter pressing tool. Small fractions (around 10-20 mg) of the pellets were equilibrated at various temperature ranging from 1400 °C to 1650 °C in a vertical resistance tube furnace (Nabertherm, RHTV 40/250/18 model, Germany) with electrical resistance of molybdenum disilicide (MoSi_2) heating elements. Fused silica crucibles and platinum wires and foils (Pt, Johnson-Matthey Noble Metals, UK, 99.99% (metal basis)) were used as the substrate material and

suspension components, respectively. Auxiliaries of the furnace and the experimental procedure have been discussed thoroughly in the previous publications [25-26]. The weight of each sample was 10-20 mg. The small size of the sample was an advantage in approaching the equilibrium and especially in the sample quenching. Special attention was paid to the accuracy of the experimental temperature. The uniform hot zone of the furnace was carefully determined by measuring the thermal profile with a calibrated S-type thermocouple (Johnson-Matthey Noble Metals, UK) at different temperatures ranging from 1000 °C to 1650 °C, and the overall temperature accuracy was estimated to be ± 2 °C for the entire experimental temperature range of interest.

The experiments were conducted with the bottom and the top of the reaction tube open to the ambient air atmosphere. Once, the pre-determined equilibration time was reached, the specimen was released and quenched rapidly into an ice-water bath (0 °C). The quenched samples were dried and mounted in an epoxy resin. Polished cross sections of the specimens were prepared by using conventional metallographic grinding and polishing techniques.

2.4 Analyses

As prepared samples were polished to obtain a flat cross-section, a conductive carbon-coating of 15nm thickness was then applied with a Leica EM SCD050 Coater (supplied by Leica Mikrosysteme GmbH, Vienna, Austria). The microstructure and phase composition of the samples were firstly examined by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectrometer (EDS). For that, a LEO 1450 (Carl Zeiss Microscopy GmbH, Jena, Germany) scanning electron microscope was employed with a linked Inca X-Sight 7366 Energy EDS analyzer (Oxford Instruments plc, Abingdon, Oxford-shire, UK). Selected samples were examined by XRPD with a PANalytical diffractometer (X'Pert Pro Powder, Almelo, Netherlands) equipped with Co radiation with a step size of 0.007° over a 2θ range of $10-70^\circ$ at room temperature.

The quantitative elemental analysis was performed on a JEOL 8530F Plus field emission electron microprobe, and the acceleration voltage applied in the analyzing was 15 kV. Full spectrometer wavelength scan was performed on each phase of the samples. The standards used for the analysis were quartz for Si, yttrium garnet for Y, lanthanum phosphate for La, and ytterbium phosphate for Yb. Oxygen was not measured, but it was calculated based on the stoichiometry by assigning the oxidation degree of Si as 4+, and Y, Yb, La as 3+. The detection limits of the elements were estimated by the analyses software to be Y, 46 ppm; La, 33 ppm; Yb 77 ppm; Si, 279 ppm. The overall detection limit of EPMA analyzes is estimated to be 0.1 wt%. Different analytical conditions were applied in analyzing SiO_2 and $\text{REM}_2\text{Si}_2\text{O}_7$ /liquid phase, aiming to achieve sufficient detection limit of the elements and to maintain the sample stability under electron radiation. The probe current was set at 10 nA in analyzing the liquid and the $\text{REM}_2\text{Si}_2\text{O}_7$ phases, and the current was changed to 200 nA when examining the SiO_2 phase. The probe beam size was 1 μm when analyzing bulk solid phases and it was changed to 5 μm when analyzing the liquid phase.

3. Results and discussion

3.1 Sintered REM-orthosilicates

Figure 1 depicts the synthesized material containing ytterbium orthosilicate, i.e., a polished section on the left side and a XRPD pattern on the right side.

Figure 1. A BSE image (a) and recorded XRPD patterns (b) of the sintered sample from the Yb₂O₃-SiO₂ system.

As shown in Figure 1(a), porous microstructure has been produced after sintering the pelletized mixture of SiO₂ and Yb₂O₃. Three phases could be detected within the BSE (back scattered electron) image, EDS analyses confirmed that the central bright phase to be Yb₂Si₂O₇, the surrounded grey phase to be Yb₂SiO₅, the sporadically distributed black phase to be SiO₂, and no residue of Yb₂O₃ was detected. The recorded XRPD patterns revealed that the major phase was Yb₂Si₂O₇, with some fraction of SiO₂ and traces of Yb₂SiO₅, which agrees well with the SEM-EDS results. Yb₂SiO₅ phase and SiO₂ phase were embedded in each other, but the Yb₂Si₂O₇ phase obviously formed starting from the core, and indicating the formation mechanism of Yb₂Si₂O₇ as:

Similar phenomena were observed in the Y₂O₃-SiO₂ and La(OH)₃-SiO₂ systems. The semi-quantitative XRPD results indicated that Y₂Si₂O₇, Yb₂Si₂O₇ and La₂Si₂O₇ accounted for 77 wt.%, 88 wt.% and 91 wt.%, respectively in the synthesized mixtures. The equilibrium experiments were carried out by taking these sintered products and additional pure SiO₂ powder as starting materials.

3.2 Phase equilibria of the REM₂O₃-SiO₂ (REM = Y/Yb/La) systems

3.2.1 The Yb₂O₃-SiO₂ system

The equilibrated and quenched samples were carefully analyzed by SEM and EDS, and selected microstructures of the Yb_2O_3 - SiO_2 system samples are shown in Figure 2.

Figure 2. Backscattered SEM images of quenched Yb_2O_3 - SiO_2 system samples of this study at: (a) 1653°C, 2h; (b) 1602°C, 4h; (c) 1550°C, 12h; (d) 1497°C, 24h; (e) 1454°C, 36h; and (f) 1399°C, 48h.

As shown in Figure 2, each sample contained two homogeneous phases, and no concentration gradients were detected within the samples and their phases. The black phase was confirmed to be SiO_2 by EDS, and the bulk bright phase was revealed to be $\text{Yb}_2\text{Si}_2\text{O}_7$. There was no liquid phase forming within the temperature range of the present study, indicating that the eutectic temperature between $\text{Yb}_2\text{Si}_2\text{O}_7$ - SiO_2 is

higher than 1653°C. The finding agrees with the phase diagram presented by Toropov [12]. Along with increasing temperature, the particle size of Yb₂Si₂O₇ phase gradually grows as well. 5-10 independent measuring points/areas from each phase were analyzed with EPMA in each sample, and results obtained are listed in Table I.

Table I. Phase compositions of equilibrium phases in the Yb₂O₃-SiO₂ system 1400-1650 °C.

N o.	T / °C*	Time /h	Phase	EPMA Result (wt.%)**		EPMA Result (mol.%)	
				SiO ₂	Yb ₂ O ₃	SiO ₂	Yb ₂ O ₃
1	1653	2	Cristobalite	99.47±0.07	0.52±0.07	99.92±0.07	0.08±0.07
			Diytterbium Disilicate	22.87±0.28	75.93±0.40	66.39±0.28	33.61±0.40
2	1602	4	Cristobalite	99.75±0.36	0.07±0.04	99.99±0.36	0.01±0.04
			Diytterbium Disilicate	23.10±0.30	76.15±0.54	66.55±0.30	33.45±0.54
3	1550	12	Cristobalite	99.42±0.06	0.57±0.06	99.91±0.06	0.09±0.06
			Diytterbium Disilicate	23.41±0.19	76.52±0.09	66.74±0.19	33.26±0.09
4	1497	24	Cristobalite	99.39±0.10	0.57±0.06	99.91±0.10	0.09±0.06
			Diytterbium Disilicate	23.33±0.33	76.67±0.27	66.62±0.33	33.38±0.27
5	1454	36	Tridymite	99.48±0.04	0.51±0.04	99.92±0.04	0.08±0.04
			Diytterbium Disilicate	22.92±0.16	76.53±0.10	66.27±0.16	33.73±0.10
6	1399	48	Tridymite	99.42±0.07	0.57±0.07	99.91±0.07	0.09±0.07
			Diytterbium Disilicate	23.03±0.14	75.93±0.22	66.55±0.14	33.45±0.22

* Standard uncertainty: $\mu(T) = \pm 2$ °C; $P_{tot} = 1$ atm; $P_{O_2}=0.21$ atm.

** Average standard deviation: $\sigma(\text{EPMA})=0.13$.

In EPMA, oxygen was not measurement but calculated based on stoichiometry by assigning Si as 4+, and Yb as 3+. The chemical compositions have been recalculated based on the measured metallic elements (Si and Yb). SiO₂ and Yb₂O₃ were considered as the terminal phases for presentation purposes. In the studied temperature range, Yb₂O₃ had larger solubility than Y₂O₃ in SiO₂ phase, maximum value was 0.57 wt.%, and temperature variations had little impact on Yb₂O₃ solubility. SiO₂ had an obvious solubility in the Y₂Si₂O₇ phase, and it firstly increase and then decrease along with increasing temperature. The standard deviations of the mean values for each phase were calculated based on its data set. The average standard uncertainty of the EPMA measurement is given as the footnote of Table I.

3.2.2 The La₂O₃-SiO₂ system

The equilibrated and quenched samples were carefully analyzed by SEM and EDS, and selected microstructures of the La_2O_3 - SiO_2 system samples are shown in Figure 3.

Figure 3, Backscattered SEM images of quenched La_2O_3 - SiO_2 system samples of this study at: (a) 1653°C, 2h; (b) 1602°C, 4h; (c) 1550°C, 12h; (d) 1497°C, 24h; (e) 1454°C, 36h; (f) 1399°C, 48h.

As shown in the figure, each of these samples contained two or three homogeneous phases, and no concentration gradients were detected within these samples. The black phase was confirmed to be SiO_2 by EDS, and the bulk bright phase has been revealed to be $\text{La}_2\text{Si}_2\text{O}_7$ or liquid oxide phase. In Figure 3(a), the formation of the liquid oxide phase agrees with the phase diagram presented by Toropov [12-14]. Along with increasing temperature, the particle size of $\text{La}_2\text{Si}_2\text{O}_7$

phase grew larger. 5-10 independent measuring points/areas from each phase were analyzed with EPMA in each sample, and the EPMA results are listed in Table II.

Table II. Phase compositions of equilibrium phases in the $\text{La}_2\text{O}_3\text{-SiO}_2$ system 1400-1650 °C.

N o.	T / °C*	Time /h	Phase	EPMA Result (wt.%)**		EPMA Result (mol.%)**	
				SiO_2	La_2O_3	SiO_2	La_2O_3
1	1653	2	Cristobalite	99.72±0.03	0.25±0.03	99.95±0.03	0.05±0.03
			Liquid Oxide	39.27±0.25	59.07±0.11	78.28±0.25	21.72±0.11
2	1602	4	Cristobalite	99.77±0.04	0.22±0.04	99.96±0.04	0.04±0.04
			Dilanthanum Disilicate	26.89±0.14	72.48±0.07	66.80±0.14	33.20±0.07
3	1550	12	Cristobalite	99.85±0.03	0.14±0.03	99.97±0.03	0.03±0.03
			Dilanthanum Disilicate	26.54±0.10	72.47±0.11	66.51±0.10	33.49±0.11
4	1497	24	Cristobalite	99.80±0.02	0.19±0.02	99.96±0.02	0.04±0.02
			Dilanthanum Disilicate	26.70±0.04	72.42±0.04	66.66±0.04	33.34±0.04
5	1454	36	Tridymite	99.75±0.05	0.22±0.04	99.96±0.05	0.04±0.04
			Dilanthanum Disilicate	26.91±0.04	72.84±0.05	66.70±0.04	33.30±0.05
6	1399	48	Tridymite	99.84±0.03	0.14±0.03	99.97±0.03	0.03±0.03
			Dilanthanum Disilicate	26.93±0.08	72.35±0.17	66.87±0.08	33.13±0.17

* Standard uncertainty: $\mu(T) = \pm 2$ °C; $P_{tot} = 1$ atm; $P_{O_2} = 0.21$ atm.

** Average standard deviation: $\sigma(\text{EPMA}) = 0.12$.

In the temperature range studied, La_2O_3 had a small solubility in SiO_2 , with the maximum value of 0.22 wt.%, and La_2O_3 solubility in SiO_2 phase increased along with temperature increasing. SiO_2 had also an obvious solubility in the $\text{La}_2\text{Si}_2\text{O}_7$ phase, and it firstly increased and then decreased along with increasing temperature. The standard deviations of the mean value for each phase has been calculated based on its data set. The average standard deviation of the EPMA measurements is given in the footnote of Table II.

3.2.3 The $\text{Y}_2\text{O}_3\text{-SiO}_2$ system

The equilibrated and quenched samples of the $\text{Y}_2\text{O}_3\text{-SiO}_2$ system were carefully analyzed by SEM and EDS and selected microstructures of the samples are shown in Figure 4.

Figure 4, Backscattered SEM images of quenched Y_2O_3 - SiO_2 system samples equilibrated at: (a) 1653°C, 2h; (b) 1602°C, 4h; (c) 1550°C, 12h; (d) 1497°C, 24h; (e) 1454°C, 36h; (f) 1399°C, 48h.

As shown in Figure 4, the samples annealed at high temperatures have two or three phases. The black phase was confirmed to be SiO_2 , and bulk bright phase was $\text{Y}_2\text{Si}_2\text{O}_7$. Tiny Y_2SiO_5 areas were found in the cores of the $\text{Y}_2\text{Si}_2\text{O}_7$ particles in figure 2 (a) and figure 2 (e), which revealed the formation mechanism of $\text{Y}_2\text{Si}_2\text{O}_7$. The microprobe analysis was focused on the local equilibria, i.e. on those areas of the samples where only two phases were present: REM orthosilicate and SiO_2 . There is no liquid in saturation with $\text{Y}_2\text{Si}_2\text{O}_7$ or SiO_2 obtained below 1653 °C, meaning that the eutectic of Liquid- $\text{Y}_2\text{Si}_2\text{O}_7$ - SiO_2 is above 1653 °C. This finding agrees with the

phase diagram reported by Toropov and Drummond [12,19]. Along with increasing temperature, the $Y_2Si_2O_7$ particle size grew, and it can be explained by the Ostwald ripening. In order to obtain the accurate chemical phase compositions, EPMA measurements were carried out on well equilibrated $Y_2Si_2O_7$ phases and SiO_2 phase domains, which located far from the intermediate Y_2SiO_5 phase. 5-10 independent measuring points/areas from each phase were analyzed in each sample to quantify the chemical composition. The EPMA results obtained from the phase equilibration experiments of the binary Y_2O_3 - SiO_2 system at SiO_2 saturation at temperatures ranging from 1400 °C to 1650 °C were listed in Table III.

Table III. Phase compositions of equilibrium phases in the Y_2O_3 - SiO_2 system 1400-1650 °C.

N o.	T / °C*	Time /h	Phase	EPMA Result (wt.%)**		EPMA Result (mol.%)**	
				SiO_2	Y_2O_3	SiO_2	Y_2O_3
1	1653	2	Cristobalite	99.98±0.08	0.004±0.003	100.00±0.08	0.00±0.003
			Diyttrium Disilicate	34.44±0.42	65.57±0.43	66.38±0.42	33.62±0.43
2	1602	4	Cristobalite	99.75±0.36	0.03±0.014	99.99±0.36	0.01±0.014
			Diyttrium Disilicate	34.13±0.12	65.15±0.23	66.32±0.12	33.68±0.23
3	1550	12	Cristobalite	99.94±0.03	0.04±0.023	99.99±0.03	0.01±0.023
			Diyttrium Disilicate	34.41±0.43	65.31±0.25	66.45±0.43	33.55±0.25
4	1497	24	Cristobalite	99.96±0.04	0.023±0.005	99.99±0.04	0.01±0.005
			Diyttrium Disilicate	34.44±0.50	65.51±0.14	66.40±0.50	33.60±0.14
5	1454	36	Tridymite	99.91±0.12	0.076±0.012	99.98±0.12	0.02±0.012
			Diyttrium Disilicate	34.29±0.23	65.12±0.15	66.43±0.23	33.57±0.15
6	1399	48	Tridymite	99.97±0.01	0.019±0.011	99.99±0.01	0.01±0.011
			Diyttrium Disilicate	34.03±0.12	65.69±0.74	66.07±0.12	33.93±0.74

* Standard uncertainty: $\mu(T) = \pm 2$ °C; $P_{tot} = 1$ atm; $P_{O_2}=0.21$ atm.

** Average standard deviation: $\sigma(EPMA) = 0.12$.

The concentrations of the elements measured with EPMA (Si and Y) were stoichiometrically converted to the concentrations of SiO_2 and Y_2O_3 , respectively, for presentation purposes. In the temperature range studied, Y_2O_3 had a very low solubility in either tridymite or cristobalite phases of SiO_2 , the maximum obtained in this study was 0.076 wt.%, and Y_2O_3 solubility in SiO_2 phase decreased along with temperature increasing. SiO_2 had an obvious solubility in the $Y_2Si_2O_7$ phase, and it firstly increased and then decreased along with increasing temperature. The standard deviation of the average composition for each phase has been calculated based on its data sets. The average standard deviation of the EPMA measurements is given in the footnote of table III.

Conclusions

Phase equilibrium information of the $\text{SiO}_2 - \text{REM}_2\text{O}_3$ ($\text{REM} = \text{Y}/\text{Yb}/\text{La}$) systems, and specifically the REM orthosilicate and SiO_2 equilibria at elevated temperatures have been experimentally studied. The sub-solidus equilibria between $\text{REM}_2\text{Si}_2\text{O}_7$ and SiO_2 obtained in this study shows that REM_2O_3 ($\text{REM} = \text{Y}, \text{Yb}, \text{La}$) solubility in SiO_2 phases is small in the temperature range of 1400-1650°C, and it was in the sequence of $\text{Yb}_2\text{O}_3 > \text{La}_2\text{O}_3 > \text{Y}_2\text{O}_3$. Correspondingly, SiO_2 had a low solubility in $\text{La}_2\text{Si}_2\text{O}_7$ at silica saturation, while it was nearly insoluble in $\text{Y}_2\text{Si}_2\text{O}_7$ and $\text{Yb}_2\text{Si}_2\text{O}_7$. No liquid oxide phase was detected in the $\text{SiO}_2 - \text{REM}_2\text{O}_3$ ($\text{REM} = \text{Y}/\text{Yb}$) systems, and the eutectic temperature between $\text{La}_2\text{Si}_2\text{O}_7$ and SiO_2 was found to exist between 1600 to 1650°C.

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