

Article

Phase Equilibria in the System $\text{CaO-SiO}_2\text{-La}_2\text{O}_3\text{-Nb}_2\text{O}_5$ at 1400°C

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Abstract: $\text{CaO-SiO}_2\text{-La}_2\text{O}_3\text{-Nb}_2\text{O}_5$ system is of great significance for the pyrometallurgical utilization of Bayan Obo tailing resources. In the present work, the phase equilibrium of this quaternary system at 1400°C was determined by a thermodynamic equilibrium experiment. On the basis of the recently determined $\text{CaO-La}_2\text{O}_3\text{-Nb}_2\text{O}_5$ phase diagram, some boundary surfaces of primary phase fields of $\text{CaO-SiO}_2\text{-La}_2\text{O}_3\text{-Nb}_2\text{O}_5$ phase diagram were modified; then, the 1400°C isothermal surface in the primary phase fields of SiO_2 , CaNb_2O_6 , $\text{Ca}_2\text{Nb}_2\text{O}_7$, and LaNbO_4 was constructed, respectively. On this basis, $\text{CaO-SiO}_2\text{-Nb}_2\text{O}_5$ pseudo-ternary phase diagrams with $w(\text{La}_2\text{O}_3) = 5\%, 10\%, 15\%$, and 20% were determined, respectively. Considering the importance of equilibrium crystallization reaction type, we proposed a new rule named *Tangent Line Rule* to judge the univariant reaction type in the quaternary phase diagram. By applying *Tangent Line Rule* and *Tangent Plane Rule* previously proposed, some univariant and bivariant crystallization reaction types in the $\text{CaO-SiO}_2\text{-La}_2\text{O}_3\text{-Nb}_2\text{O}_5$ phase diagram were determined, respectively. The current work can provide original data for the establishment of a thermodynamic database of Nb-bearing and REE-bearing slag system; the proposed *Tangent Line Rule* will promote the application of a spatial quaternary phase diagram.



Citation: Liu, C.; Qiu, J.; Liu, Z. Phase Equilibria in the System $\text{CaO-SiO}_2\text{-La}_2\text{O}_3\text{-Nb}_2\text{O}_5$ at 1400°C . *Metals* **2021**, *11*, 1892. <https://doi.org/10.3390/met11121892>

Academic Editor: Alexander McLean

Received: 27 October 2021

Accepted: 20 November 2021

Published: 24 November 2021

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Keywords: $\text{CaO-SiO}_2\text{-La}_2\text{O}_3\text{-Nb}_2\text{O}_5$; phase equilibria; rare earth; slag

1. Introduction

Bayan Obo deposit in northern China is a famous polymetallic ore deposit in the world. Until now, more than 71 kinds of elements existing in over 170 types of mineral phases have been detected in this deposit [1]. Among these valuable elements, niobium (Nb) and rare earth elements (REE) are two typical elements with huge reserves: the proven reserves of Nb and REE rank second and first in the world, respectively [2]. However, such a considerable amount of mineral reserve did not bring the expected metal production—an important reason is that the coexistence of complex mineral phases makes it difficult to predict the property of slag system at high temperatures [3], which has delayed the development of related processes. Consequently, almost all niobium resources and partial rare earth resources in Bayan Obo mineral can only be discarded into tailings. Over time, the accumulated tailings have not only caused waste of resources, but also brought potential harm to the environment [4]. In order to achieve the separation of Nb and REE elements from these tailing resources, some pyrometallurgical processes have been proposed recently [5–7]. Due to the special composition of tailings, $\text{CaO-SiO}_2\text{-La}_2\text{O}_3\text{-Nb}_2\text{O}_5$ slag system has proved to be a basic system in related pyrometallurgical processes. However, the lack of a related phase diagram has restricted the development of related processes.

For a quaternary phase diagram, it is necessary to discuss related representation types. In order to completely represent the real phase equilibrium, there are two types of spatial quaternary phase diagrams [8]: an *isothermal tetrahedron* phase diagram like Figure 1 and a *liquidus tetrahedron* phase diagram like Figure 2. The *isothermal tetrahedron*

phase diagram can express almost all the phase equilibrium information at a constant temperature, viz. single-liquid phase region, tie-lines in two-phase region, tie-triangles in three-phase region, and four-phase tetrahedron region [8]. The composition of solid solution phase can also be represented in this form of phase diagram. According to Figure 1, as long as the total composition of a slag is known, the related equilibrium phase relation and phase composition at this temperature can be clearly determined. Using the *Lever Rule*, we can even calculate the proportion of each equilibrium phase. However, as far as the *liquidus tetrahedron* phase diagram shown in Figure 2 is concerned, some detailed information at each temperature such as tie-lines, tie-triangles, and tie-tetrahedrons can no longer be expressed—the main purpose of the *liquidus tetrahedron* phase diagram is to show the liquidus temperature of each composition point in different primary phase fields. Nevertheless, *liquidus tetrahedron* phase diagram is still an indispensable expression of quaternary system—an important reason is that it is the only way to discuss the equilibrium *crystallization reaction type* in the phase diagram, which will be described in the following paragraph.

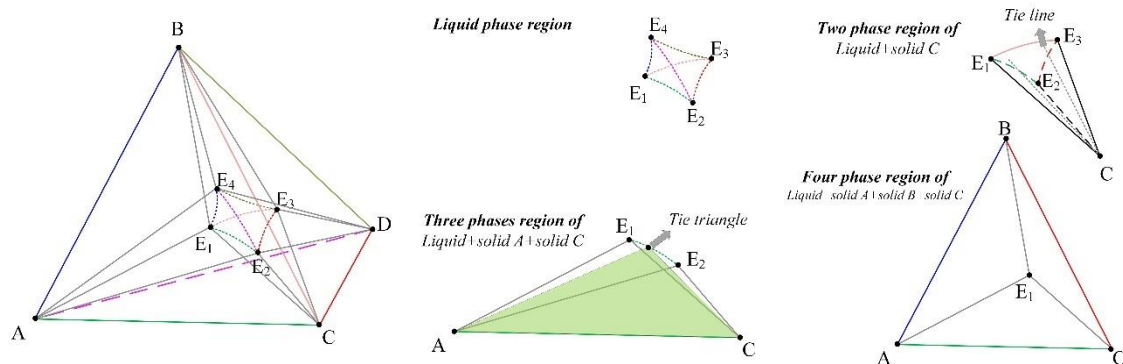


Figure 1. Isothermal tetrahedron phase diagram for quaternary system.

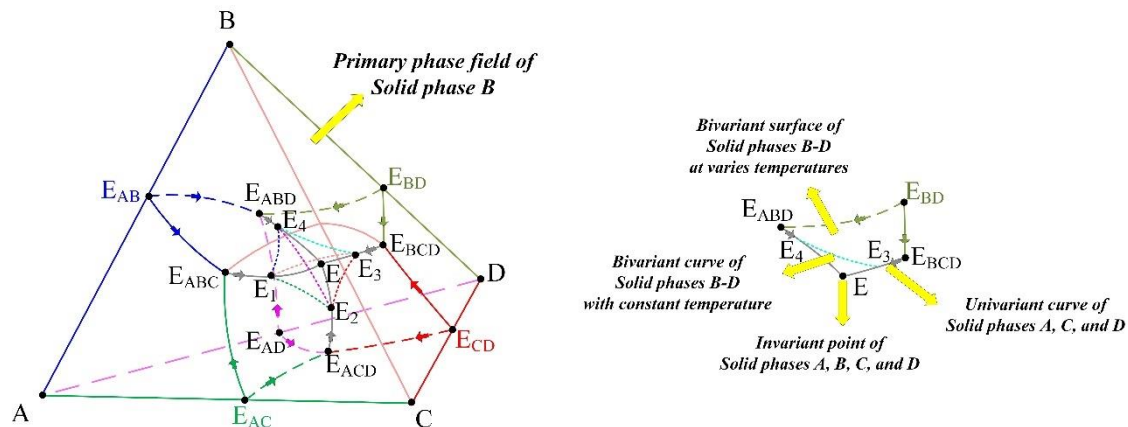


Figure 2. Liquidus tetrahedron phase diagram for quaternary system with liquid region at constant temperature (E1–E4).

Generally, some solid phase will crystallize from the liquid phase in sequence as temperature falls. When there are more than two kinds of solid phases in equilibrium with the liquid phase, the *crystallization reaction type* can be quite different: for instance, in A-B binary system, it can be Liquid = A + B, Liquid + A = B, or Liquid + B = A [9]. For quaternary systems, the *crystallization reaction type* will be more complex because there may be multiple solid phases at the same time, as listed in Table 1. Since the *crystallization reaction type* can be reflected in the instantaneous change of liquid phase composition as temperature falls, *liquidus tetrahedron* phase diagram proved to be an effective method to show the crystallization reaction type. Until now, some relevant rules for determining the

type of invariant or bivariant reaction have already been proposed [10,11], but the rule for univariant reaction in a quaternary phase diagram is still unknown.

Table 1. Crystallization reaction of quaternary phase diagram.

Crystallization Reaction	Free Degree	Typical Phase Equilibria	Rule
Invariant reaction (point)	0	Liquid phase + A + B + C + D	Lever Rule [10]
Univariant reaction (line)	1	Liquid phase + A + B + C	Unknown
Bivariant reaction (surface)	2	Liquid phase + A + B	Tangent Surface (line) Rule [11]

Besides spatial tetrahedral phase diagram, *pseudo-ternary* phase diagram is also widely used for representing the equilibrium phase relation in quaternary systems. Once *isothermal tetrahedron* phase diagram or *liquidus tetrahedron* phase diagram is determined, the *pseudo-ternary isothermal section* phase diagram or *pseudo-ternary liquidus* phase diagram can be easily obtained by intercepting these spatial *tetrahedron* phase diagrams by using different pseudo-ternary planes, respectively. However, it has to be said that since the pseudo-ternary phase diagram can only show a part of the spatial tetrahedral phase diagram, some information will inevitably be discarded—*pseudo-ternary isothermal section* phase diagram can only show the type of phase region, but cannot show the specific composition of each equilibrium phase (This is because the real equilibrium phase is not located in the pseudo-ternary plane); *pseudo-ternary liquidus* phase diagram can only show the primary phase field and related liquidus temperature, but cannot be used to discuss the type of crystallization reaction.

No matter what type of phase diagram is used, the related sub-system information is helpful for the construction of the multicomponent phase diagram. Table 2 shows the available studies on the sub-system phase diagrams of CaO-SiO₂-La₂O₃-Nb₂O₅ system. In the literature, only the CaO-SiO₂ system has experienced complete thermodynamic evaluation, while the experimental phase equilibrium data of Nb or REE containing systems are more or less lacking—in fact, this is the most important reason why these systems have not been thermodynamically assessed at present. The authors' team has systematically studied the CaO-SiO₂-La₂O₃-Nb₂O₅ quaternary phase diagram in recent years—the results are also listed in Table 2. Previously, most experiments were carried out below 1300 °C to obtain more information about primary phase fields, liquidus surfaces, the invariant reaction type, etc. On this basis, we think it is time to perform experiments above 1300 °C to provide more phase diagram information of this quaternary system now.

Table 2. Available studies on the CaO-SiO₂-La₂O₃-Nb₂O₅ system and its subsystems.

	System	Ref No.		System	Ref No.
Binary system	CaO-SiO ₂	[12–17]	Ternary system	CaO-SiO ₂ -La ₂ O ₃	[18]
	CaO-La ₂ O ₃	[19]		CaO-La ₂ O ₃ -Nb ₂ O ₅	[20–23]
	CaO-Nb ₂ O ₅	[24–27]		CaO-SiO ₂ -Nb ₂ O ₅	[28]
	La ₂ O ₃ -Nb ₂ O ₅	[29]		La ₂ O ₃ -SiO ₂ -Nb ₂ O ₅	
	La ₂ O ₃ -SiO ₂	[30,31]	Quaternary system	CaO-SiO ₂ -La ₂ O ₃ -Nb ₂ O ₅	[11,32–34]
	SiO ₂ -Nb ₂ O ₅	[35]			

The equilibrium experiment is the most scientific method used to study the phase equilibrium of slag systems, which has been successfully applied in many systems [36–42]. In the present work, the phase equilibrium of the $\text{CaO-SiO}_2\text{-La}_2\text{O}_3\text{-Nb}_2\text{O}_5$ system at 1400 °C with $w(\text{La}_2\text{O}_3)$ less than 25% was studied by this method. On the basis of the known phase diagram of sub-ternary systems, the *liquidus tetrahedron* phase diagram of $\text{CaO-SiO}_2\text{-La}_2\text{O}_3\text{-Nb}_2\text{O}_5$ quaternary system with 1400 °C isothermal surfaces were constructed. Then, some *pseudo-ternary liquidus* phase diagrams of $\text{CaO-SiO}_2\text{-}w\text{La}_2\text{O}_3\text{-Nb}_2\text{O}_5$ systems were obtained. In addition, a new rule named *Tangent Line Rule* was proposed to discuss the univariant reaction type of quaternary phase diagram. On this basis, some univariant reaction types of the $\text{CaO-SiO}_2\text{-La}_2\text{O}_3\text{-Nb}_2\text{O}_5$ system were judged based on the constructed spatial phase diagram. Besides, some bivariant reaction types corresponding to some modified bivariant surfaces were also discussed based on the *Tangent Surface Rule* proposed before [11].

2. Experimental Procedure

Powders CaO , SiO_2 , Nb_2O_5 , and La_2O_3 with purity 99.99% (provided by the Sinopharm Chemical Regent Co., Ltd. Beijing, China) were used as the raw material of equilibrium experiment. Approximate 1 g sample was placed in the platinum crucible in a MoSi_2 furnace (Precondar Co., Ltd, Luoyang, China), and then heated to 1600 °C and kept for 3 h for the sample to achieve homogeneous so that it can achieve equilibrium faster in the subsequent process; after that, the sample was cooled to 1400 °C and kept for 24 h. Then, the sample was quenched in ice-water to remain the phase equilibrium at experimental temperature. The equilibrium experiment was performed in air.

The Electron Probe Micro Analyzer (EPMA, type: JXA-8530F, JEOL Ltd., Akishima-shi, Japan) was then used to identify the phase equilibrium of the sample and measure the composition of each equilibrium phase. The composition of each equilibrium phase was calculated from the average value of six points. XRD (X'pert PRO type produced by Malvern Panalytical B.V., Almelo, The Netherlands) was used to help identify the type of equilibrium phase. Some details of the EPMA and XRD were as follows: EPMA—accelerating voltage = 15 kV, WD = 10.9 mm, beam current = 10 nA, standard samples $\text{Ca}(\text{CaCO}_3)$, $\text{Si}(\text{SiO}_2)$, $\text{Nb}(\text{Nb})$, $\text{La}(\text{LaPO}_4)$ from Chinese Academy of Geological Sciences, respectively; XRD—scanning range = 5–90 degrees.

There are three standards for whether the equilibrium was confirmed: 1. The crystalline phase was fully developed and there is no poor quenching area in the sample; 2. Six EPMA points were performed for each phase, and these six compositions were almost the same; 3. In the previous work, we found 24 h and 48 h have no obvious effect on the equilibrium state, i.e., 24 h is enough for the current system to achieve equilibrium.

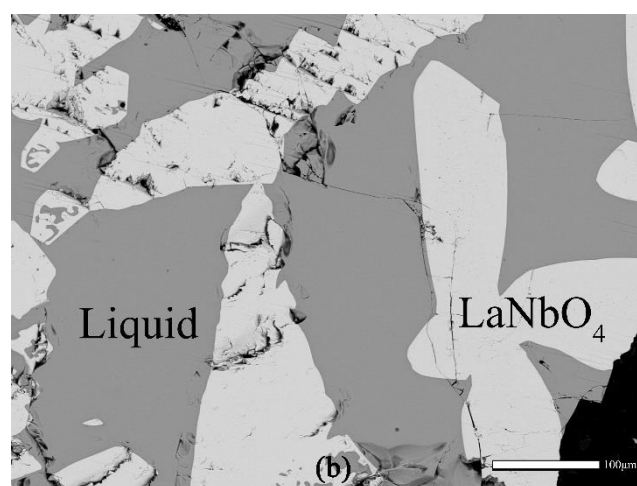
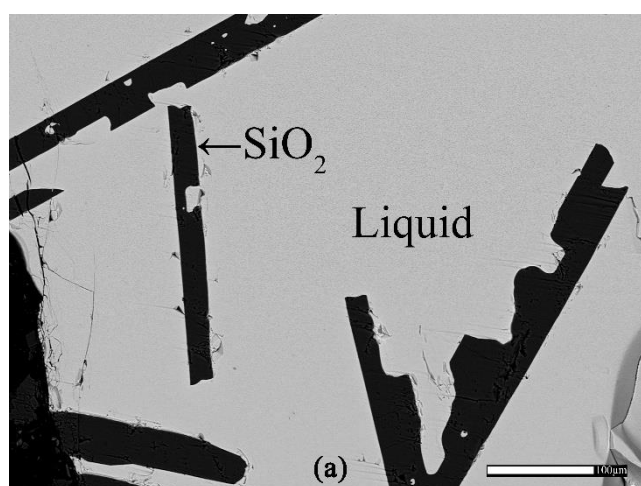
3. Experimental Results

According to the experimental result, five kinds of phase equilibria were determined from 25 samples. Table 3 lists the EPMA composition of each equilibrium phase; Figures 3 and 4 show the typical EPMA micrographs and XRD results, respectively. The details of phase equilibria are as follows.

For the phase equilibrium of “liquid phase+ SiO_2 ” shown in Figure 3a, the solid phase SiO_2 was more inclined to form a strip shape. Besides, the backscattered composition contrast of SiO_2 is almost black because there are no heavy elements in it. Figure 3b shows a typical “liquid phase+ LaNbO_4 ”. In some samples, a small amount of Ca and Si elements were detected in the LaNbO_4 phase. Figure 3c,d shows the morphology of CaNb_2O_6 and $\text{Ca}_2\text{Nb}_2\text{O}_7$ phases. Because the atomic number of Nb is much higher than that of Ca, it is difficult to distinguish CaNb_2O_6 and $\text{Ca}_2\text{Nb}_2\text{O}_7$ from each other only by the composition contrast; nevertheless, we could still distinguish them from their EPMA composition. Moreover, XRD analysis can also help verify the identification of CaNb_2O_6 and $\text{Ca}_2\text{Nb}_2\text{O}_7$. The obtained composition of liquid phase in the samples was then used to construct the *liquidus tetrahedron* phase diagram of the $\text{CaO-SiO}_2\text{-La}_2\text{O}_3\text{-Nb}_2\text{O}_5$ system.

Table 3. Composition of equilibrium phases in the samples, mass%.

No.	Phase	CaO	SiO ₂	Nb ₂ O ₅	La ₂ O ₃	No.	Phase	CaO	SiO ₂	Nb ₂ O ₅	La ₂ O ₃
#1	Liquid	21.27%	35.94%	37.49%	5.30%	#14	Liquid	23.47%	12.56%	58.40%	5.57%
	SiO ₂		100.00%				CaNb ₂ O ₆	17.39%		82.61%	
#2	Liquid	16.07%	19.61%	59.07%	5.26%	#15	Ca ₂ Nb ₂ O ₇	23.26%		70.09%	5.78%
	SiO ₂		100.00%				Liquid	20.78%	14.38%	56.22%	8.61%
#3	Liquid	14.99%	22.50%	52.85%	9.66%	#16	CaNb ₂ O ₆	17.42%		82.58%	
	SiO ₂		100.00%				Liquid	11.81%	11.19%	51.14%	25.86%
#4	Liquid	10.37%	17.51%	56.52%	15.60%	#17	LaNbO ₄	0.93%	1.20%	43.40%	54.47%
	SiO ₂		100.00%				Liquid	6.45%	11.22%	49.63%	32.70%
#5	Liquid	8.95%	20.71%	50.43%	19.91%	#18	LaNbO ₄			43.91%	56.09%
	SiO ₂		100.00%				Liquid	16.43%	11.30%	47.47%	24.80%
#6	Liquid	24.38%	53.29%	6.40%	15.93%	#19	LaNbO ₄	1.63%	1.55%	42.98%	53.84%
	SiO ₂		100.00%				Liquid	15.27%	14.71%	41.32%	28.70%
#7	Liquid	18.74%	38.40%	26.42%	16.43%	#20	LaNbO ₄			43.48%	56.52%
	SiO ₂		100.00%				Liquid	12.55%	11.15%	50.59%	25.70%
#8	Liquid	35.52%	59.49%	3.45%	1.55%	#21	LaNbO ₄	1.86%	2.40%	43.32%	52.42%
	SiO ₂		100.00%				Liquid	13.37%	14.50%	42.92%	29.21%
#9	Liquid	32.35%	54.90%	6.85%	5.91%	#22	LaNbO ₄			43.81%	56.19%
	SiO ₂		100.00%				Liquid	22.87%	13.94%	50.23%	12.96%
#10	Liquid	24.21%	41.97%	28.47%	5.35%	#23	Ca ₂ Nb ₂ O ₇	20.95%		70.55%	8.49%
	SiO ₂		100.00%				Liquid	28.11%	15.61%	50.35%	5.92%
#11	Liquid	21.37%	38.40%	30.14%	10.10%	#24	Ca ₂ Nb ₂ O ₇	23.22%		69.96%	6.82%
	SiO ₂		100.00%				Liquid	20.65%	12.26%	49.62%	17.47%
#12	Liquid	19.48%	28.57%	46.72%	5.23%	#25	Ca ₂ Nb ₂ O ₇	20.79%		69.32%	9.89%
	SiO ₂		100.00%				Liquid	33.71%	18.75%	39.71%	7.84%
#13	Liquid	22.22%	49.06%	13.16%	15.56%	#25	Ca ₂ Nb ₂ O ₇	24.61%		70.80%	4.59%
	SiO ₂		100.00%								

**Figure 3.** Cont.

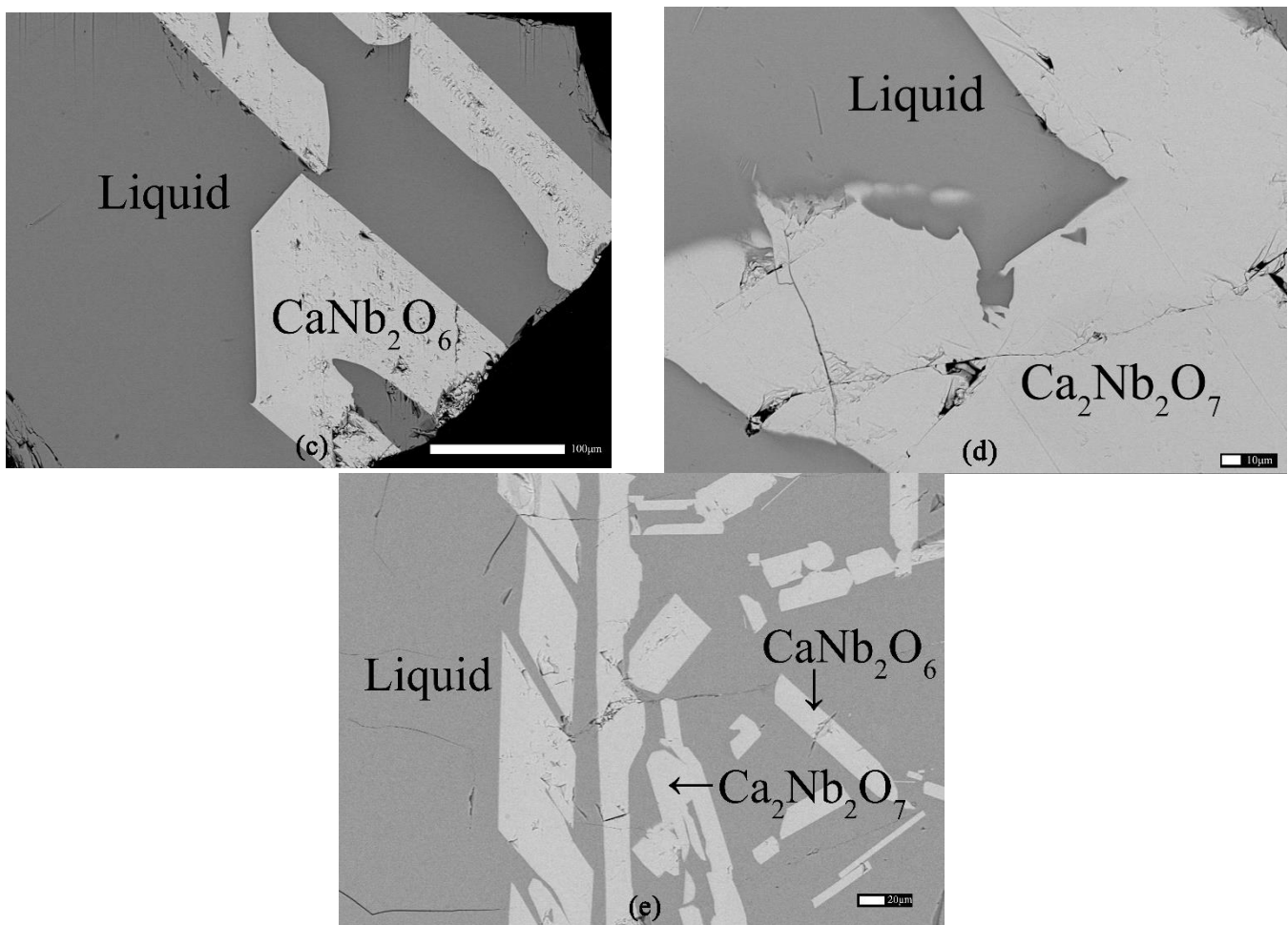


Figure 3. Typical EPMA micrographs of the samples (a) Liquid phase+ SiO_2 (Slag No.1) (b) Liquid phase+ LaNbO_4 (Slag No.16). (c) Liquid phase+ CaNb_2O_6 (Slag No.15) (d) Liquid phase+ $\text{Ca}_2\text{Nb}_2\text{O}_7$ (Slag No.22) (e) Liquid phase+ CaNb_2O_6 + $\text{Ca}_2\text{Nb}_2\text{O}_7$ (Slag No.14).

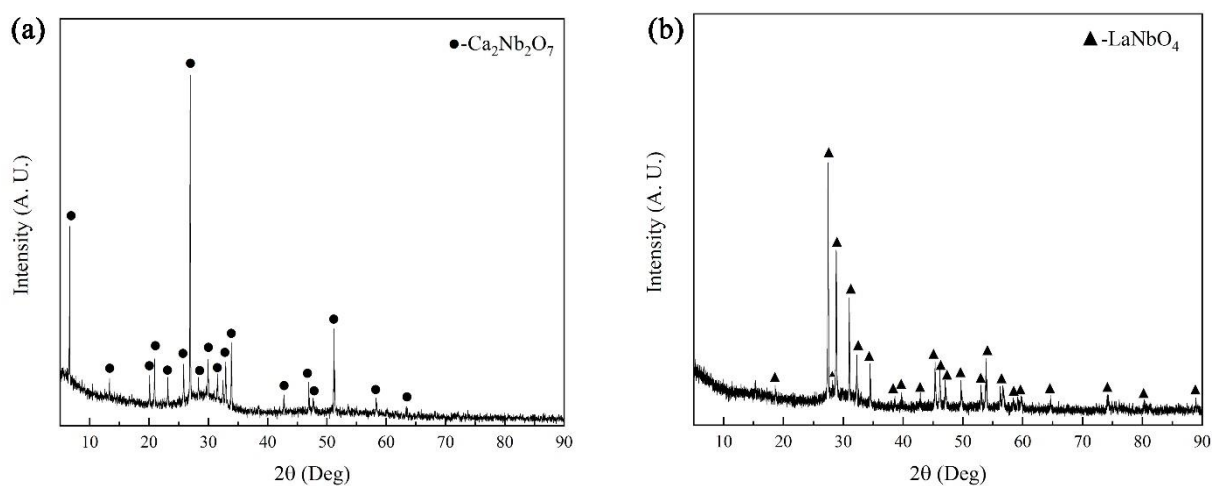


Figure 4. Cont.

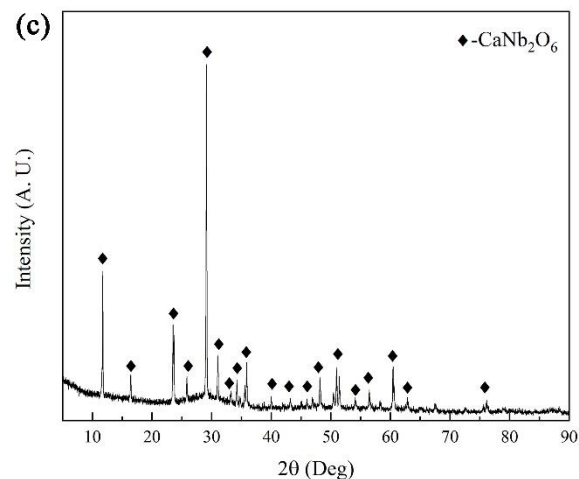


Figure 4. Typical XRD results of the samples (a) Liquid phase+ CaNb_2O_6 (Slag No.15) (b) Liquid phase+ LaNbO_4 (Slag No.16) (c) Liquid phase+ $\text{Ca}_2\text{Nb}_2\text{O}_7$ (Slag No.22).

4. Phase Diagram of the $\text{CaO-SiO}_2\text{-La}_2\text{O}_3\text{-Nb}_2\text{O}_5$ System

In the previous work [11–34], the author determined the primary phase fields of SiO_2 , CaNb_2O_6 , $\text{Ca}_2\text{Nb}_2\text{O}_7$, and LaNbO_4 in the $\text{CaO-SiO}_2\text{-La}_2\text{O}_3\text{-Nb}_2\text{O}_5$ phase diagram. At that time, the phase equilibrium of the $\text{CaO-La}_2\text{O}_3\text{-Nb}_2\text{O}_5$ system was not clear; consequently, some boundary information of bivariant surfaces in the $\text{CaO-SiO}_2\text{-La}_2\text{O}_3\text{-Nb}_2\text{O}_5$ phase diagram was merely speculated rather than accurately determined. In the current work, on the basis of the recently determined phase diagram of the $\text{CaO-La}_2\text{O}_3\text{-Nb}_2\text{O}_5$ system [20], these bivariant surfaces were modified. Moreover, the isothermal surface at 1400°C in the primary phase fields of SiO_2 , CaNb_2O_6 , $\text{Ca}_2\text{Nb}_2\text{O}_7$, and LaNbO_4 were constructed, respectively. Finally, some *pseudo-ternary liquidus* phase diagram of $\text{CaO-SiO}_2\text{-Nb}_2\text{O}_5$ pseudo-ternary system with different $w(\text{La}_2\text{O}_3)$ was obtained by intercepting the constructed $\text{CaO-SiO}_2\text{-La}_2\text{O}_3\text{-Nb}_2\text{O}_5$ *liquidus tetrahedron* phase diagram. For convenience, CaO , SiO_2 , Nb_2O_5 and La_2O_3 were sometimes abbreviated to C, S, N, and L in the following manuscript, respectively.

4.1. Liquidus Tetrahedron Phase Diagram of $\text{CaO-SiO}_2\text{-La}_2\text{O}_3\text{-Nb}_2\text{O}_5$ System

Figure 5 shows the modified primary phase fields of the $\text{CaO-SiO}_2\text{-La}_2\text{O}_3\text{-Nb}_2\text{O}_5$ system. The colorful surfaces are bivariant surfaces: LN-S(olive), CN-S(orange), $\text{C}_2\text{N-LN}$ (magenta), $\text{C}_2\text{N-CN}$ (gray), and LN-CN(cyan), respectively; the last three of them have been modified as they are adjacent to the $\text{CaO-La}_2\text{O}_3\text{-Nb}_2\text{O}_5$ system, while the other two bivariant surfaces are still the previous results [11].

It can be seen from Figure 5 that, in the low basicity region of the $\text{CaO-SiO}_2\text{-La}_2\text{O}_3\text{-Nb}_2\text{O}_5$ system ($w(\text{CaO})/w(\text{SiO}_2)$ less than 0.65), there is a wide primary phase field of SiO_2 . The two boundary lines shown in Figure 6 are the liquidus lines at 1400°C in the primary phase field of SiO_2 in the ternary phase diagrams of $\text{CaO-SiO}_2\text{-Nb}_2\text{O}_5$ [28] and $\text{CaO-SiO}_2\text{-La}_2\text{O}_3$ [18], respectively. On this basis, the 1400°C isothermal surface inside primary phase field of SiO_2 of the $\text{CaO-SiO}_2\text{-La}_2\text{O}_3\text{-Nb}_2\text{O}_5$ system was determined. The dash lines are tie-lines in the two-phase region of Liquid+ SiO_2 at 1400°C . Then, the bivariant line with liquidus temperature of 1400°C on the CN-S bivariant surface was obtained, namely the green line in Figure 6. Since the CN-S bivariant surface is the interface between the primary phase fields of CN and S, the obtained CN-S bivariant line can be further used to construct the 1400°C isothermal surface in the primary phase field of CN.

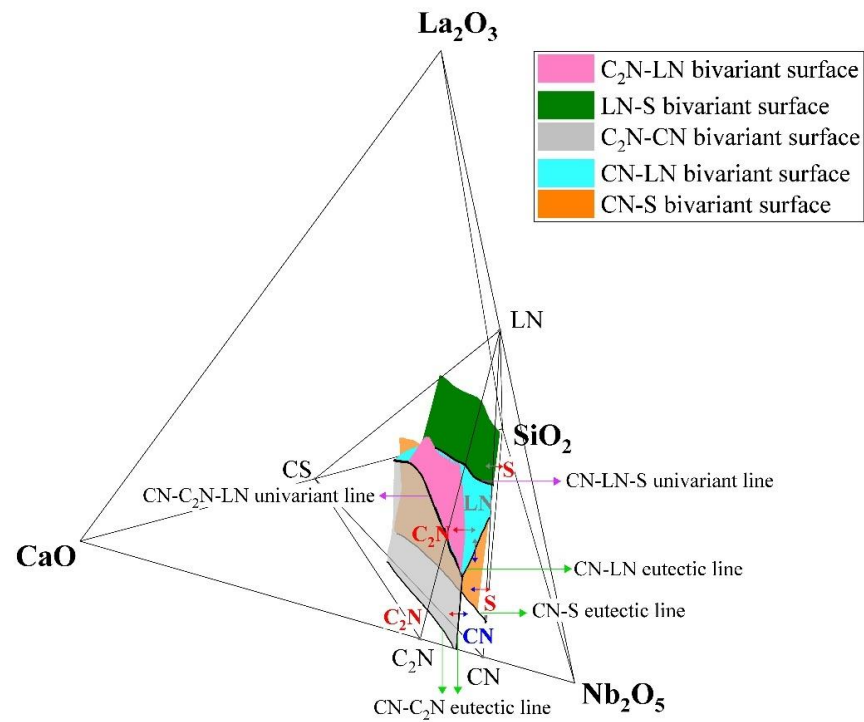


Figure 5. Primary phase fields of the CaO-SiO₂-La₂O₃-Nb₂O₅ system.

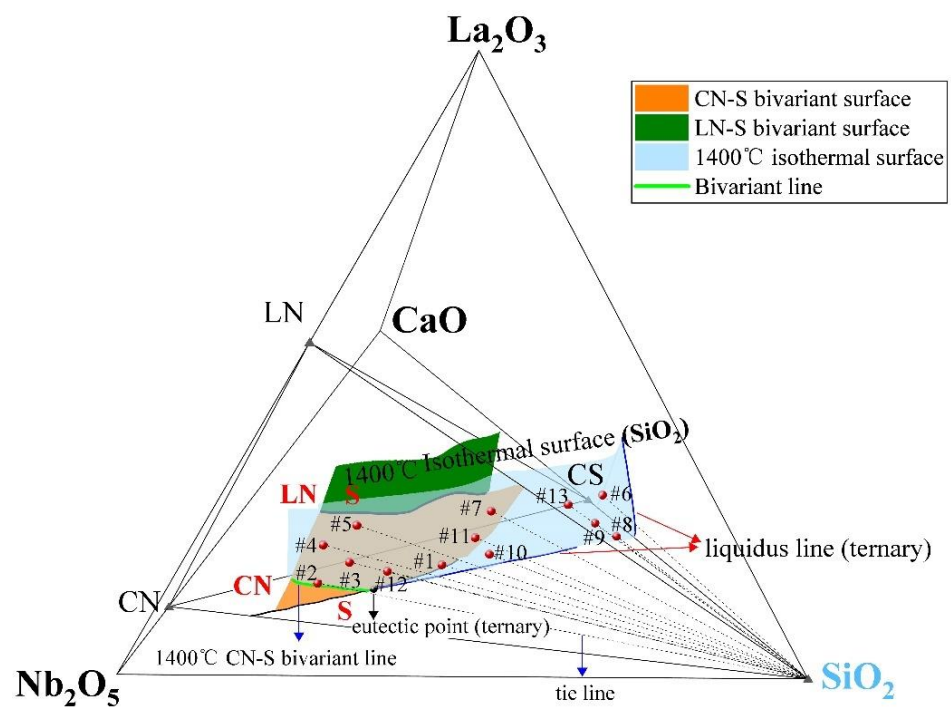


Figure 6. 1400 °C isothermal surface in the primary phase field of SiO₂.

As shown in Figure 5, with the increase of basicity, the primary phase field of low $w(\text{La}_2\text{O}_3)$ region changes from SiO₂ to CaNb₂O₆ and then to Ca₂Nb₂O₇, while that in the high $w(\text{La}_2\text{O}_3)$ region changes from SiO₂ to LaNbO₄. Figure 7 shows the 1400 °C isothermal surfaces in the phase fields of CN (magenta surface) and LN (green surface), respectively. From the isothermal surface of LN, it can be predicted that there will be a wide primary phase field of LN in the high La₂O₃ content region. On the basis of the 1400 °C isothermal surface in the primary phase field of CN, the 1400 °C bivariant line (green line)

on the CN- C_2N bivariant surface was obtained and then used to construct the 1400 °C isothermal surface in the primary phase field of C_2N , as shown in Figure 8. On the basis of the 1400 °C liquidus line in the primary phase field of C_2N in CaO-SiO₂-Nb₂O₅ [28] phase diagram, the 1400 °C red isothermal surface in the primary phase field of C_2N in CaO-SiO₂-La₂O₃-Nb₂O₅ phase diagram was determined.

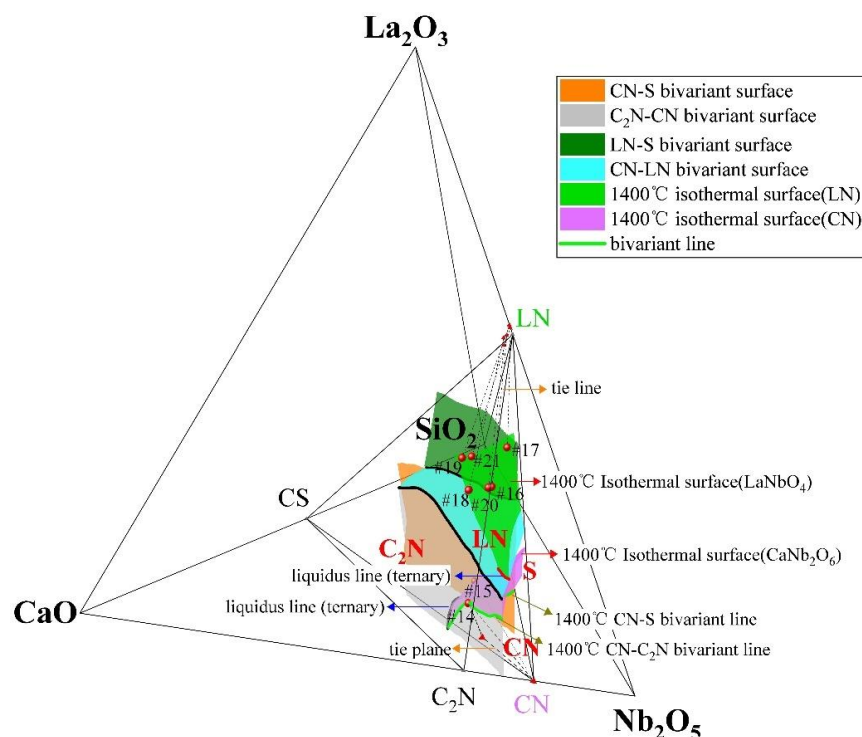


Figure 7. 1400 °C isothermal surface in the primary phase fields of CaNb₂O₆ and LaNbO₄.

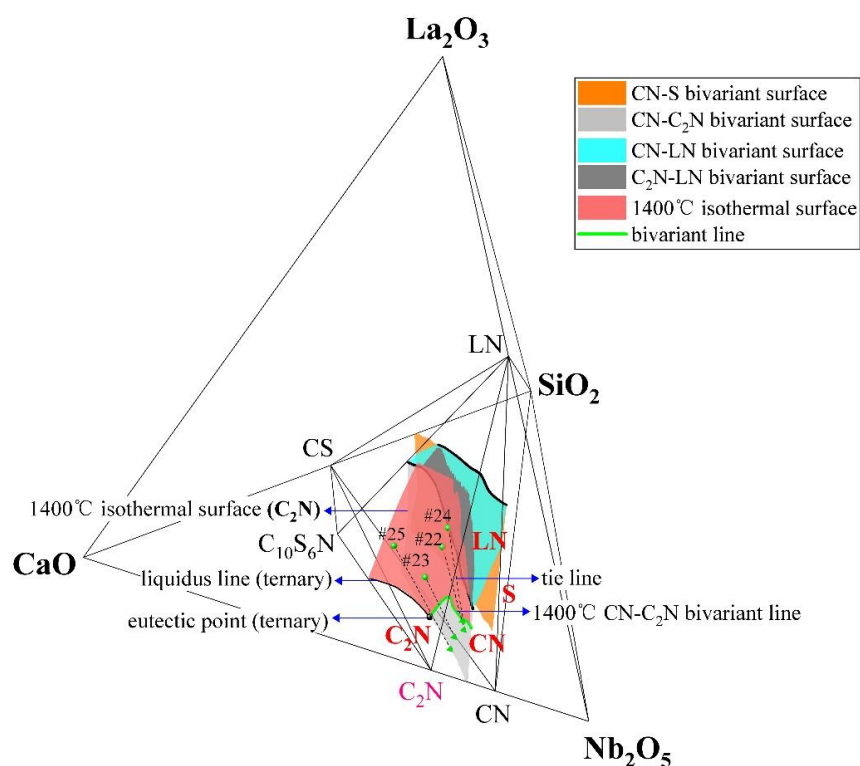


Figure 8. 1400 °C isothermal surface in the primary phase field of Ca₂Nb₂O₇.

4.2. Pseudo-Ternary Liquidus Phase Diagram of CaO-SiO₂-Nb₂O₅ Pseudo-Ternary System

On the basis of the constructed *liquidus tetrahedron* phase diagrams shown in Figure 5 to Figure 8, some *pseudo-ternary liquidus* phase diagrams of CaO-SiO₂-Nb₂O₅ pseudo-ternary system with different $w(\text{La}_2\text{O}_3)$ were determined, as shown in Figure 9.

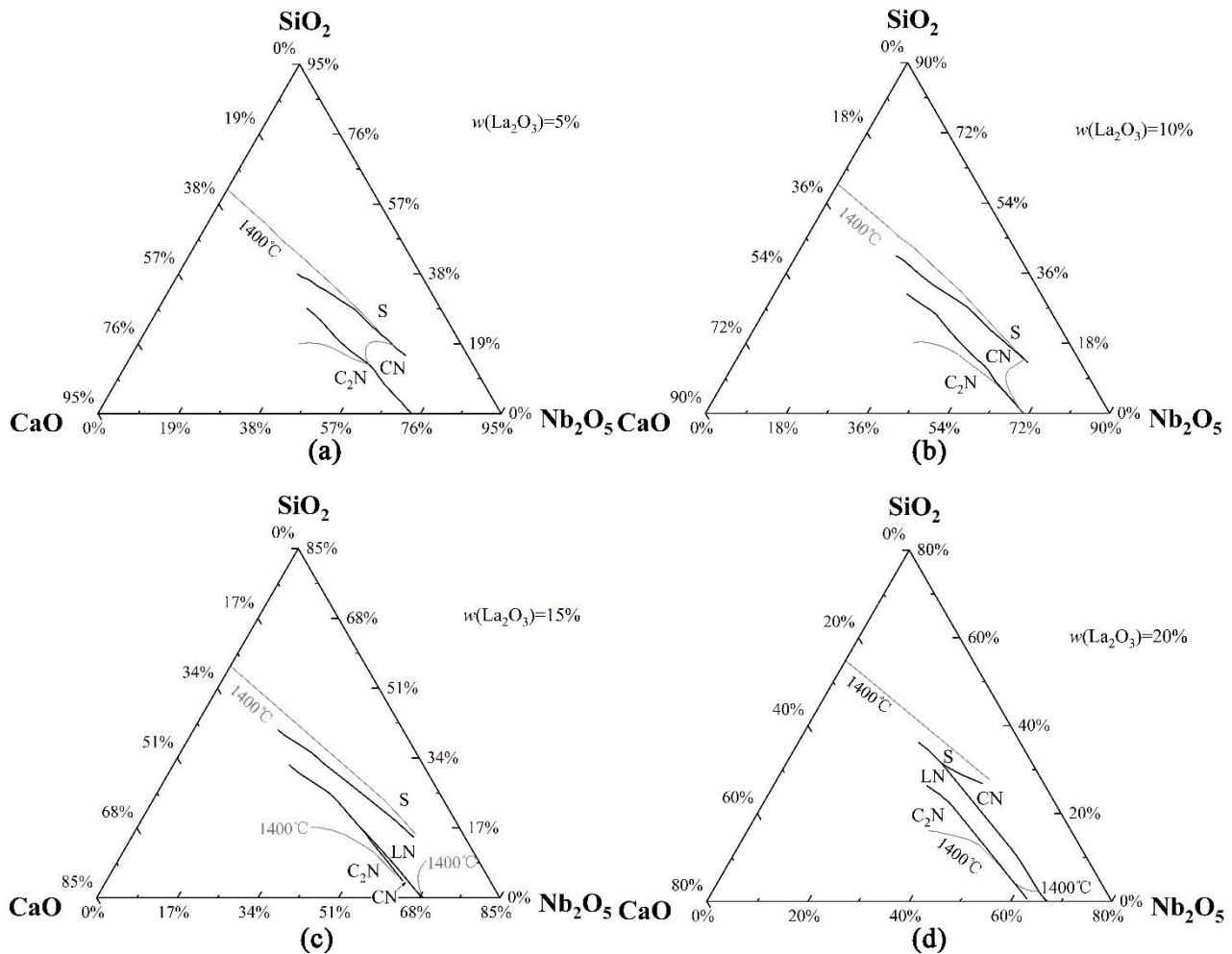


Figure 9. Pseudo-ternary liquidus phase diagrams of CaO-SiO₂-(5%, 10%, 15%, 20%)La₂O₃-Nb₂O₅ system (a) CaO-SiO₂-5%La₂O₃-Nb₂O₅ (b) CaO-SiO₂-10%La₂O₃-Nb₂O₅ (c) CaO-SiO₂-15%La₂O₃-Nb₂O₅ (d) CaO-SiO₂-20%La₂O₃-Nb₂O₅.

5. Univariant and Bivariant Reaction Type of CaO-SiO₂-La₂O₃-Nb₂O₅ System

In this section, some bivariant reaction types of the CaO-SiO₂-La₂O₃-Nb₂O₅ system were determined according to the *Tangent Surface Rule* [11]. Then, a *Tangent Line Rule* that can be used to discuss the univariant reaction type of quaternary phase diagram was proposed and applied to the CaO-SiO₂-La₂O₃-Nb₂O₅ system.

5.1. Bivariant Reactions

According to the *Tangent Surface Rule*, the crystallization reaction type of bivariant surface A-B in a quaternary system can be determined by the relative position of the intersection point of the *tangent plane passing through any point on this bivariant surface* and *corresponding Alkemade line A-B* [43]. When the intersection point is inside the *Alkemade line A-B*, the bivariant reaction type will be eutectic reaction Liquid = A + B; when the intersection point is outside the *Alkemade line A-B*, the bivariant reaction type will be peritectic reaction Liquid + A = B or Liquid + B = A.

Figure 10 shows the modified primary phase fields of the CaO-SiO₂-La₂O₃-Nb₂O₅ system. The bivariant surfaces of CN-C₂N(gray), CN-LN(cyan), and C₂N-CN(magenta)

were modified on the basis of the $\text{CaO-La}_2\text{O}_3\text{-Nb}_2\text{O}_5$ phase diagram [20]. According to the *Tangent Surface Rule*, the whole bivariant surfaces of $\text{C}_2\text{N-LN}$ and CN-LN can be determined as eutectic surfaces with crystallization reactions $\text{Liquid} = \text{C}_2\text{N} + \text{CN}$ and $\text{Liquid} = \text{CN} + \text{LN}$, respectively. For the $\text{C}_2\text{N-CN}$ bivariant surface, the crystallization reaction type in the yellow region in Figure 10 can be determined as peritectic $\text{Liquid} + \text{C}_2\text{N} = \text{CN}$, while in other regions, the reaction type will change to eutectic $\text{Liquid} = \text{C}_2\text{N} + \text{CN}$. As for the bivariant surfaces of CN-S and LN-S , since they were not modified, the crystallization reaction types are not different from that previously determined, namely, both of them are determined as eutectic reactions.

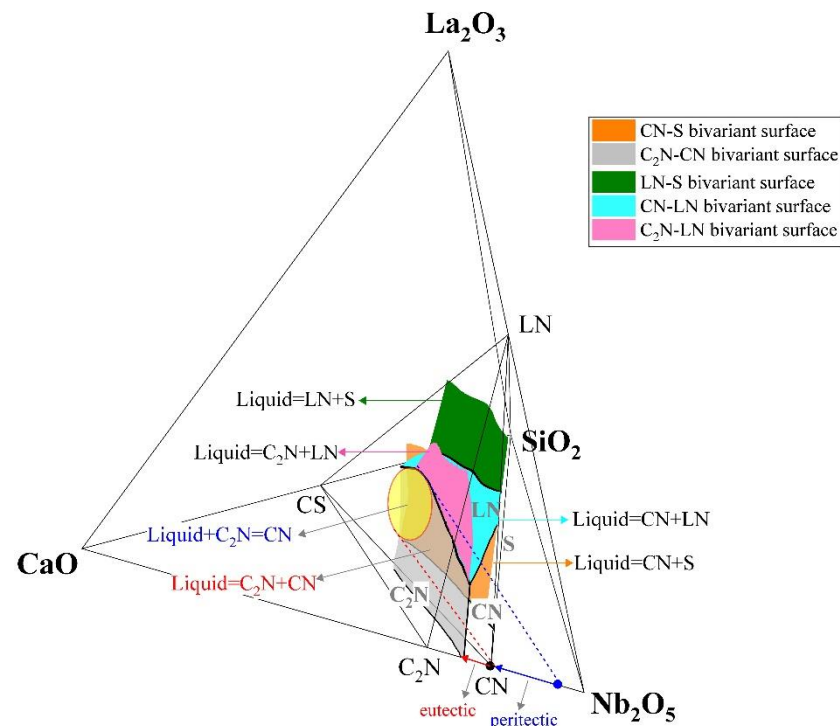


Figure 10. Schematic diagram for bivariant crystallization reaction type of $\text{CaO-SiO}_2\text{-La}_2\text{O}_3\text{-Nb}_2\text{O}_5$ phase diagram.

5.2. Univariant Reactions

Figure 11 shows a schematic diagram for the *Tangent Line Rule* in the quaternary system A-B-C-D . The curve $\text{E}_{\text{ABC-Q-P-E}_{\text{ABCD}}}$ is the univariant line corresponding to *Alkemade triangle* A-B-C . For the relative position of tangent line of curve $\text{E}_{\text{ABC-Q-P-E}_{\text{ABCD}}}$ and *Alkemade triangle* A-B-C , there are three typical positions: points $\text{S}_{\text{Q-ABC}}$, $\text{S}_{\text{P-Q}}$, and $\text{S}_{\text{P-ABCD}}$, which correspond to three kinds of univariant reaction type, viz. $\text{Liquid} = \text{A} + \text{B} + \text{C}$, $\text{Liquid} + \text{A} = \text{B} + \text{C}$, and $\text{Liquid} + \text{A} + \text{B} = \text{C}$, respectively. The reason why the univariant reaction type can be determined from the relative position is that the related intersection point is the total composition of instantaneous crystallization phases at each univariant temperature. The deduction process is as follows.

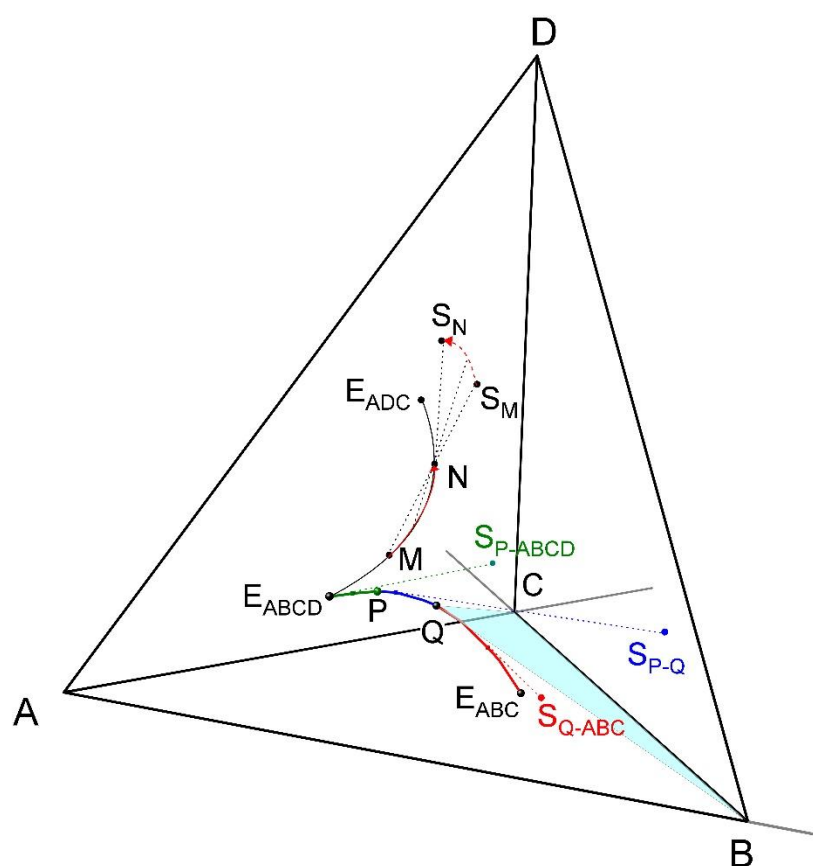


Figure 11. Schematic diagram for the *Tangent Line Rule* applicable to quaternary phase diagram.

$E_{ADC-N-M-E_{ABCD}}$ is the univariant line corresponding to the *Alkemade triangle* A-D-C; for any liquid point on this univariant line, the liquid phase will be in equilibrium with three solid phases: A, D, and C. Point S_M is the intersection point of the secant line MN and *Alkemade triangle* A-D-C; point S_N is the intersection point of the tangent line (passing through point N) and the *Alkemade triangle* A-D-C. When a slag sample with total composition at point N achieves equilibrium at temperature T_M (the univariant temperature at point M), there will be a four-phase coexistence of Liquid_M + A + C + D. The total composition of solid phases A, C, and D be at point S_M . When the discussed equilibrium temperature is close to T_N , the total composition of the solid phases will change in the direction of $S_M \rightarrow S_N$. Therefore, S_N can represent the total composition of instantaneous crystallization phase at T_N when the temperature is slightly disturbed to $T_N + dT$ (the value of dT is close to infinitesimal). According to the ternary *Lever Rule*, the reaction type corresponding to the three intersection points can be further determined, respectively, i.e., Liquid = A + B + C, Liquid + A = B + C, and Liquid + A + B = C introduced above.

Figure 12 shows the univariant lines in the $\text{CaO-SiO}_2\text{-La}_2\text{O}_3\text{-Nb}_2\text{O}_5$ phase diagram. According to the proposed *Tangent Line Rule*, the whole univariant line corresponding to *Alkemade triangle* CN-LN-S can be determined as eutectic line, i.e., $\text{Liquid} = \text{CN} + \text{LN} + \text{S}$. As for the univariant line corresponding to *Alkemade triangle* $\text{C}_2\text{N-CN-LN}$, the univariant reaction type can be quite different depending on its composition change. In the low $w(\text{Nb}_2\text{O}_5)$ region, as the related intersection points are outside of the *Alkemade triangle* $\text{C}_2\text{N-CN-LN}$ (just like any point on curve A-B), the univariant reaction proved to be a quasi-peritectic reaction, namely, $\text{Liquid} + \text{C}_2\text{N} = \text{LN} + \text{CN}$. In the high $w(\text{Nb}_2\text{O}_5)$ region, since the related intersection points become inside the *Alkemade triangle* $\text{C}_2\text{N-CN-LN}$ (just like any point on curve B-C), the univariant reaction will change to eutectic reaction, namely, $\text{Liquid} = \text{C}_2\text{N} + \text{CN} + \text{LN}$.

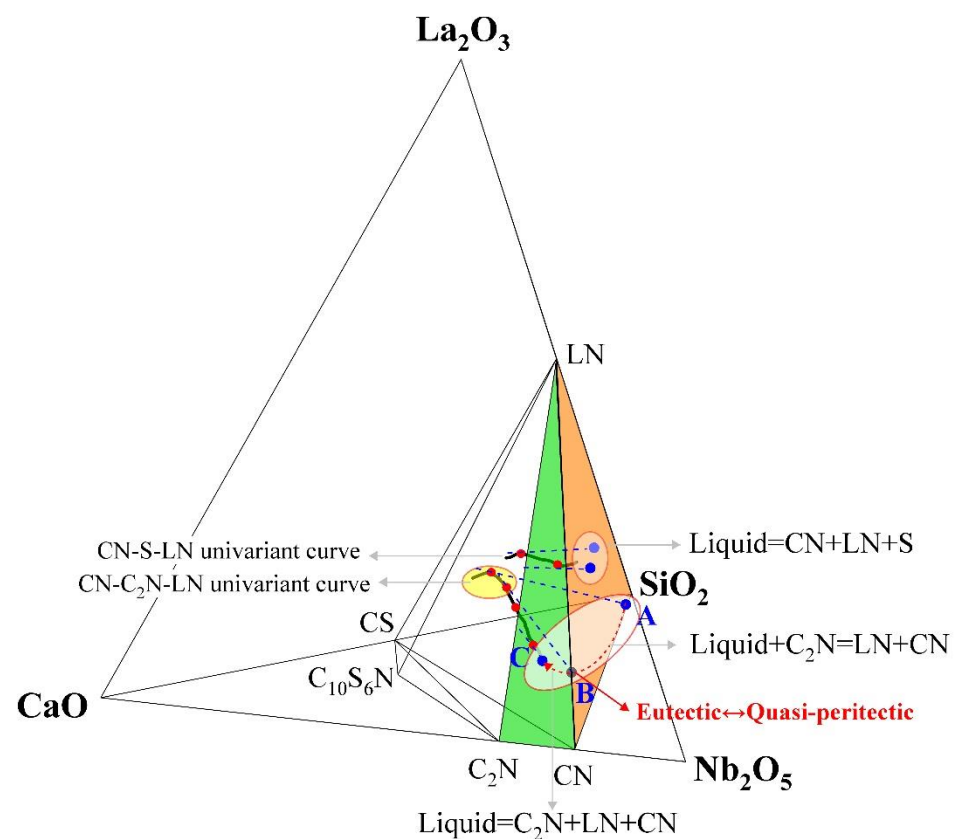


Figure 12. Schematic diagram for univariant crystallization reaction type of CaO-SiO₂-La₂O₃-Nb₂O₅ phase diagram.

6. Conclusions

In the present work, the phase equilibrium of the CaO-SiO₂-La₂O₃-Nb₂O₅ system at 1400 °C was experimentally studied. The primary phase fields of CaNb₂O₆, Ca₂Nb₂O₇, and LaNbO₄ were modified; the isothermal surfaces in the primary phase fields of SiO₂, CaNb₂O₆, Ca₂Nb₂O₇, and LaNbO₄ at 1400 °C were constructed, respectively. A new rule named *Tangent Line Rule* was proposed to discuss the univariant reaction type of quaternary phase diagram and applied to the CaO-SiO₂-La₂O₃-Nb₂O₅ phase diagram. The univariant line of CaNb₂O₆-SiO₂-LaNbO₄ proved to be a uniform eutectic line, while the univariant line of Ca₂Nb₂O₇-CaNb₂O₆-LaNbO₄ changed from a quasi-peritectic line to eutectic line with the increase of $w(\text{Nb}_2\text{O}_5)$. The bivariant surfaces of CaNb₂O₆-LaNbO₄, CaNb₂O₆-SiO₂, Ca₂Nb₂O₇-LaNbO₄, and LaNbO₄-SiO₂ were always eutectic surfaces, while the bivariant surface of Ca₂Nb₂O₇-CaNb₂O₆ changed from peritectic surface to eutectic surface with the increase of $w(\text{Nb}_2\text{O}_5)$.

Author Contributions: Data curation, C.L. and J.Q.; Formal analysis, C.L., J.Q. and Z.L.; Funding acquisition, C.L. and Z.L.; Investigation, C.L. and J.Q.; Methodology, C.L. and J.Q.; Project administration, C.L. and Z.L.; Software, J.Q. and Z.L.; Writing—original draft, C.L. and J.Q.; Writing—review & editing, J.Q. and Z.L. All authors have read and agreed to the published version of the manuscript.

Funding: This work was funded by the National Natural Science Foundation of China [grant numbers 51874082], and China Postdoctoral Science Foundation Funded Project [grant numbers 2020M680966].

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: This work was supported by the National Natural Science Foundation of China [grant numbers 51874082], and China Postdoctoral Science Foundation Funded Project [grant numbers 2020M680966].

Conflicts of Interest: The authors declare no conflict of interest.

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