Phase relationships in the La_2O_3–SrO–Nb_2O_5 system

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The phase relationships in the La_2O_3–SrO–Nb_2O_5 system were studied. The isothermal section at 1400°C of this system was determined. Within this system, two niobates, $LaSr_2Nb_2O_{8.5}$ (1-2-2) with hexagonal structure and $LaSr_2NbO_6$ (1-2-1) with cubic structure occurred. Same family compounds, $YSr_2Nb_2O_{8.5}$ and $LaSr_2Ta_2O_{8.5}$, could be also synthesized. In the SrO-rich area of the SrO–Nb_2O_5 subsystem, a tetragonal solid solution with a composition range of $Sr_{2-4}NbO_{4.5-6.5}$ (i.e. 66.7–80 at.% SrO) was also observed.

1. Introduction

As is well known, a number of niobates can be formed from niobium oxide, alkaline-earth oxides and/or rare-earth oxides. Many of these niobates possess perovskite [1] or tungsten brande [2] structure, and thus exhibit interesting electric properties. This leads to interest in the study of compound formation of niobates and phase relationships in the La_2O_3–SrO–Nb_2O_5 system.

In the ternary systems rare-earth oxides–alkaline-earth oxides–M_2O_5 (M = V, Nb, Ta), only the phase diagram for the Gd_2O_3–BaO–Nb_2O_5 system has been published [3]. Unfortunately, no ternary compound was reported in this system, except for two solid solutions in the BaO-rich area. In the La_2O_3–SrO–Nb_2O_5 system, there exists four La-niobates 1-0-5, 1-0-3, 1-0-1, 3-0-1 (La:Sr:Nb) in the La_2O_3–Nb_2O_5 subsystem and four Sr-niobates, 0-1-5, 0-1-2, 0-1-1, 0-5-4 in the SrO–Nb_2O_5 subsystem. The phase diagrams of these two binary systems have been published [4,5], but there still exists some uncertainty in the SrO-rich area of the SrO–Nb_2O_5 system [5]. No information is available for the La_2O_3–SrO–Nb_2O_5 ternary system and the La_2O_3–SrO binary system. The present work was undertaken to study the phase relationships in this ternary system.

2. Experimental

The starting powders used were La_2O_3, $SrCO_3$ and Nb_2O_5 (Alfa Chemicals) all with 99.9% purity. La_2O_3 powder was calcined at 1100°C for 2 h before use. The compositions studied are listed in table 1. The mixtures of powders were milled in an agate mortar with isopropanol as medium, dried and then isostatically pressed into pellets under 50000 psi. The pellets were heated in air at 1200–1650°C for solid state reaction. The liquid area was measured by observations of the melting behavior of compositions.

An automatic X-ray diffractometer (Rigaku) was used to analyse the phase compositions after heating and grinding off the surface layer of the pellets. The lattice parameters were determined with silicon as standard and corrected by the least-squares method.

3. Results and discussion

Table 1 lists the compositions investigated, the heating conditions and the phase compositions by X-ray analysis. For the La_2O_3–SrO binary system, all samples were heated in air at 1400–1650°C. As a result, only one compound $2La_2O_3$–SrO (4-1-0) was found. La_2O_3–2SrO (1-1-0) had been reported [6]

Table 1
Phase analysis of compositions after heating

Compositions (in at. ratio)				Heating conditions (in air)		Phase analysis of compositions by X-ray [a)]
La	Sr	Nb	O	T (°C)	t (h)	
La_2O_3–SrO–Nb_2O_5						
5	2	1	12	1400	4	La_2O_3, 1-2-1
3	3	1	10	1400	4	1-2-1, 4-1-0, SrO
				1650	3	1-2-1, 4-1-0, SrO
2	5	1	10.5	1400	4	SrO, 1-2-1, 4-1-0
				1650	3	SrO, 1-2-1, 4-1-0
1	11	3	20	1500	4	1-2-1, 0-2-1s.s., SrO
1	5	2	11.5	1400	4	0-2-1s.s., 1-2-1
1	2	1	6	1400	5	1-2-1, 3-0-1 (trace)
				1500	5	1-2-1, 3-0-1 (trace)
3	1	1	8	1500	4	1-2-1, 3-0-1, La_2O_3
3	2.5	2	12	1400	4	1-2-1, 3-0-1
				1500	3	1-2-1, 3-0-1
1	3	2	9.5	1500	4	1-2-2, 1-2-1, 0-2-1s.s.
1	5	4	16.5	1400	5	1-2-2, 0-5-4, 0-2-1s.s.
				1500	5	1-2-2, 0-5-4, 0-2-1s.s.
1	4.5	4	16	1400	5	1-2-2, 0-5-4, 0-2-1-s.s. (trace)
				1500	5	1-2-2, 0-5-4, 0-2-1s.s. (trace)
1	2	2	8.5	1400	3	1-2-2, 1-2-1 (trace), 3-0-1 (trace)
				1550	5	1-2-2
1	3	3	12	1500	6	1-2-2, 0-1-1
2	1	2	9	1400	3	1-2-2, 3-0-1, 1-0-1
3	3	4	17.5	1400	3	1-2-2, 3-0-1, 1-0-1
2	1	3	11.5	1200	3	1-2-2, 1-0-1, 0-1-1
				1300	3	1-0-1, 1-2-2, 0-1-1
				1400	3	1-0-1, 1-2-2, 0-1-1
1	2	3	11	1200	3	1-2-2, 1-0-1, 0-1-1
				1300	3	1-2-2, 1-0-1, 0-1-1
				1400	3	melted
1	2	3.5	12.25	1250	3	0-1-2, 0-1-1, 1-0-1
				1400	3	melted
2	1	5	16.5	1200	3	1-0-1, 0-1-2, 1-0-3
				1300	3	partly melted
				1400	3	melted
1	2	5	16	1200	3	0-1-2, 1-0-1
				1300	3	0-1-2, 1-0-1
				1400	3	melted
1	2	9	26	1250	3	0-1-2, 0-1-5, 1-0-3
				1400	3	melted
1	1	8	22.5	1250	3	1-0-5, 0-1-5, 1-0-3
				1400	3	melted
1	1	18	47.5	1250	5	Nb_2O_5, 1-0-5, 0-1-5 (trace)
				1400	3	melted
La_2O_3–SrO						
6	1	0	10	1400	4	4-1-0, La_2O_3
2	1	0	4	1400	4	4-1-0, SrO
4	3	0	9	1400	4	4-1-0, SrO
1	1	0	2.5	1500	4	SrO, 4-1-0
				1650	3	SrO, 4-1-0
1	2	0	3.5	1400	4	SrO, 4-1-0
SrO–Nb_2O_5						
0	5	4	15	1400	5	0-5-4
0	3	2	8	1400	5	0-5-4, 0-2-1
0	2	1	4.5	1500	4	0-2-1
0	3	1	5.5	1500	4	0-2-1s.s.
0	4	1	6.5	1500	3	0-2-1s.s.
0	5	1	7.5	1500	4	0-2-1-s.s., SrO
0	7	1	9.5	1500	3	SrO, 0-2-1s.s.

[a)] The numbers represent the compounds with the composition ratio of La:Sr:Nb.

Table 2
X-ray data for $4SrO–Nb_2O_5$

$d_{obs.}$ (Å)	$d_{cal.}$ (Å)	I/I_0	$h\,k\,l$
4.777	4.766	2	1 1 1
4.135	4.130	3	2 0 0
2.9211	2.9202	100	2 2 0
2.3848	2.3831	2	2 2 2
2.0650	2.0649	27	4 0 0
2.0634	2.0615	15	0 0 4
1.6858	1.6855	31	4 2 2
1.6846	1.6842	16	2 2 4
1.5886	1.5887	1	3 3 3
1.4601	1.4601	13	4 4 0
1.4585	1.4589	7	4 0 4
1.3964	1.3961	1	5 3 1
1.3059	1.3058	9	6 0 2
1.3043	1.3041	5	2 0 6

tetragonal: $a_0 = 8.260 \pm 0.004$ Å
$c_0 = 8.246 \pm 0.004$ Å

to form by heating in argon, however, it was not obtained in air in our experiments. The limited solid solution of $2La_2O_3–SrO$ (4-1-0) reported [6] was not checked in the present work. In the SrO-rich area of the $SrO–Nb_2O_5$ system, a new phase $4SrO–Nb_2O_5$ (0-2-1) was observed. The structure was identified to be tetragonal with $a = 8.260$ Å and $c = 8.246$ Å as listed in table 2. It might be derived from a cubic structure, because the separation of some X-ray peaks from those of the cubic pattern occurred, e.g. $hkl = 400$ and 004, 422 and 224, 440 and 404, 602 and 206. This new phase can form a tetragonal solid solution region with a composition range, $Sr_{2-4}Nb_2O_{4.5-6.5}$ (i.e. 66.7–80 at.% SrO). Other Sr-niobates and all La-niobates [4,5] have been confirmed in the present work.

From the results of the phase composition analysis listed in table 1, the subsolidus phase relationships in the $La_2O_3–SrO–Nb_2O_5$ system could be established. There exists two compounds $LaSr_2Nb_2O_{8.5}$ (1-2-2) and $LaSr_2NbO_6$ (1-2-1). Pure single-phase 1-2-2 could be obtained only at 1500°C after 5 h, otherwise it always was contaminated with traces of the other phases 1-2-1 and 3-0-1 at 1400°C. The compound 1-2-2 has a hexagonal structure with $a = 5.6584$ Å and $c = 19.385$ Å, which is the same as $La_{0.67}\square_{0.33}Sr_2(VO_4)_2$ ($a = 5.628$ Å, $c = 20.00$ Å) [7]. According to the latter composition, it would be 1-3-3. The composition 1-3-3, however, always contained a little $Sr_2Nb_2O_7$ (0-1-1) second phase. X-ray data of 1-2-2 and the corresponding vanadate are listed in table 3 for comparison. Other family compounds, $LaSr_2Ta_2O_{8.5}$ with $a = 5.6506$ Å, $c = 19.448$ Å and $YSr_2Nb_2O_{8.5}$ with $a = 5.6605$ Å, $c = 19.052$ Å

Table 3
X-ray data for $LaSr_2Nb_2O_{8.5}$; comparison with $La_{0.67}\square_{0.33}Sr_2(VO_4)_2$ [7]

$LaSr_2Nb_2O_{8.5}$				$La_{067}\square_{0.33}Sr_2(VO_4)_2$	
$d_{obs.}$ (Å)	$d_{cal.}$ (Å)	I/I_0	$h\,k\,l$	d (Å)	I/I_0
3.0376	3.0405	100	1 0 5	3.07	100
2.8256	2.8292	56	1 1 0	2.81	65
			0 0 9	2.222	<2
2.1873	2.1866	6	2 0 4	2.189	<2
			1 1 6	2.145	<2
2.0706	2.0712	42	2 0 5	2.074	50
1.8025	1.8026	30	1 0 10	1.841	45
1.6713	1.6712	26	1 2 5	1.673	40
1.6336	1.6334	7	3 0 0	1.625	30
1.5204	1.5203	14	0 2 10	1.541	30
1.4145	1.4146	8	2 2 0	1.407	25
1.3393	1.3392	8	1 2 10	1.355	20
1.2828	1.2826	3	1 3 5	1.281	30

hexagonal: $a_0 = 5.6584 \pm 0.0008$ Å
$c_0 = 19.385 \pm 0.005$ Å

$a_0 = 5.628$ Å
$c_0 = 20.00$ Å

Table 4
X-ray data for $YSr_2Nb_2O_{8.5}$ and $LaSr_2Ta_2O_{8.5}$

$YSr_2Nb_2O_{8.5}$				$LaSr_2Ta_2O_{8.5}$			
$d_{obs.}$ (Å)	$d_{cal.}$ (Å)	I/I_0	$h\ k\ l$	$d_{obs.}$ (Å)	$d_{cal.}$ (Å)	I/I_0	$h\ k\ l$
3.0105	3.0085	100	1 0 5	3.0447	3.0449	100	1 0 5
2.8291	2.8302	58	1 1 0	2.8256	2.8253	73	1 1 0
2.0616	2.0614	43	2 0 5	2.0711	2.0711	44	2 0 5
1.7776	1.7758	20	1 0 10	1.8075	1.8073	20	1 0 10
1.6668	1.6663	30	1 2 5	1.6702	1.6704	30	1 2 5
1.6333	1.6340	10	3 0 0	1.6314	1.6312	13	3 0 0
1.5057	1.5042	12	0 2 10	1.5225	1.5224	12	0 2 10
1.4153	1.4151	10	2 2 0	1.4126	1.4127	10	2 2 0
1.3293	1.3283	8	1 2 10	1.3401	1.3402	12	1 2 10
1.2810	1.2805	7	1 3 5	1.2815	1.2815	8	1 3 5
hexagonal: $a_0 = 5.6605 \pm 0.0006$ Å $c_0 = 19.052 \pm 0.004$ Å				$a_0 = 5.6506 \pm 0.0002$ Å $c_0 = 19.448 \pm 0.002$ Å			

Table 5
X-ray data for $LaSr_2NbO_6$

d (Å)	I/I_0	$h\ k\ l$
2.9436	100	2 2 0
2.0810	21	4 0 0
1.6996	24	4 2 2
1.6015	4	3 3 3
1.4707	8	4 4 0
1.4066	2	5 3 1
1.3157	6	6 2 0
1.2020	2	4 4 4
cubic: $a_0 = 8.324 \pm 0.004$ Å		

could also be synthesized. The latter was only stable up to 1300°C. The X-ray data of both compounds are also listed in table 4.

$LaSr_2NbO_6$ has a cubic structure with $a = 8.324$ Å, which is the same as the $(NH_4)_3FeF_6$ structure. It is similar to the member of the cryolite family close to the perovskite structure [8]. Other family compounds such as $LaSr_2TaO_6$ ($a = 8.27$ Å), $DyBa_2NbO_6$ ($a = 8.453$ Å), YBa_2NbO_6 ($a = 8.436$ Å) and so on have been reported [9,10]. The X-ray data of $LaSr_2NbO_6$ are listed in table 5, its lattice parameter is two times as large as that of the simple perovskite (ABO_3).

In the Nb_2O_5-rich area of the ternary system, many compositions melted at lower temperatures, showing

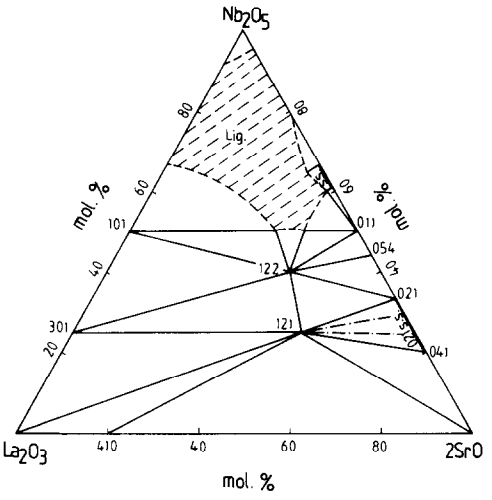

Fig. 1. Isothermal section at 1400°C for the La_2O_3–SrO–Nb_2O_5 system.

that there exists a liquid region. The 1400°C isothermal section of this region (fig. 1) was determined by the observation of the melting behavior of those compositions.

4. Conclusions

The phase relationships at 1400°C in the La_2O_3–SrO–Nb_2O_5 system were determined. Two compounds, $LaSr_2Nb_2O_{8.5}$ with a hexagonal structure and

$LaSr_2NbO_6$ with a cubic $(NH_4)_3FeF_6$ structure occurred in this system. Two similar compounds were also synthesized. In the SrO-rich area of the SrO–Nb_2O_5 subsystem, a tetragonal solid solution with the composition $Sr_{2-4}NbO_{4.5-6.5}$ (i.e. 66.7–80 at.% SrO) was also observed.

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