CHEMISTRY LETTERS, pp. 1331-1334, 1973. Published by the Chemical Society of Japan

SYNTHESIS OF LANTHANOID ALUMINATES (β-Al_2O_3 TYPE) USING ARC PLASMA FLAME

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New compounds with approximate formulas, $La_2O_3 \cdot 7Al_2O_3$, $Pr_2O_3 \cdot 7Al_2O_3$, $Nd_2O_3 \cdot 8Al_2O_3$ and $Sm_2O_3 \cdot 7Al_2O_3$, have been obtained through melting by arc plasma flame and separated into their own single phases by a proper chemical treatment. All of the compounds have the β-Al_2O_3 type structure. Excepting only $La_2O_3 \cdot 7Al_2O_3$, these compounds have the β-Al_2O_3 type structure at temperatures higher than 1500°C.

Existence of compounds with the β-Al_2O_3 type structure in the alkali oxide-alumina and the lanthanoid oxide-alumina systems has already been known. In the former system, compounds ($R_2O \cdot nAl_2O_3$; R=Na, K) have been found as the so-called β-Al_2O_3, β'-Al_2O_3 and β''-Al_2O_3 in which n=11$^{1)}$, n=7$^{2)}$ and n=5$^{2)}$, respectively. The crystal structure of β'-Al_2O_3 and β''-Al_2O_3 is of the β-Al_2O_3 type. In the latter system, compounds ($Ln_2O_3 \cdot mAl_2O_3$; Ln=La, Ce, Pr, Nd and Sm) with the β-Al_2O_3 type found up to date are only those of m=11$^{3-5)}$.

The purpose of this study is to examine the existence of any other phase having the β-Al_2O_3 type structure besides $Ln_2O_3 \cdot 11Al_2O_3$ in the Ln_2O_3-Al_2O_3 system, as reported for the R_2O-Al_2O_3 system.

The purity of $Ln_2O_3$$^{6)}$ and α-Al_2O_3 used in this experiment was higher than 99.9%. Powders (325 mesh under) of Ln_2O_3 and Al_2O_3 were weighed to several molar ratios and mixed by mortar grinding. The mixed powder was formed into pellets, 5mm in diameter and 1mm in thickness, by pressing at 10 ton/cm^2. The pellets were then sintered in air at 1000°C for five hours. The sintered pellets were subsequently transferred into an arc plasma flame furnace as shown schematically in Fig. 1. A Linde Type LPS 15/50H arc plasma equipment was used. The pellets were heated till they melted into drops almost spherical in shape (2-3mm in diameter). Subsequently the melt was rapidly solidified by terminating the arc current. The specimens obtained by the above method were examined by an X-ray diffractometer equipped with a pulse height analyzer using CuKα radiation. The X-ray patterns for specimens having an initial molar ratio Ln_2O_3:Al_2O_3 of 1:6, 1:7 and 1:8 resembled closely that of β-Al_2O_3. Although the new compound with the β-Al_2O_3 type structure could be detected at the above molar ratio, all the samples also contained some amount of $LnAlO_3$. A pure monophase of the β-type structure could not be realized under any experimental condition.

A chemical separation method as shown in Fig. 2 was employed to remove $LnAlO_3$ as the impurity. A sample having an initial molar ratio of Ln_2O_3:Al_2O_3=1:7 was used

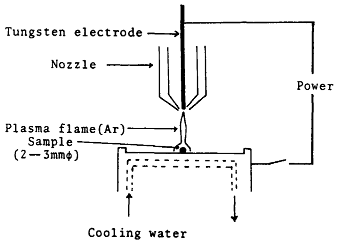


Fig. 1 The apparatus of arc plasma melting.

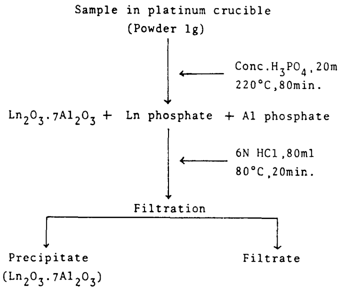


Fig. 2 The procedure of chemical treatment.

for this chemical treatment, because a large quantity of the new compound could be detected at this molar ratio. The samples obtained by the arc plasma melting were dissolved in conc. H_3PO_4 at 220°C for 80 minutes. The resulting residue mainly consisted of the new β-Al_2O_3 type compound and a slight amount of Ln-phosphate and Al-phosphate. The residue was treated in 6N HCl at 80°C for 20 minutes to remove the trace of impurities. After filtration and washing, a precipitate containing only the monophase with the β-Al_2O_3 type structure was obtained, and subsequently analyzed by the X-ray fluorescence method. The results of the chemical analysis and the cell parameter determination of the new lanthanoid compounds are shown in Table 1.

Table 1. The analytical values and cell dimensions of new lanthanoid aluminates

	a(Å)	c(Å)	c/a
$La_2O_3 \cdot 6.96Al_2O_3$	5.549	22.060	3.975
$Pr_2O_3 \cdot 7.00Al_2O_3$	5.555	22.000	3.960
$Nd_2O_3 \cdot 8.14Al_2O_3$	5.552	21.970	3.957
$Sm_2O_3 \cdot 6.80Al_2O_3$	5.536	21.950	3.965

Errors of analysis in chemical analysis are within 0.5%.

Compounds with a composition of $Ln_2O_3 \cdot 7$(or 8)Al_2O_3 were found only for Ln=La, Pr, Nd and Sm but not for the other kinds of lanthanoid. Such the compounds could not be obtained through solid state reaction, but readily produced by the melting method.

The X-ray diffraction patterns of specimens, as cast and after chemical separation, are shown in Figs. 3-1 and 3-2, respectively. Thereby the Nd_2O_3-Al_2O_3 sample was taken up as a typical example. Figure 3-1 shows a pattern of the mixture of $Nd_2O_3 \cdot 8Al_2O_3$ and $NdAlO_3$. The characteristic lines of the latter compound are indicated by a symbol P. The cell dimensions and lattice spacings of all the compounds obtained were determined from X-ray diffraction patterns taken by CuKα_1 or CuKα radiation at room temperature with a 114.6mm diameter Debye-Scherrer powder camera. Cohen's analytical method was applied to determine the accurate cell dimensions. The relative intensity of the diffraction lines was measured using an X-ray diffractometer equipped with a scintillation counter.

The X-ray diffraction data of $Ln_2O_3 \cdot 7$(or 8)Al_2O_3 were compared with those of $Ln_2O_3 \cdot 11Al_2O_3$. For comparison between $La_2O_3 \cdot 7Al_2O_3$ and $La_2O_3 \cdot 11Al_2O_3$, their lattice spacings and the relative intensities of their diffraction lines are shown in Table 2. The data of the two compounds are generally not in agreement between the both. This is particularly outstanding for the diffraction lines with strong intensity. For example the intensities of $d_{obs.}$=3.680Å, 2.754Å, 2.696Å and 1.542Å in $La_2O_3 \cdot 7Al_2O_3$ do not correspond to those of $d_{obs.}$=3.85Å, 2.75Å, 2.70Å and 1.548Å in $La_2O_3 \cdot 11Al_2O_3$, respectively (lines indicated by underline). With regard to the lattice spacing of the strongest intensity in each diffraction pattern, $d_{obs.}$=2.637Å for one compound is not consistent with $d_{obs.}$=1.548Å for the other compound. In Table 3, X-ray diffraction data of $Nd_2O_3\cdot8Al_2O_3$ and $Nd_2O_3\cdot11Al_2O_3$5) are shown. In this case too the compounds are different with respect to the lattice spacings and the intensities. Several lines in the pattern such as 3.272Å, 2.771Å, 1.711Å, 1.604Å and 1.567Å in $Nd_2O_3\cdot8Al_2O_3$ are not observed in $Nd_2O_3\cdot11Al_2O_3$. The intensities of the lines with the lattice spacings, 3.649Å, 2.742Å, 2.196Å and 1.540Å (indicated by underline) observed in the former, are apparently different from those of 3.67Å, 2.76Å, 2.21Å and 1.541Å observed in the latter.

As the data of the lower and the higher angle sides have not been reported about $La_2O_3\cdot11Al_2O_3$ and $Nd_2O_3\cdot11Al_2O_3$, a detailed comparison of the crystal data could not be performed. However from the above results, it seems established that the crystal structures of $La_2O_3\cdot7Al_2O_3$ and $Nd_2O_3\cdot8Al_2O_3$ are different from those of $La_2O_3\cdot11Al_2O_3$ and $Nd_2O_3\cdot11Al_2O_3$. The diffraction data of $Pr_2O_3\cdot7Al_2O_3$ and $Sm_2O_3\cdot7Al_2O_3$ are similar to those of $La_2O_3\cdot7Al_2O_3$ and $Nd_2O_3\cdot8Al_2O_3$. Thus it is apparent that the compounds, $La_2O_3\cdot7Al_2O_3$, $Pr_2O_3\cdot7Al_2O_3$, $Nd_2O_3\cdot8Al_2O_3$ and $Sm_2O_3\cdot7Al_2O_3$ exist in form of crystals with the β-Al_2O_3 type structure similar to that of $Ln_2O_3\cdot11Al_2O_3$ even though their molar ratios are fairly far from that of $Ln_2O_3\cdot11Al_2O_3$.

The powder samples of the new compounds were heated in an electric furnace at 1500°C in air for 20 hours. After cooled down slowly to room temperature, the

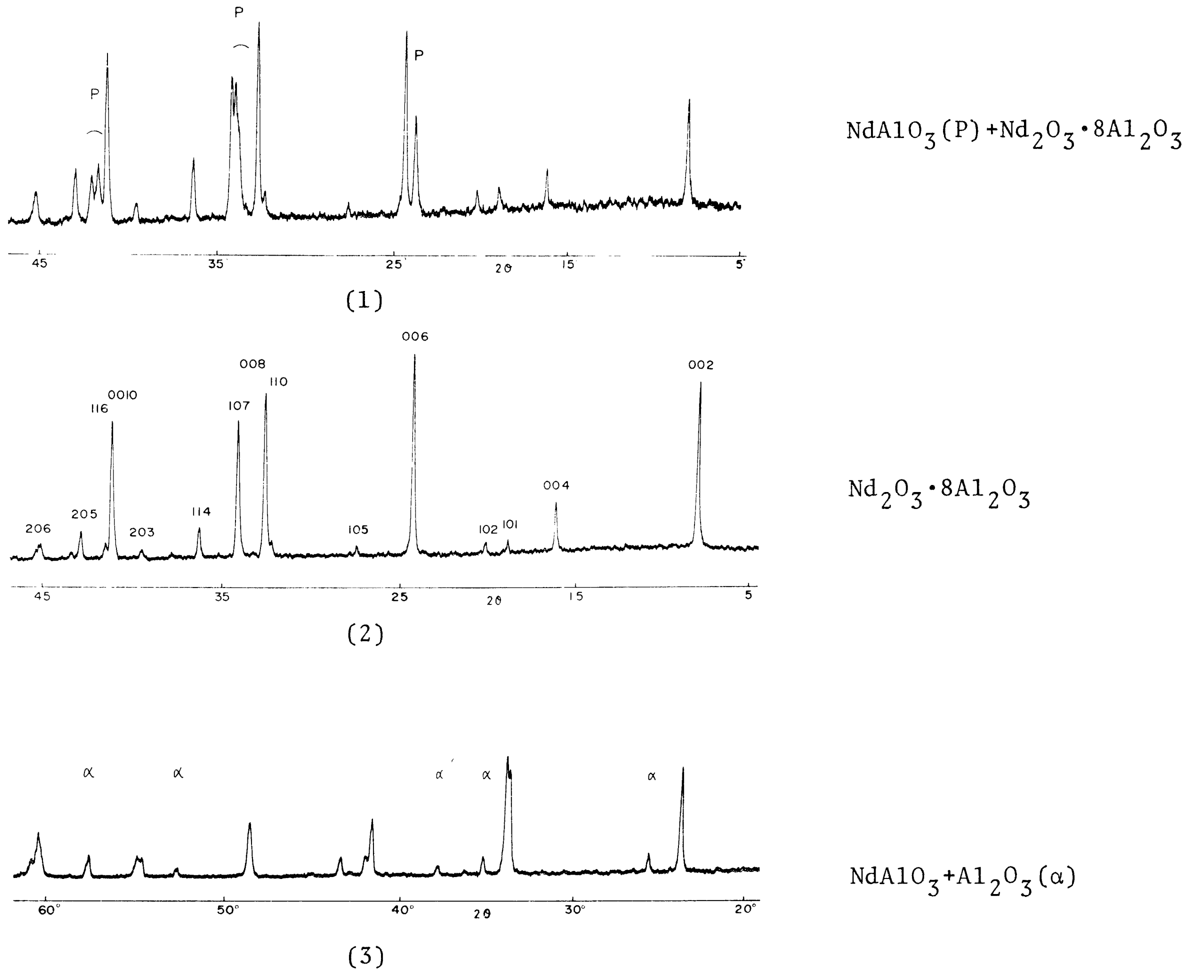
Table 2. X-ray powder diffraction data of $La_2O_3\cdot7Al_2O_3$ and $La_2O_3\cdot11Al_2O_3$

$La_2O_3\cdot7Al_2O_3$ a=5.549A,c=22.061A				$La_2O_3\cdot11Al_2O_3$ a=5.556A,c=22.030A	
h k l	$d_{obs.}$	$d_{cal.}$	I/I_o	$d_{obs.}$	I/I_o
0 0 2	11.080	11.031	80		
0 0 4	5.523	5.515	28		
1 0 1	4.709	4.696	12		
1 0 2	4.411	4.406	11		
1 0 3	4.040	4.023	5		
0 0 6	3.680	3.677	90	3.85	35
				3.43	31
1 0 5	3.258	3.250	5		
1 1 0	2.773	2.775	16		
0 0 8	2.754	2.758	79	2.75	37
1 1 2	2.696	2.691	5	2.70	87
1 0 7	2.637	2.635	100	2.66	85
1 1 4	2.486	2.479	32		
				2.40	48
2 0 3	2.286	2.284	9	2.30	23
0 0 10 2 0 4	2.205	2.206 2.203	83	2.20	69
1 0 9	2.185	2.184	13		
2 0 5	2.114	2.110	23	2.12	44
2 0 6 1 0 10	2.015	2.011 2.006	25	2.02	37
0 0 11	1.987	2.005	1		
1 0 11	1.851	1.851	14	1.90	44
0 0 12	1.838	1.838	5	1.862	23
1 1 10 1 2 4	1.728	1.727 1.725	4	1.725	23
2 0 9	1.717	1.716	7	1.701	33
0 3 0	1.600	1.602	5		
0 0 14 2 1 7	1.576	1.576 1.574	47	1.573	50
2 0 11 3 0 4	1.542	1.540 1.538	46	1.548	100
1 0 14	1.498	1.497	4		
1 0 15	1.406	1.406	7		
2 2 0	1.390	1.387	14	1.396	46
0 0 16	1.379	1.379	7	1.344	35
2 0 14	1.318	1.318	20	1.321	35
2 2 8	1.239	1.239	3	1.267	23
1 1 16	1.235	1.235	9		
0 0 18	1.229	1.226	1		
2 0 16	1.196	1.196	3	1.212	21
1 0 18 4 0 3	1.187	1.188 1.186	9	1.201	35
4 0 5	1.161	1.159	1		
2 0 17 2 2 11	1.142	1.142 1.141	5	1.144	31
3 0 14 1 1 18	1.121	1.123 1.121	9	1.123	23
0 0 20 4 0 8	1.103	1.103 1.101	33		
2 0 19 1 4 1	1.046	1.045 1.047	3		
2 2 14	1.043	1.041	5		
4 0 11	1.032	1.031	7		
1 0 21 1 1 20	1.026	1.027 1.025	10	1.015	42
2 0 20 0 0 22	1.002	1.002 1.003	4		
1 0 22	0.982	0.982	2		
1 0 25	0.868	0.868	5		
2 2 20	0.864	0.863	13		
2 0 25	0.828	0.828	50		

Table 3. X-ray powder diffraction data of $Nd_2O_3\cdot8Al_2O_3$ and $Nd_2O_3\cdot11Al_2O_3$

$Nd_2O_3\cdot8Al_2O_3$ a=5.551Å,c=21.97Å				$Nd_2O_3\cdot11Al_2O_3$	
h k l	$d_{obs.}$	$d_{cal.}$	I/I_o	$d_{obs.}$	I/I_o
0 0 2	11.00	10.99	76		
0 0 4	5.471	5.493	24		
1 0 1	4.718	4.696	13		
1 0 2	4.404	4.404	9		
1 0 3	4.012	4.019	5		
0 0 6	3.649	3.662	73	3.67	20
1 0 5	3.272	3.243	11		
1 1 0	2.771	2.776	14		
0 0 8	2.742	2.746	69	2.76	32
1 1 2	2.688	2.691	3		
1 0 7	2.624	2.628	100	2.64	100
1 1 4	2.473	2.477	35	2.48	50
2 0 3	2.284	2.284	10	2.29	16
0 0 10 2 0 4 1 1 6	2.196	2.197 2.202 2.212	75	2.21	42
1 0 9	2.171	2.177	9		
2 0 5	2.112	2.109	24	2.12	50
2 0 6 1 0 10	2.012	2.009 1.998	32	2.02	46
1 0 11	1.850	1.844	17	1.84	20
2 0 9	1.718	1.713	4	1.723	17
1 0 12	1.711	1.711	10		
0 3 0	1.604	1.602	15		
2 1 7	1.571	1.572	31	1.576	44
0 0 14	1.567	1.569	18		
3 0 14 2 0 11	1.540	1.538 1.536	57	1.541	85
				1.464	6
1 0 14	1.491	1.492	6		
1 0 15	1.400	1.401	12		
2 2 0	1.392	1.388	19	1.393	40
0 0 16	1.372	1.373	11		
				1.349	5
2 0 14 1 0 16	1.317	1.314 1.320	19	1.319	26
2 2 8	1.239	1.239	9		
0 0 18	1.226	1.221	3	1.233	14
1 0 18 4 0 3	1.184	1.183 1.186	11	1.187	14
4 0 5	1.160	1.159	3		
				1.142	10
3 0 14	1.117	1.121	13	1.119	14
0 0 20	1.098	1.099	17	1.101	10
2 2 14 2 0 19	1.039	1.040 1.042	9	1.043	14
4 0 11	1.030	1.030	8	1.033	12
1 0 21	1.022	1.022	11		
0 0 22	0.998	0.999	8		
1 0 25	0.864	0.865	7		
2 2 20	0.861	0.861	9		
2 0 25	0.825	0.825	42		

samples were examined by X-ray diffraction. In Fig. 3-3, the pattern of the $Nd_2O_3 \cdot 8Al_2O_3$ powder after the above treatment is shown as a typical example. There is no pattern corresponding to β-Al_2O_3, but that of the mixture of $NdAlO_3$ and α-Al_2O_3 (indicated by α in Fig. 3-3) is found. On the other hand, when $Nd_2O_3 \cdot 8Al_2O_3$ was quenched from higher than 1500°C to room temperature, this compound did not decompose. The above results show that the compound $Nd_2O_3 \cdot 8Al_2O_3$ has high temperature phase. The compounds $Pr_2O_3 \cdot 7Al_2O_3$ and $Sm_2O_3 \cdot 7Al_2O_3$ have the same high temperature phase as $Nd_2O_3 \cdot 8Al_2O_3$ has. However, $La_2O_3 \cdot 7Al_2O_3$ with β-Al_2O_3 type did not decompose by the heat treatment described above.



(1)

(2)

(3)

Fig. 3 The X-ray diffraction patterns.
(1) Specimen obtained by the arc plasma melting.
(2) Specimen after chemical seperation treatment.
(3) Specimen reheated at 1500°C.

References
1) C. A. Beevers and M. A. S. Ross, Z. Krist., 97, 57 (1937).
2) G. Yamaguchi and K. Suzuki, Bull. Chem. Soc. Japan, 41, 93 (1968).
3) R. S. Roth and S. Hasko, J. Amer. Ceram. Soc., 41, 146 (1958).
4) I. A. Bondar and N. V. Vinogradova, Izu. An. SSSR, Ser. Khim., 785 (1964).
5) N. A. Godina and E. K. Keler; Izu, Akad. Nauk, Ser. Khim., 1, 24 (1966).
6) Pr_6O_{11} was used in the case of Ln=Pr.

(Received September 29, 1973)