

Synthesis of Ba-V-O New Compound Containing Low Valence State Vanadium Ions

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ABSTRACT

A new compound containing low valence state vanadium ions (av. +2.57), $BaV_{14}O_{19}$, was synthesized by solid state reaction at 1773 K under flowing Ar. The X-ray diffraction peaks of $BaV_{14}O_{19}$ can be indexed on monoclinic unit cells with the lattice parameters of $a=7.654 \text{ \AA}$, $b=12.639 \text{ \AA}$, $c=7.011 \text{ \AA}$, $\beta=107.85^\circ$. $BaV_{14}O_{19}$ has definite composition and does not show any nonstoichiometry. $BaV_{14}O_{19}$ is stable and not oxidized at ambient condition although it contains large amount of low valence state vanadium ions.

Key words : low valence state vanadium, barium vanadate, solid state reaction

1. INTRODUCTION

Vanadium has $3d^34s^2$ electrons in its outer shell and its ion shows various valence states from +2 to +5. A lot of studies have been reported in detail on their crystal structures and physical properties of various vanadium oxides. However, there are a few reports on complex vanadium oxides containing low valence state vanadium ions, while many complex vanadium oxides containing high valence state vanadium ions have been studied. In the Ba-V-O system (see Fig. 1 [1 ~ 17]), a few compounds containing low valence state vanadium ions have been also reported so far.

When the ratio of the number of cation to that of O^{2-} increases with decreasing the charge of cation, for example $V_2O_5(V^{3+}) \rightarrow VO(V^{2+})$, interstices between adjacent O^{2-} decrease by filling of cation, and the cation becomes closer each other. The shorter the distance between cation and cation becomes, the more the possibility of overlapping between d-orbitals of cations increases. An example of the formation of metal-metal bond in oxide can be seen in Nb_6 octahedron of NbO [18]. Such oxides having metal-metal bond are interesting since they can be positioned between ionic compounds and intermetallic compounds groups. In the sight of crystal chemistry, the formation of anomalous polyhedron led by metal-metal bond is expected. In addition, their physical properties, especially electrical and magnetic properties, would be also remarkable.

The ionic radii of titanium and vanadium ions are

larger than that of other transition metals as iron, nickel and cobalt with the same number of electrical charge [19]. From this point of view, transition metal ions in IV~V group would be more suitable to form metal-metal bonds in complex oxides. In addition, the low valence state vanadium ion does not seem to be so unstable because VO and V_2O_3 are not oxidized speedily at ambient condition. The possible occurrences of new compounds containing low valence state vanadium ions are expected.

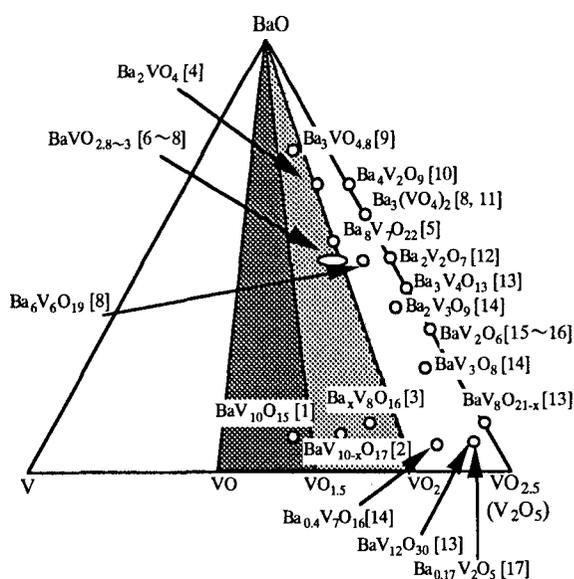


Fig. 1. Ternary phases in Ba-V-O system.

This paper reports the occurrences of a new compound containing low valence state vanadium ions, which was found in our study in the ternary Ba-V-O system.

2. EXPERIMENTAL

BaCO₃, V₂O₅ and V powders were used as starting materials for preparing BaV₁₄O₁₉. The amount of oxygen on the surface of V powder was measured previously by the thermogravimetric analysis and that was counted. The appropriate mixture was pelletized and put in a Mo foil to avoid a reaction with carbon heater. Then, the sample was calcined at 1773 K for 12 h in flowing Ar using a radio frequency induction heating furnace. The sample after the heat treatment was ground and reheated under the same condition.

The X-ray powder diffraction (XRD) pattern of the product was recorded using graphite monochromated CuK α radiation. The lattice parameters were calculated by the least-squares method using diffraction peaks collected with the step increment of 0.002°. Silicon powder was used as an internal standard. The

ITO method was used for indexing the XRD peaks of the product. Transmission electron diffraction (TED) images were taken by JEM-2000EX II, operating at 200 kV. Thermogravimetric analysis was performed in air between room temperature and 1273 K.

3. RESULTS and DISCUSSIONS

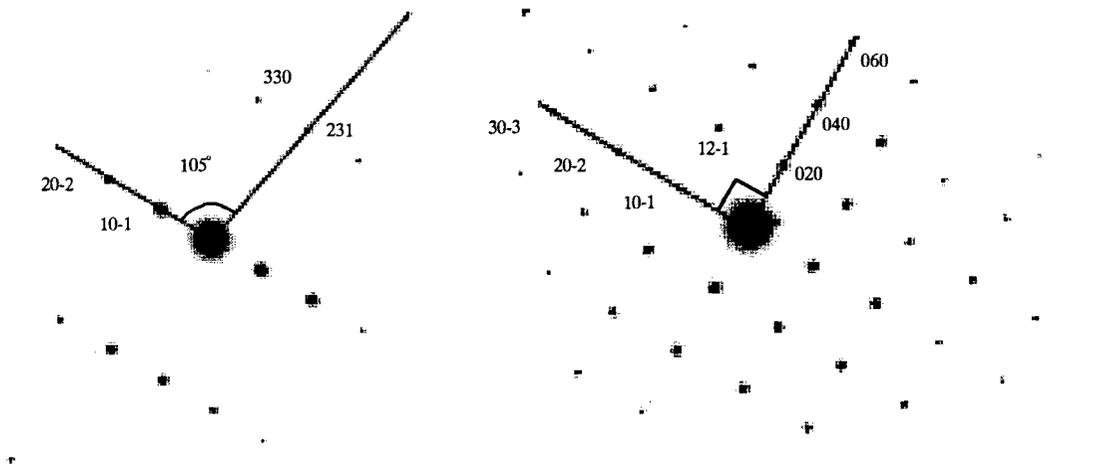
A black product was obtained after the heat treatment. The XRD pattern of the product was different from that of other Ba-V-O ternary compounds reported. All diffraction peaks could be indexed on a monoclinic cell by the ITO method, and the lattice parameters were calculated to be $a=7.654$ Å, $b=12.639$ Å, $c=7.011$ Å, $\beta=107.85^\circ$. The diffraction data is listed in Table I.

TED images are shown in Fig. 2. Diffraction images could be indexed using the lattice parameters mentioned above, and the observed face angles were consistent with the calculated values well. As the result, the lattice parameters, $a=7.654$ Å, $b=12.639$ Å, $c=7.011$ Å, $\beta=107.85^\circ$, prove to be adequate.

Both XRD patterns and TED images showed 0k0 reflections with $k=2n$, indicating that the crystal

Table I
X-ray powder diffraction data of BaV₁₄O₁₉
monoclinic, $a=7.654$ Å, $b=12.639$ Å, $c=7.011$ Å, $\beta=107.85^\circ$

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs} /Å	<i>d</i> _{cal} /Å	I/I0	<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs} /Å	<i>d</i> _{cal} /Å	I/I0	<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs} /Å	<i>d</i> _{cal} /Å	I/I0
0	2	0	6.304	6.320	1	2	5	-1	2.0902	2.0893	1	2	7	1			
1	3	0	3.651	3.647	8	2	2	2	2.0414	2.0385	100	1	8	-1	1.5256	1.5243	3
2	0	0		3.643		3.643	5	0		-1		1.5238					
1	2	1	3.566	3.559	30	3	3	-2	1.9840	1.9840	5	4	3	1	1.5251	1.5251	2
0	3	1		3.563		3.561	1	6		-1		1.5165					
2	1	-1	3.343	3.337	19	3	2	1	1.9686	1.9808	2	1	1	4	1.5180	1.5182	2
0	0	2		3.339		3.339	3	4		-1		1.5181					
1	1	-2	3.161	3.160	23	1	0	3	1.8926	1.9659	4	2	4	-4	1.5067	1.5059	3
0	4	0		3.156		3.160	0	3		3		1.5065					
2	2	0	2.954	2.951	9	2	3	-3	1.8569	1.9671	4	1	7	2	1.4832	1.4822	2
0	2	2		2.952		2.952	1	6		1		1.4832					
2	0	-2	2.7864	2.7811	16	1	6	1	1.7814	1.8914	2	3	6	1	1.4373	1.4822	23
2	1	1		2.7811		2.7811	4	1		-1		1.4490					
2	3	-1	2.6752	2.7849	6	1	5	2	1.7424	1.8558	4	2	8	0	1.4277	1.4494	17
1	4	-1		2.7859		2.7859	4	0		-2		1.4475					
2	2	-2	2.5497	2.6747	8	2	4	2	1.7310	1.7796	2	1	3	4	1.4021	1.4361	3
1	3	-2		2.6747		2.6747	0	6		2		1.4372					
1	4	1	2.3885	2.5477	10	3	5	0	1.7424	1.7513	3	1	6	3	1.4277	1.4372	2
3	0	-1		2.5467		2.5467	1	7		0		1.4357					
2	4	0	2.3640	2.3869	6	4	2	0	1.7310	1.7501	2	3	5	2	1.4021	1.4264	2
1	5	0		2.3881		2.3881	3	4		1		1.4279					
3	1	0	2.3373	2.3849	3	0	7	1	1.6698	1.7429	4	0	8	2	1.3929	1.4279	1
2	3	1		2.3849		2.3849	2	0		-4		1.4279					
0	5	1	2.2956	2.3612	7	2	0	-4	1.6698	1.7309	4	3	2	3	1.3787	1.4001	2
3	2	-1		2.3621		2.3621	2	1		-4		1.4008					
1	0	-3	2.1064	2.3370	3	0	0	4	1.6698	1.6684	4	0	7	3	1.3787	1.4019	2
1	3	2		2.3370		2.3370	2	1		3		1.4017					
0	4	2	2.1925	2.2929	14	2	2	-4	1.6698	1.6695	4	4	5	-3	1.3787	1.4021	2
0	1	3		2.2929		2.2929	1	4		3		1.4021					
2	1	-3	2.1064	2.2943	4	1	4	3	1.6698	1.6692	4	2	8	-2	1.3787	1.3930	1
1	2	-3		2.2943		2.2943	4	1		-3		1.3930					
0	6	0	2.1064	2.1908	4	4	1	-3	1.6698	1.6702	4	1	9	0	1.3787	1.3789	2
2	1	-3		2.1908		2.1908	2	7		-1		1.3789					
1	2	-3	2.1064	2.1924	4	2	7	-1	1.6698	1.6228	4	0	9	1	1.3787	1.3742	2
0	6	0		2.1924		2.1924	1	6		0		1.3742					
3	3	0		2.1065		3	3	2		1.5985							
				2.1040		1	7	-2		1.6003							
						4	4	-2		1.6002							

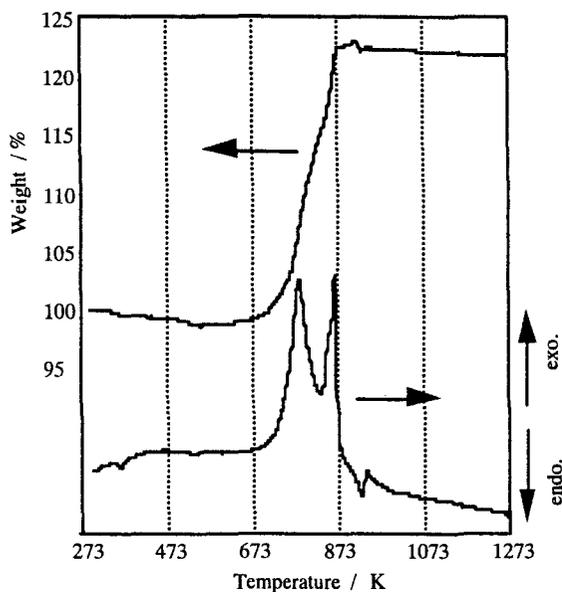
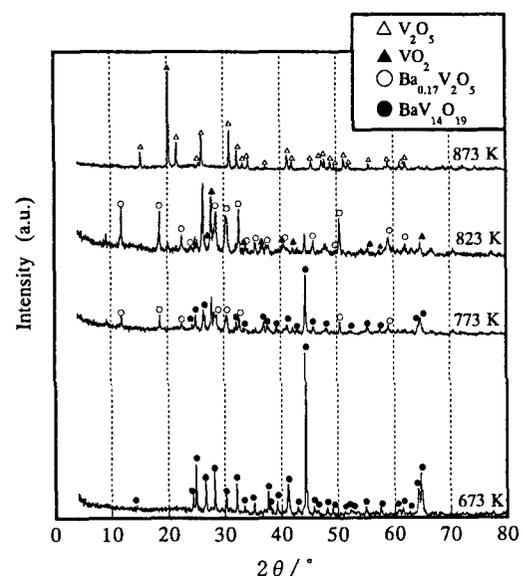
Fig. 2. TED images of $\text{BaV}_{14}\text{O}_{19}$.

structure of the product has a symmetry axis of screw diad. Diffraction peaks and images satisfy no other extinction rule, thus space group $P2_1$ (No.4) or $P2_1/m$ (No.11) is possible.

Nonstoichiometry of Ba or V, as demonstrated in $\text{Ba}_x\text{V}_8\text{O}_{16}$ [3] and $\text{BaV}_{10-x}\text{O}_{17}$ [2], were not confirmed because diffraction peaks did not shift without reference to heating temperature, heating time and changes of Ba/V ratio in starting composition. There was a possibility of oxygen nonstoichiometry caused by the use of BaCO_3 which generates reducing CO gas. However, this was excluded by the fact that the use of $\text{Ba}_2\text{V}_2\text{O}_7$ instead of BaCO_3 gave the same product and did not show any shift of diffraction peaks. The composition of the product was determined to be $\text{BaV}_{14}\text{O}_{19}$ from the starting composition giving a single

phase. A quantitative analysis of Ba/V ratio was also performed on a single phases sample by EDAX, but Ba/V ratio was so small that we could not determine the strict composition.

The result of thermogravimetric analysis in air with temperature increasing up to 1273 K is shown in Fig. 3. $\text{BaV}_{14}\text{O}_{19}$ showed a weight increase of 23.8% between 673 K and 873 K. The XRD patterns of samples after heat treatments at 673 K, 773 K, 823 K and 873 K are shown in Fig. 4. The weight increase of $\text{BaV}_{14}\text{O}_{19}$ started around 673 K. In this point, specific changes or peak shifts were not seen in the XRD pattern. At 773 K, $\text{Ba}_{0.17}\text{V}_2\text{O}_5$ appeared along with $\text{BaV}_{14}\text{O}_{19}$. The diffraction peaks of $\text{BaV}_{14}\text{O}_{19}$ disappeared at 823 K, and $\text{Ba}_{0.17}\text{V}_2\text{O}_5$, VO_2 and an unknown phase coexisted. Finally, the existence of only V_2O_5 was seen in the XRD

Fig. 3. TG and DTA curves for $\text{BaV}_{14}\text{O}_{19}$ in air at a rate of $10^\circ\text{C}/\text{min}$.Fig. 4. XRD patterns of $\text{BaV}_{14}\text{O}_{19}$ after heat treatments at various temperatures in air

pattern of the sample heated at 873 K. It was not made sure that what compound contained Ba at this point.

From the XRD patterns, the weight increase of $\text{BaV}_{14}\text{O}_{19}$ with increasing temperature is due to the oxidation of vanadium ions. The exothermal peak is also consistent with this result. After the heat treatment at 873K, the valence state of vanadium ions would be nearly +5 taking account of the fact that there was no $\text{Ba}_{0.17}\text{V}_2\text{O}_5$ phase at the end of oxidation of $\text{BaV}_{14}\text{O}_{19}$. Assuming that all vanadium ions are +5 at the end of weight increase and the Ba/V ratio is 1/14, the composition of sample before the oxidation is calculated to be $\text{BaV}_{14}\text{O}_{18.86}$, which is almost the same to the starting composition $\text{BaV}_{14}\text{O}_{19}$. The average valence state of vanadium ions is +2.57 in $\text{BaV}_{14}\text{O}_{19}$, and a complex oxide containing low valence state vanadium ions was confirmed to exist in Ba-V-O system.

$\text{BaV}_{14}\text{O}_{19}$ was not oxidized in air below 573 K. When $\text{BaV}_{14}\text{O}_{19}$ was kept at ambient conditions for several months, there was no change of the XRD pattern or no broadening of diffraction peaks. $\text{BaV}_{14}\text{O}_{19}$, containing low valence state vanadium ions, is very stable though VO and V_2O_3 are gradually oxidized at ambient condition.

4. CONCLUSIONS

$\text{BaV}_{14}\text{O}_{19}$ containing low valence state vanadium ions was synthesized by solid state reaction. The average valence state of vanadium ions is +2.57 and the lattice parameters are $a=7.654 \text{ \AA}$, $b=12.639 \text{ \AA}$, $c=7.011 \text{ \AA}$, $\beta=107.85^\circ$. Possible space group of $\text{BaV}_{14}\text{O}_{19}$ is thought to be $P2_1$ or $P2_1/m$ from its extinction rule. $\text{BaV}_{14}\text{O}_{19}$ is stoichiometric and stable at ambient conditions though $\text{BaV}_{14}\text{O}_{19}$ contains low valence state vanadium ions. Since the detailed crystal structure is not known yet, the structure analysis using single crystal is needed in further study.

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