THE Bi_2O_3-V_2O_5 SYSTEM AND CRYSTAL DATA ABOUT SOME BISMUTH VANADATES

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ABSTRACT

The equilibrium diagram of the Bi_2O_3-V_2O_5 system has been studied by DTA and X-ray diffraction in the concentration range 12.5-100 mol % V_2O_5.
To determine the formula of some bismuth vanadates we have used the Tammann graphs of the invariant reactions and the results of the X-ray diffraction by monocrystals.
Seven compounds were found ; $Bi_2V_8O_{23}$ exists between 450 and 514°C ; $BiVO_4$ and Bi_5VO_{10} melt congruently ; the other compounds $Bi_6V_4O_{19}$, $Bi_7V_3O_{18}$, $Bi_{14}V_4O_{31}$ and $Bi_{14}V_2O_{26}$ melt incongruently ; three polymorphic transformations of $Bi_6V_4O_{19}$ are observed.
The liquidus of our binary system is very close to that published recently by Blinovskov and Fotiev (Zh.Neorg.Khim,1987,32,254) but many differences exist between the number of the compounds and their formula.
The crystal data of $Bi_6V_4O_{19}\alpha$ and $Bi_7V_3O_{18}$ have been established ; a structural formula of the last compound was proposed in accordance with its possible perovskite structure : $Bi_3\left[Bi_{0.5}V_{1.5}\square\right]O_9$.
Monocrystals of another vanadate Bi_3VO_7 were found and analysed although this compound does not exist in the equilibrium diagram.

INTRODUCTION

Oxides of bismuth and vanadium find frequent use, alone or mixed, as oxidation catalysts. Some of bismuth vanadates, as $BiVO_4$, are particularly interesting materials because of their optical, electrical and ferroelastical properties.
Two studies of the Bi_2O_3-V_2O_5 system were published before. In 1964, Smolyaninov and Belyaev (1) found four compounds : 7 $Bi_2O_3 \cdot V_2O_5$ and $BiVO_4$ melt congruently ; $Bi_4(V_2O_7)_3$ and $Bi(VO_3)_3$ melt incongruently ; only the liquidus is drawn in their diagram. More recently , in 1987, Blinovskov and Fotiev (2) have published a more detailed study of this system between 14 and 100 mol % V_2O_5; four compounds were also found : two forms of $BiVO_4$ $\alpha \xrightleftharpoons{255°C} \beta \xrightleftharpoons{947°C}$ liq; three forms of $Bi_4V_2O_{11}$ $\alpha \xrightleftharpoons{440°C} \beta \xrightleftharpoons{555°C} \gamma \xrightleftharpoons{880°C}$ liq+ $Bi_8V_2O_{17}$; $Bi_8V_2O_{17}$ which melt incongruently at 920°C and $Bi_{12}V_2O_{23}$ which melt congruently at 940°C.
In this study of the Bi_2O_3-V_2O_5 system the thermal and crystallographic results were used both to establish the equilibrium diagram.

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Table 1

Composition of the liquid phase on the invariant reaction

Température °C	V_2O_5 mol %	Name of the invariant reaction
660	88%	eutectic
868	38%	peritectic
860	37%	eutectic
890	31%	peritectic
908	25%	peritectic

Table 2

Crystallographic data about some bismuth vanadates

$Bi_6V_4O_{19}\alpha$ orthorhombic, Amm2
a = 34.3 (2), b = 5.77 (5), c = 15.79 (9) Å
$d_{exp.}$ = 5.6 , d_{calc} = 5.62 Z = 6
The powder diagram is indexed.

$Bi_{3.5}V_{1.5}O_9$ (or $Bi_7V_3O_{18}$) monoclinic, one of the space groups C
a = 5.529 (5), b = 5.612, c = 8.12 (1) Å ;
β = 109.87 (9), d_{exp} = 7.0, d_{calc} = 6.67, Z = 1
The powder diagram is indexed.

Bi_3VO_7 monoclinic
a = 6.82 , b = 3.9 , c = 6.9 Å ; β = 108°
with d = 7.5 , Z = 1. It is impossible to index the powder diagram ; this compound does not belong to the equilibrium diagram.

$Bi_{14}V_4O_{31}$ (4) monoclinic, space group C2, Cm or C2/m
a = 19.72 , b = 11.459, c = 80.16 Å ; β = 90.5° ;
d_{exp} = 8.0 , d_{calc} = 7.97 , Z = 24.
with c = 10.02 Å , the powder diagram is correctly indexed.

10 mol % V_2O_5 cubic, a = 10.09 Å

5 mol % V_2O_5 cubic, a = 10.15 Å

EXPERIMENTAL

DTA was performed with a Netsch apparatus Model 404 M; Pt,10% Rh-Pt thermocouples and platinum or alumina crucibles were used; the reference material was alumina and the sample weight was 150mg. The calibration of the temperatures were achieved with $K_2Cr_2O_7$ (397°C), K_2SO_4 (585,1069°C), and NaCl (801°C); the heating rate was 10° min, the temperatures were given at ± 3°C.

The mixtures were obtained by sintering the two oxides at 700°C for two days. It is also possible to put the two oxides directly in the crucible and to carry out the thermal analysis; then, an exothermic phenomenon appears about 650°C. In all the cases, two or three heating curves were carried out on each mixture. The powders and the single crystals were studied by X-Ray diffraction with respectively a Siemens diffractometer and a Weissenberg camera ($\lambda Cu_{K\alpha}$).

RESULTS

1) Phase diagram (see figure)

It was studied in the concentration range 12.5-100 mol % V_2O_5. Seven compounds were found. To determine the formula of some bismuth vanadates, we have used the Tammann graphs of the invariant reactions (see table 1) and also the results of the X-Ray diffraction by single crystals.

2) Crystallographic data (table 2)

Single crystals of some of these compounds were obtained by slow cooling from the melt; their qualities were too bad to undertake a structural study but sufficient to determine the unit cell dimensions and sometimes the space group; the densities were performed by pycnometry. All these data led to a possible chemical formula for the studied compounds.

DISCUSSION

- The liquidus of the Bi_2O_3-V_2O_5 is very close to that published by Blinovskov and Fotiev (2) but many differences exist between the number of the compounds and their formula.

- The formula of $Bi_2V_8O_{23}$ was determined by the Tammann graphs of the invariant reactions at 450 and 514°C.

- Bierlein and Sleight (3) have indicated that the heat transformation monoclinic $BiVO_4 \rightleftharpoons$ tetragonal $BiVO_4$ is very small and cannot be seen by DTA.

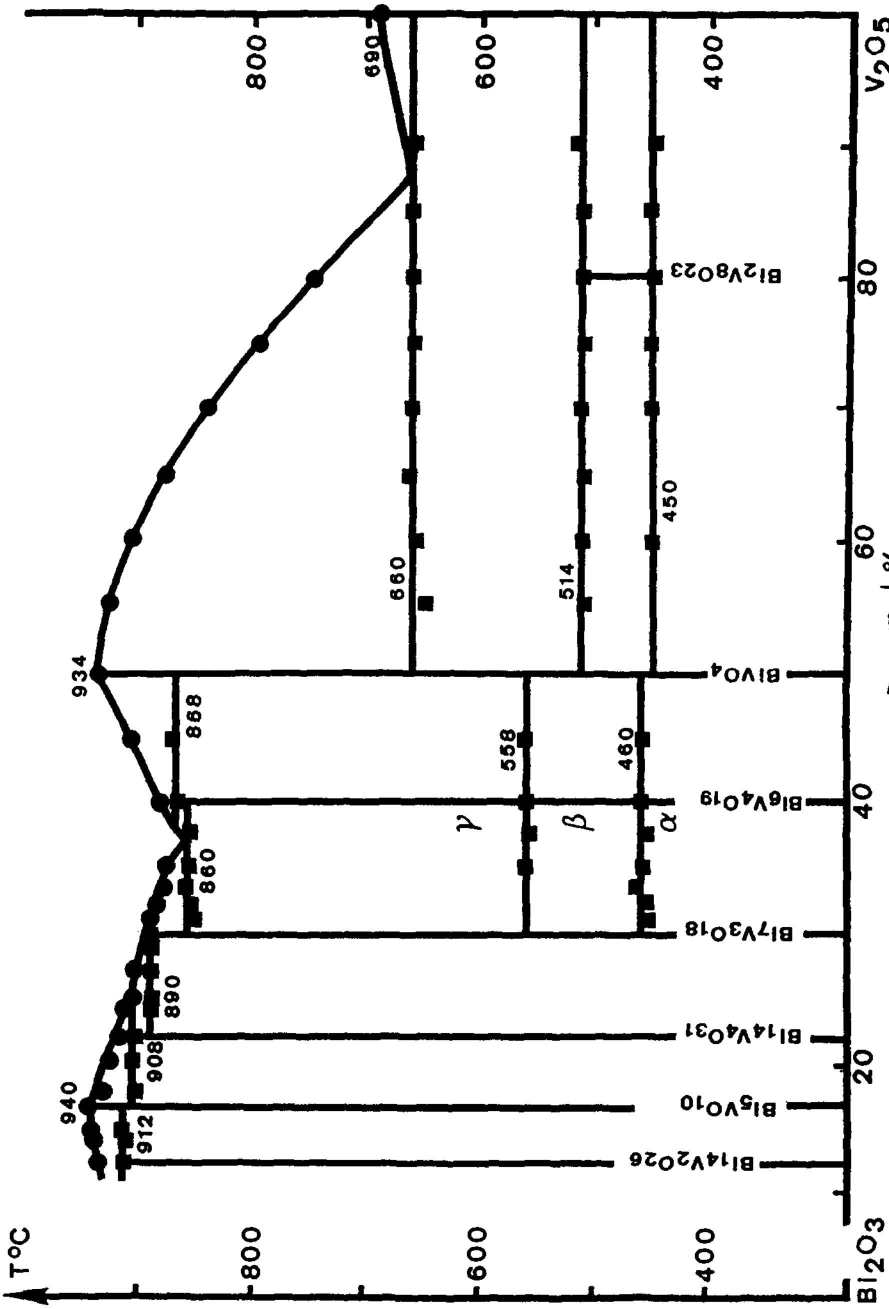

Fig. 1. Phase diagrame of the system Bi_2O_3 - V_2O_5

- Phase transitions, ionic conductivity and structure of $Bi_4V_2O_{11}$ were recently studied (5,6); the structure was perovskite type (5,6) and ionic conductivity was attributed to a possible mobility of some oxygen ions (6); at room temperature, the unit cell is orthorhombic (no space group was indicated), but a structural approach was realized in a pseudo-cell ao/3, bo/3, c = 5.533, 5.661, 15.288 Å (6) or 5.614, 5.540, 15.30 Å (7). However, the volume of this pseudo-cell, 474 $Å^3$, is twice as much as the one of $Bi_{3.5}V_{1.5}O_9$ cell, 237 $Å^3$ (table 2); this last formula may be written $Bi_3 [Bi_{0.5}V_{1.5}\square] O_9$ or $Bi [Bi_{0.17}V_{0.5}\square_{0.33}] O_3$ by analogy with the well-known $Gd [Fe] O_3$ compound which has a perovskite type structure (V = 230 $Å^3$); the vacant octahedral sites may explain the ionic conductivity. Furthermore, a better value of Z is calculated with $Bi_{3.5}V_{1.5}O_9$ formula (table 2) than with $Bi_4V_2O_{11}$ formula (with the pseudo cell dimensions Z = 1.52 for d = 7.0).

- At a close composition of $Bi_8V_2O_{17}$ (2), single crystals of $Bi_{14}V_4O_{31}$ were obtained (22.2 instead of 20 mol % V_2O_5) (4); the value of Z for $Bi_8V_2O_{17}$ is 42.5 and for $Bi_{14}V_4O_{31}$, it is 24 which is a better one.

- In the composition range 0-12.5 mol % V_2O_5 a cubic phase was recognized (table 2). In the litterature, Sekiya et al.(8) claimed out that there is a solid solution of V_2O_5 in the δ Bi_2O_3 which is cubic ; Khachani et al.(9) claimed out that a sillenite phase $Bi^{3+}_{12}[V^{5+}_{0.8-x}Bi^{5+}_x\square_{0.2}] O_{20}$ with pentavalent bismuth exists in this composition range. The Bi_2O_3-V_2O_5 diagram has not been studied in this composition range because of the possibility of not having a binary system.

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