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STUDY OF BINARY SYSTEMS $TlVO_3$-MVO_3 : M = Li, Na

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ABSTRACT

Using DTA and X-ray diffraction, two new compounds $TlNa_2V_3O_9$ and $TlLi_2V_3O_9$ have been found in these systems. The thallium metavanadate $TlVO_3$ did not exist under two allotropic forms as found before, in the binary system Tl_2O-V_2O_5. Besides, the interpretation of the thermal effects in the binary system $TlVO_3$-$NaVO_3$ was completely different from a previous one. This may arise from the difference of compounds synthesis methods used in the two studies.

$TlNa_2V_3O_9$ and $TlLi_2V_3O_9$ showed a solid state decomposition; their X-ray powder diagrams did not allow to characterize them, because of the continuous presence of the initial compounds $TlVO_3$ and MVO_3.

The examination of the pyroxene structures types occured in the alkaline metavanadates agreed with the existence of such defined mixed compounds : $TlLi_2(VO_3)_3$ and $TlNa_2(VO_3)_3$.

INTRODUCTION

The metavanadates of alkaline or pseudo-alkaline metals (Tl^+, NH_4^+...) have a pyroxene structure formed by infinite chains of corner-shared VO_4 tetrahedra. According to Hawthorne and Calvo (1) three kinds of chains should be distinguished for $LiVO_3$, $NaVO_3$ and the other metavanadates : $LiVO_3$ and $NaVO_3$ belong to the monoclinic C2/c group * while KVO_3, $RbVO_3$, $CsVO_3$, NH_4VO_3 and $TlVO_3$ belong to the orthorhombic Pbcm group. Some mixed metavanadates with univalent ions were known; the main method to characterize them is to establish the binary phase diagram between simple metavanadates. From crystallographic and structural data, we may expect that defined compounds exist in $TlVO_3$-$LiVO_3$ and $TlVO_3$-$NaVO_3$ systems while more or less waste solid solutions should appear between $TlVO_3$ and the other metavanadates.

MEASURING METHODS

$LiVO_3$, $NaVO_3$ and $TlVO_3$ were synthesized under a dry process by direct reaction between Li_2CO_3, Na_2CO_3 and recrystallized Tl_2CO_3 with V_2O_5.

* the orthorhombic form of $NaVO_3$ did not appeared by dry process and its structure were not known (10).

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Thallium(I) and vanadium(I) contents were determined by chemical analysis(2). Direct and differential thermal analysis were conducted with about 15 and 2g of product; platinum crucibles were used (3). Three experiments on the same mixture were made to reach correct results; those ones were infered from thermal phenomenon raised up at heating.

RESULTS AND DISCUSSION

1) Melting points of $LiVO_3$, $NaVO_3$ and $TlVO_3$ were respectively 610,618 and 426°C (± 2°C). No allotropic transformation was found for $LiVO_3$, $NaVO_3$ and even for $TlVO_3$; for the last compound, this result was inconsistent with the data claimed by Belyaev and al (4). An explanation may be allowed to this desagreement. Considering the relative volatility of thallium(I) salts, we may reasonably think that the thallium(I) metavanadate used by Belyaev and al was soiled with another thallium(I) vanadate richer in V_2O_5; this allowed the apparition of a thermal phenomenon with a weaker amplitude around 360°C due to an eutectic equilibrium (stable or metastable)on the DTA curves, according with the binary system $Tl_2O-V_2O_5$(2). Furthermore we may point out the absence of allotropic transformation for $TlVO_3$ which is mentionned in the study of binary system $TlVO_3-AgVO_3$(5),and in the numerous works about "$TlVO_4$" (in fact $TlVO_3$(2)) synthesized with Tl_2O_3 and V_2O_5 (6-9).

2) $TlVO_3-LiVO_3$ system (fig.1)

Two invariant phenomena, very closed in temperature and sometimes separable with difficulty are shown; the first one, quite weak, at 332°C(± 2°C) and the second one at 363°C(± 2°C). According to the X-Ray analysis we could put forward the following interpretation; at 363°C, an eutectic equilibrium occurs : liq E (20% $LiVO_3$) $\rightleftharpoons$ $TlVO_3+LiVO_3$; the composition of E point is determined by extrapolation of liquidus curve and Tammann diagram; at 332°C the invariant equilibrium could represent the solid state decomposition of a mixed metavanadate $TlLi_2(VO_3)_3$ characterized by some new lines on the X-Ray powder diagram(table 1); for all mixtures that showed the 332°C phenomenon during heating, extra lines on the X-Ray powder diagrams occured which were more intense after long annealing at 250°C. However, the most intense lines of $TlVO_3$ and $LiVO_3$ powder diagrams were present and led to think that the 330°C phenomena is not totally reversible.

2) $TlVO_3-NaVO_3$ system (fig.2)

As in the former diagram, two invariant phenomena occured at 388 and 400°C(+ 2°C) but the Tammann graphics were better; the first one was weaker than the second one; a same explanation was given. At 400°C an eutectic equilibrium occured; liq E (10% $NaVO_3$) $\rightleftharpoons$ $NaVO_3$ + $TlVO_3$. At 388°C, the invariant

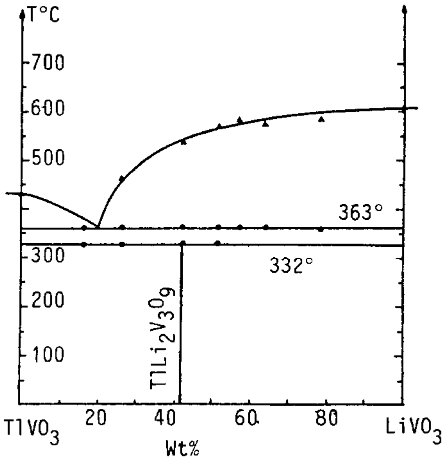

Figure 1

d (Å)	I/Io
7.90	m
5.73	w
5.41	w
4,62	vs
3.95	s
3,60	m
3.24	vs
2.83	m
2,73	w
2.64	w
2.54	w
2.49	w

Table 1

vs:very strong;s:strong;m:medium;
w:weak;vw:very weak

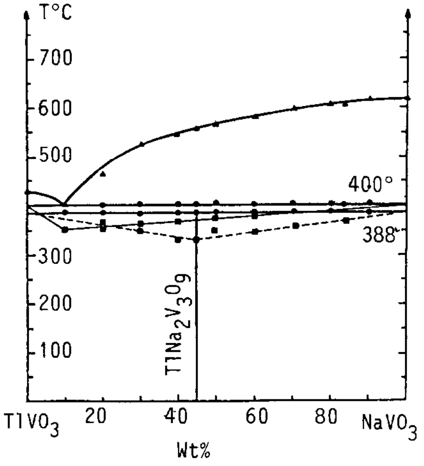

Figure 2

d(Å)	I/Io
7.230	w
5.686	vw
5.177	w
5.147	w
4.872	m
3,322	m
3.310	vw
3,290	f
3.154	vs
3.102	vw
3.060	w
3.041	vw
2.999	vw
2.984	vw
2.887	vs
2.767	s
2.754	vw

Table 2

equilibrium could represent the solid state decomposition of a mixed compound $TlNa_2(VO_3)_3$ characterized by new lines on the powder diagrams of the mixtures (table 2); the diagram interpretation is quite different from the previous one (4) although observed phenomena were similar; an explanation was already given.

Other mixed metavanadates including $NaVO_3$ were found by different studies : $Na_3K(VO_3)_4$ and $NaK(VO_3)_2$ (10); $NaK_2(VO_3)_3$ and $Na_2K(VO_3)_3$ (11); $NaK(VO_3)_2$ (12); $Na_2K(VO_3)_3$ (13); $NaK(VO_3)_2$ (14). The structure of the $NaK(VO_3)_2$ compound was the only one clearly established by Idler and al (15). Another compound $CsNa(VO_3)_2$ was also found in the binary system $CsVO_3$-$NaVO_3$ (11).

CONCLUSION

Two new compounds $TlLi_2V_3O_9$ and $TlNa_2V_3O_9$ were found in the two binary diagrams $TlVO_3$-$LiVO_3$ and $TlVO_3$-$NaVO_3$ which have been totally established.

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