Mat. Res. Bull., Vol. 22, pp. 477-481, 1987. Printed in the USA.
0025-5408/87 $3.00 + .00

$Nb_2Te_2O_9$ AND $Ta_2Te_2O_9$: TWO NEW MIXED OXIDES OF Te(IV)

M. Gaitán, A. Jerez, C.Pico and M.L. Veiga
Departamento Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense, 28040-Madrid, Spain

(Received October 17, 1986; Refereed)

ABSTRACT

$Nb_2Te_2O_9$ and $Ta_2Te_2O_9$ were prepared by solid state reactions between amorphous TeO_3(s) and metallic pentoxides of Nb and Ta. A crystallographic analysis carried out by X-ray diffraction showed that these compounds are isostructural (space group: $P2_1/C$. a = 6.883 A, b = 7.853 A, c = 14.591 A, β = 103.66 for $Nb_2Te_2O_9$ and a = 7.10 A, b = 7.48 A, c = 14.62 A, β = 102.9 for $Ta_2Te_2O_9$). The IR spectra and thermal decomposition processes of both mixed oxides were studied.

MATERIALS INDEX: oxides, tellurium, niobium, tantalum

INTRODUCTION

On the basis of the well known antecedents in the V-Te-O system (1), we have attempted to synthesize new compounds of Nb-Te-O_2 and Ta-Te-O_2 systems that could really have interest on their theoretical structural aspects as on their possible catalytic applications in oxidation processes, which could be expected in wiew of that demonstrated for other related systems such as V_2O_5-$M^{IV}O_2$ (2,3) and Mo^{V}-Te^{IV}-O_2 (4). Studies (5,6) of Galy group about mixed oxides of Te and V (α- and β-$VTeO_4$, $V_2Te_2O_9$) have shown the existence of several solid phases in which predominates the lower (IV) oxidation state of Tellurium. Then, it was reasonable to expect that the heaviest elements of this group, Nb and Ta showed some chemical and structural analogies.

On the other hand, our experience with oxocompounds of Sb and Te (7) has shown that it was easy to obtain mixed oxides of Te(IV) with the electronically related elements of the V group, Sb(V), Nb(V) and Ta(V), as well as with others of their own group in Te_3SeO_8 (8) and $Te_2O_3(SeO_4)$ (9).

Recently, contributions of Bart (10) on the systems Nb-Te-O_2 and Ta-Te-O_2, with X-ray diffraction and spectroscopics results of some phases not characterized, and Galy (11), on the oxide $Te_3Nb_2O_{11}$, point to the need of a systematic study in this field of new materials.

EXPERIMENTAL

$Nb_2Te_2O_9$ and $Ta_2Te_2O_9$ were prepared by reacting TeO_3 and Nb_2O_5 or Ta_2O_5 in a sealed vycor tube at 740 C, during 8 h, with controlled cooling rate of 50oC/h:

$2\ TeO_3\ (s) + Nb_2O_5\ (s) \longrightarrow Nb_2Te_2O_9\ (s) + O_2\ (g)$

$2\ TeO_3\ (s) + Ta_2O_5\ (s) \longrightarrow Ta_2Te_2O_9\ (s) + O_2\ (g)$

TeO_3 was prepared by thermal decomposition of Te(OH) (12). The other chemicals and reagents used for chemical analysis were supplied by Merck.

In these conditions the oxides are obtained as microcrystalline products. The synthesis of $Nb_2Te_2O_9$ monocrystalls was performed in a three-zone furnace using a 700-740 C temperature gradient and $TeCl_4$ as transport agent.

X-Ray diffraction data for the products were obtained with a Siemens Kristalloflex powder diffractometer powered by a D-500 generator (W has been used as internal standard and employing Ni filtered CuKα radiation). Thermogravimetric studies were carried out with a Mettler TA3000 apparatus and run under nitrogen flow. The IR absorption spectra were recorded in a Perkin-Elmer 1330 spectrophotometer using KBr based pellets. Finally, chemical analysis were performed following the usual procedures (13). Densities were determined by a picnometric method using CCl as inmersion liquid.

RESULTS AND DISCUSSION

The reaction products obtained in both processes were pale-yellow ($Nb_2Te_2O_9$) and brown ($Ta_2Te_2O_9$) microcrystalline solids. Chemical analysis, performed out according to the usual procedures (13), gave the following results: for $Nb_2Te_2O_9$: Nb 30.8%; Te 44.0%; O 25.2%; (theoretical calculation: Nb 31.76%; Te 43.62%; O 24.61%). For $Ta_2Te_2O_9$: Ta 46.8%; Te 34.0%; O 19.2%; (theoretical calculation: Ta 47.55%; Te 33.53%; O 18.92%). Oxygen content was calculated by difference.

The solid densities were 4.88 $g.cm^{-3}$ ($Nb_2Te_2O_9$) and 6.59 $g.cm^{-}$ ($Ta_2Te_2O_9$).

A previous crystallographic study of $Nb_2Te_2O_9$ was performed in a Phillips four-circle automatic diffractometer. The crystalls are monoclinic (spacial group $P2_1/C$) with cell parameters a = 6.883 A, b = 7.853 A, c = 14.591 A, ß = 103.66 ; Z = 4; d = 4.95 $g.cm^{-3}$.

The reflections observed in the X-Ray diffraction diagram of $Ta_2Te_2O_9$ were corrected with respect to the internal standard (W). In table 1 are gathered the corresponding spacings and relative intensities. A comparison between this diagram and that for $Nb_2Te_2O_9$ suggest that both oxides are isostructural. Based on this assumption, we have indexed the observed reflections of $Ta_2Te_2O_9$ as listed in Table 1. The refined lattice parameters and other crystallographic data are given in Table 2.

TABLE 1.- X-Ray diffraction pattern of $Ta_2Te_2O_9$

d(exp)	h	k	l	d(calc)	I(obs)	d(exp)	h	k	l	d(calc)	I(obs)
6.63	0	1	1	6.628	9	2.210	0	3	$\bar{3}$	2.209	7
5.64	1	0	$\bar{2}$	5.638	4	2.205	3	1	0	2.204	7
5.16	0	1	2	5.162	10	2.183	1	3	2	2.181	6
4.56	1	1	1	4.554	11	2.101	2	2	3	2.101	3
4.51	1	1	$\bar{2}$	4.504	12	2.063	3	0	2	2.063	6
3.843	1	1	2	3.848	5	2.045	0	3	4	2.044	3
3.746	0	2	0	3.743	6	2.027	1	1	6	2.027	7
3.621	0	2	1	3.621	22	2.023	2	3	0	2.024	6
3.565	0	0	4	3.563	26	1.994	3	2	2	1.993	4
3.502	1	0	$\bar{4}$	3.505	25	1.967	2	3	1	1.968	2
3.460	2	0	0	3.459	13	1.959	3	1	$\bar{5}$	1.959	6
3.429	2	0	$\bar{2}$	3.430	10	1.924	2	1	5	1.924	5
3.293	1	2	0	3.292	41	1.899	2	2	$\bar{6}$	1.899	12
3.219	0	1	4	3.217	56	1.879	3	0	$\bar{6}$	1.879	17
3.174	1	1	$\bar{4}$	3.174	21	1.855	0	4	1	1.856	4
3.119	1	2	$\bar{2}$	3.119	21	1.835	1	2	6	1.836	3
2.944	2	1	1	2.943	6	1.828	1	0	$\bar{8}$	1.827	16
2.874	1	2	2	2.874	18	1.822	3	1	$\bar{6}$	1.823	11
2.819	2	0	$\bar{4}$	2.819	6	1.807	1	4	0	1.807	8
2.713	1	1	4	2.714	20	1.791	1	1	7	1.791	7
2.682	1	1	$\bar{5}$	2.682	17	1.781	0	0	8	1.782	6
2.581	0	2	4	2.581	11	1.765	4	0	$\bar{1}$	1.765	2
2.557	1	2	$\bar{4}$	2.558	10	1.758	2	2	5	1.758	4
2.529	2	2	$\bar{2}$	2.529	5	1.730	4	0	0	1.730	8
2.460	0	3	1	2.458	4	1.723	1	4	$\bar{3}$	1.723	7
2.421	1	0	$\bar{6}$	2.420	4	1.717	3	1	4	1.717	12
2.406	2	1	3	2.404	6	1.713	3	3	$\bar{2}$	1.713	11
2.365	2	1	$\bar{5}$	2.364	3	1.687	3	1	$\bar{7}$	1.687	4
2.347	1	3	0	2.348	7	1.668	2	3	4	1.668	4
2.327	1	1	5	2.328	4	1.657	0	4	4	1.657	4
2.298	1	2	4	2.299	8	1.632	4	1	1	1.633	4
2.264	0	1	6	2.264	11	1.609	2	4	$\bar{3}$	1.610	5

TABLE 2.- Cristallographic data for $Ta_2Te_2O_9$

a = 7.10(0) A
b = 7.48(7) A
c = 14.62(7) A
ß = 102.9(9)°

space group : $P2_1/C$
Z = 4
d = 6.67 $g.cm^{-3}$

Thermal decomposition runs of both oxides were similar, with weight losses of 53.8% ($Nb_2Te_2O_9$) and 40.3% ($Ta_2Te_2O_9$), at temperatures between 770 and 900 C. Decomposition processes can be formulated as:

$$Nb_2Te_2O_9(s) \xrightarrow[\text{- 54.56\% calc.}\\ \text{- 53.8 \% exp.}]{770 - 900\ C} Nb_2O_5(s) + 2\ TeO_2(g)$$

$$Ta_2Te_2O_9(s) \xrightarrow[\text{- 41.94\% calc.}\\ \text{- 40.3 \% exp.}]{770 - 900\ C} Ta_2O_5(s) + 2\ TeO_2(g)$$

Solid residues are identified by X-Ray diffraction as metallic pentoxides.

TABLE 3.- Infrared spectroscopic data (in cm-1) for $M_2Te_2O_9$ (M = Ta, Nb).

$Ta_2Te_2O_9$	$Nb_2Te_2O_9$
965(m)*	925(m)
832(vs)	820(vs)
	770(sh)
715(sh)	715(sh)
	670(b)
650(b)	630(w)
	615(sh)
470(w)	460(sh)
	435(w)
385(w)	

* vs : very strong; m : medium; w : weak; b : broad; sh : shoulder.

The IR absorption bands, whose frequencies are given in Table 3, seem to confirm the structural relation derived from the X-ray diffraction diagrams. Spectra of $Nb_2Te_2O_9$ and $Ta_2Te_2O_9$ were similar, with bands in the same regions that show displacement of vibrations toward higher wavenumbers in the heaviest element oxide. The proximity of the absorption bands did not allow to assign the registered vibrations without a more precise knowledge of the crystal structures of these materials.

REFERENCES

1. Berry, F.J. and Brett, M.E., Inorg. Chem. Acta, 68, 25, (1983) and references therein.

2. Kozlowski, R., Pettifer, R.F. and Thomas, J.M., J. Chem. Soc. Chem. Commun., 438, (1983).

3. Roozeboom, F., Fransen, T., Mars, P. and Gellings, P.J., Z. Anorg. Allg. Chem., 449, 25, (1979).

4. Bart, J.C.J. and Giordano, N., J. Catal., 64, 356, (1980).

5. Galy, J., Nat. Bur. Stand. Spec. Publ., 364, 19, (1972) and references therein.

6. Darriet, J. and Galy, J., J. Cryst. Struct. Comm., 2, 237, (1973).

7. Alonso, J.A., Castro, A., Jerez, A., Pico, C. and Veiga, M.L., J. Chem. Soc. Dalton, 2225, (1985).

8. Pico, C., Castro, A., Veiga, M.L., Gutierrez-Puebla, E., Monge, M.A. and Ruiz-Valero, C., J. Solid State Chem., 63, 0000, (1986).

9. Gaitán, M., Jerez, A., Pico, C. and Veiga, M.L., Mat. Res. Bull., 20, 1069, (1985).

10. Bart, J.C.J. and Petrini, G., Z. Anorg. Allg. Chem., 465, 51, (1980); ibid., 466, 81, (1980).

11. Galy, J. and Lundqvist, O., J. Solid State Chem., 27, 279, (1979).

12. Pico, C., Veiga, M.L. and Gutiérrez-Rios, E., An. Quim., 73, 816, (1977).

13. K. Kodama, "Methods of Quantitative Inorganic Analysis", Interscience, New York, (1963).