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THE THERMAL DECOMPOSITION OF FREEZE-DRIED TANTALUM AND MIXED LITHIUM-NIOBIUM OXALATE*

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ABSTRACT

A digital modification of a Perkin–Elmer thermobalance is described. This apparatus was used in conjunction with other thermal analysis equipment to study the thermal decomposition of $NH_4Ta(C_2O_4)_3 \cdot 2H_2O$ prepared by freeze-drying a commercial solution of the material. The major decomposition is in the region of 100–300°C and the reaction is too complex to evaluate any intermediate steps. The amorphous oxide product crystallizes around 750°C. This oxide is intimately mixed with carbon formed during the decomposition. The carbon burns off around 700–800°C. However, if the decomposition is performed in hydrogen, the carbon remains and at about 1200°C tantalum carbide is formed.

A freeze-dried mixture of lithium and niobium oxalate was investigated to determine its suitability as a starting material for the preparation of lithium niobate. The decomposition of this material is compared to that of the conventional mixture of lithium carbonate and niobium oxide. The initial decomposition of the freeze-dried material around 100–400°C leads to a mixture of lithium carbonate and niobium oxide but this subsequently reacts at about 500°C to form lithium niobate. The conventional mixture of these materials does not react until around 750°C. Surface area and electron micrographs indicate that lithium niobate having a particle size of 0.05 nm or larger can be prepared from the freeze-dried material.

INTRODUCTION

The freeze-dry process has recently been shown to be applicable to the production of ceramic raw materials[1]. The process had difficulties coping with the high acidities necessary to suppress the hydrolysis of highly charged ions. Consequently these ions are kept in aqueous solution by complexing action. Two such ions of interest are tantalum and niobium. Solutions of these ions are commercially available as the oxalate complex. The thermal decomposition of the freeze-dried tantalum oxalate material was investigated along with an equimolar mixture of the analogous niobium

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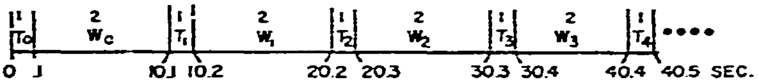
complex and lithium oxalate. The latter mixture should serve as a suitable material for the preparation of lithium niobate. In this respect the decomposition has been compared with that of an equimolar mixture of lithium carbonate and niobium oxide used for the more conventional production of lithium niobate.

EXPERIMENTAL

The Perkin–Elmer thermobalance was modified in order to obtain the data in digital form for subsequent computer processing. The equipment used for this purpose is the same as reported earlier[2]. The actual utilization is different, however, because of the unique temperature sensor and calibration of the Perkin–Elmer apparatus. The platinum furnace winding serves also as the temperature sensor. It forms one side of a bridge circuit and the other side is driven by the output voltage from the programming potentiometer. This same voltage is used to supply the temperature portion of the digital equipment. It is directly related to temperature by use of the magnetic standards recommended by Perkin–Elmer.



PER CENT WEIGHT	°C	Mg/MIN	°C
$\frac{100\,W_0}{W_0}$	$\frac{T_0+T_1}{2}$	$\frac{60(W_0-W_1)}{10.1}$	T_1
$\frac{100\,W_1}{W_0}$	$\frac{T_1+T_2}{2}$	$\frac{60(W_1-W_2)}{10.1}$	T_2
$\frac{100\,W_2}{W_0}$	$\frac{T_2+T_3}{2}$	$\frac{60(W_2-W_3)}{10.1}$	T_3

Fig. 1. Timing sequence employed by digital thermobalance.

The two input voltages are converted to frequency and counted for predetermined times in an established pattern. Fig. 1 illustrates the particular pattern used in this investigation. The temperature signal is counted for 0.1 sec and then automatically switched to the weight signal for ten sec. This pattern is cycled repeatedly in a completely automatic fashion. The output data is constantly punched on paper tape for input to the computer. The necessary quantities for the conventional thermal-analysis plots are determined as indicated in Fig. 1. The digital equipment can readily be used for kinetic studies by simply not using the temperature portion and following the weight as a function of time under isothermal conditions.

A sample consisting of about 1 mg each of alumel, nickel, Perkalloy, iron, and Hisat 50 is placed on the balance and a small permanent magnet placed in position to give rise to an apparent weight gain. As the sample is heated these materials pass through their individual Curie temperatures and loose their magnetic attraction. This is reflected in the weight signal as an apparent weight loss. A program was written which would take the weight and voltage data and determine the values of a and b in the following equation:

$$°C = aV + b.$$

The linearity of the relationship was established by the use of the controls provided by the manufacturer for this purpose. Fig. 2 shows the computer output plot of this program. The mV-reading on the ordinate corresponds directly to weight. The program establishes the measured Curie temperature for each of the materials based on the intersection of tangent lines from the point of maximum slope in the loss and from the minimum slope in the following base line. These points and intercepts are

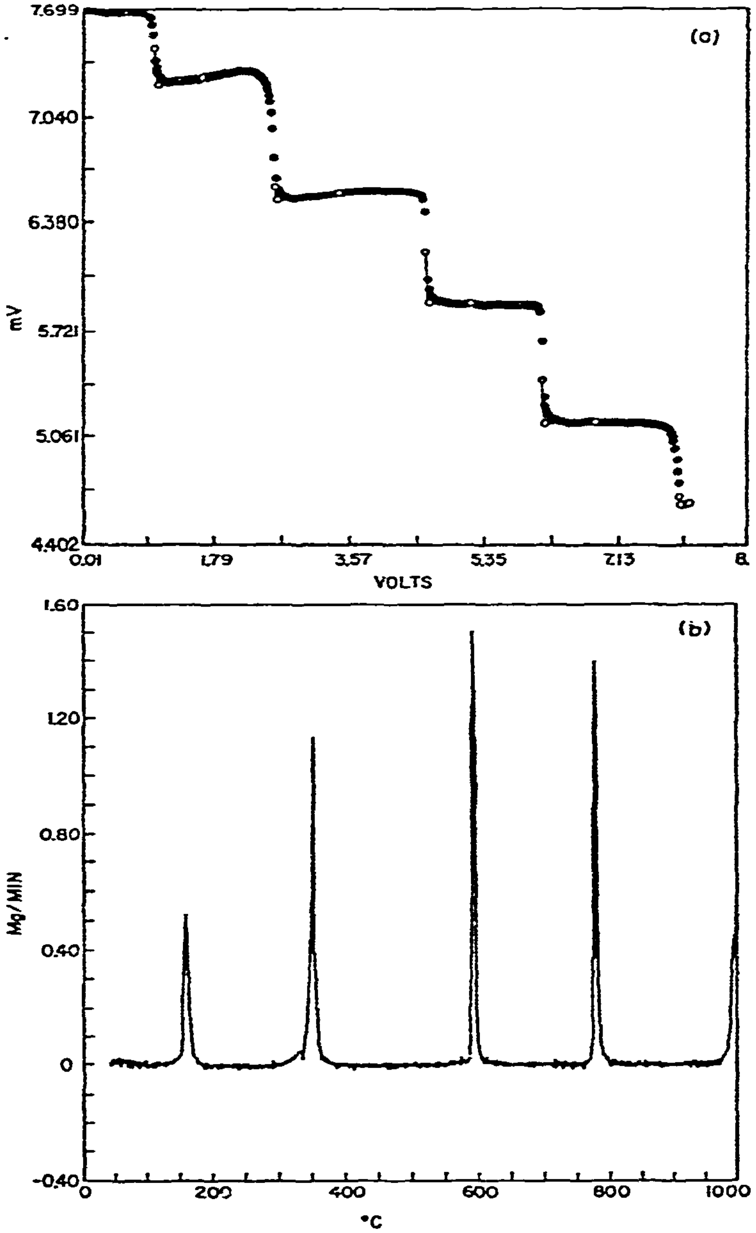


Fig. 2. Sample computer output plots of a calibration run; (*a*) weight *vs.* voltage; (*b*) rate of weight loss *vs.* temperature.

shown as open circles in Fig. 2. The voltage of the intercept is placed in the above equation along with the appropriate value of the Curie temperature. The five resulting equations are solved for *a* and *b* by a least-squares technique and the computer gives the best values along with the plot. In this favorable example the agreement is within a degree for each of the five Curie temperatures. All runs can then be processed by the computer to give the conventional output plots of % weight loss *vs.* temperature and rate of weight loss *vs.* temperature. The time averaging feature of the digital apparatus is particularly valuable for the latter plot since the differentiation greatly amplifies the noise in the original data. A sample of the differential plot for the same calibration run is also shown in Fig. 2.

A heating rate of 10°/min was employed for the thermogravimetry, differential thermal analysis, and evolved gas analysis. The DTA used the Fisher apparatus in conjunction with a Leeds and Northrup DC amplifier and X–Y recorder. The sample for EGA was placed in a platinum crucible and suspended in a platinum furnace tube. The system was continuously pumped and the gases monitored by repeatedly scanning the mass range of 1–50 using a Veeco SPI–10 residual gas analyser. The pressure was kept below 10^{-4} torr during the entire heating cycle.

Samples were heated in air for thirty minutes at various temperatures. X-ray diffraction patterns of the calcined samples were determined using a GE XRD-3 diffractometer and Cr $K\alpha$ radiation. The surface areas of these samples were also measured with a Perkin–Elmer Sorptometer using the BET nitrogen adsorption technique.

The sample powders were prepared starting from 1.13M tantalum oxalate solution (Kawecki Chemical Co.) and from an equimolar mixture of 0.67M niobium oxalate solution (Kawecki Chemical Co.) and 0.91M lithium oxalate solution (City Chemical Co.). The resulting spherical agglomerates are strongly hygroscopic and were stored in sealed containers.

Emission spectrographic analysis was performed on both freeze-dried materials and the results are presented in Table I.

RESULTS AND DISCUSSION

Fig. 3 presents the differential thermogravimetric curve for ammonium trisoxalatotantalate in flowing oxygen. The curve obtained in nitrogen was similar. Table II gives some weight-loss data at selected points. The overall weight loss is seen to correlate well with the value calculated on the basis of the dihydrate. It is difficult to say whether the dihydrate is the stable species resulting from the freeze-drying or whether it is the product of the subsequent equilibration with the atmosphere. The weight losses appear to overlap so much that it is fruitless to attempt to identify the intermediates on the basis of the weight-loss data. The weight loss at high temperature, around 750°C, is interesting. It represents a loss of approximately 1.7%. The calculated weight losses corresponding to the loss of a molecule of carbon dioxide, carbon monoxide, and water are 8.8, 5.6, and 3.6%, respectively. From these data it

TABLE I

RESULTS OF EMISSION SPECTROGRAPHIC ANALYSIS OF OXIDES PREPARED FROM THE FREEZE-DRIED OXALATE

wt.%	*Impurity in*	
	$LiNbO_3$	*Ta_2O_5*
0.X	Ca, Zr	Nb
0.0X	Al	Si, K
0.00X	K	Mg, Cu, Al, Fe, Na, Mn
0.000X	Na, Si, Cu, Fe, Mg, Ag	—

TABLE II

WEIGHT LOSS DATA FOR THE THERMAL DECOMPOSITION OF $NH_4Ta(C_2O_4)_3 \cdot 2H_2O$

	°C	*%wt. Loss*		
		O_2	*N_2*	*Theoretical*
?	210	40.7	38.7	—
$Ta_2O_{5(a)}+XC$	500	54.2	54.4	—
$Ta_2O_{5(c)}$	1000	56.0	56.0	56.1

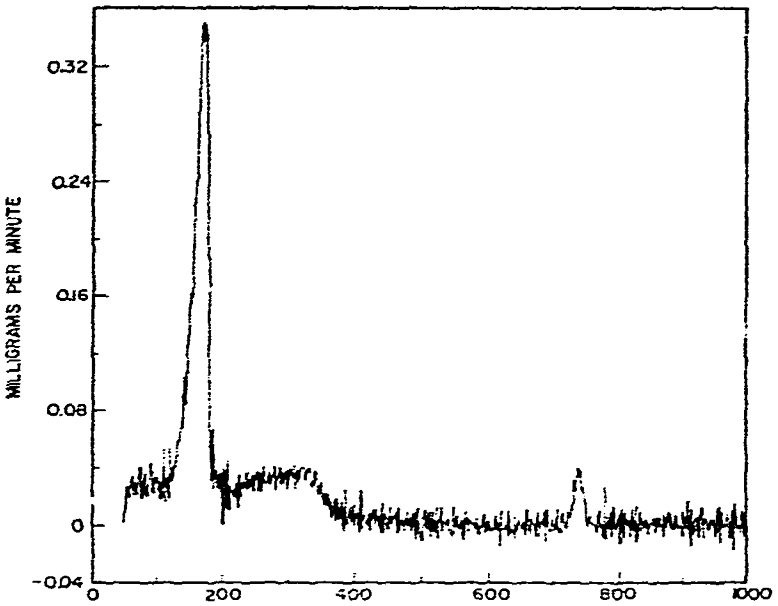


Fig. 3. DTG plot for $NH_4Ta(C_2O_4)_3 \cdot 2H_2O$ heated in O_2 (3.49 mg).

would appear that this weight loss corresponded to the loss of half a molecule of water, probably bound as hydroxide. The evolved gas analysis presented in Fig. 4, however, clearly indicates that the gases evolved in this temperature region are carbon monoxide and carbon dioxide. It is concluded therefore that the weight loss corre-

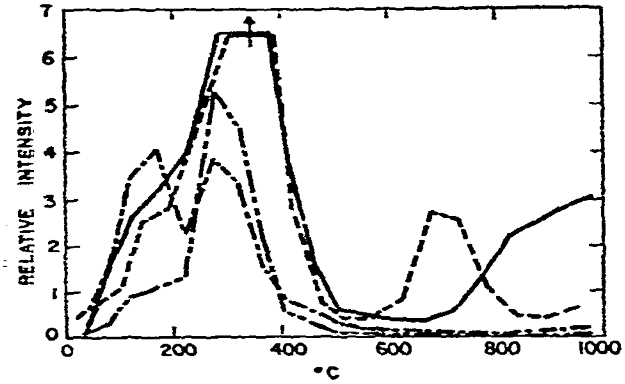


Fig. 4. EGA plots for $NH_4Ta(C_2O_4)_3 \cdot 2H_2O$; mass nos., 17 —·—, 18 —··—, 28– – –, 44 —.

sponds to the removal of carbon formed by the disproportionation of carbon monoxide during the low-temperature decomposition. Carbon monoxide is unstable with respect to carbon dioxide and carbon below about 800°C. The loss of water and ammonia are clearly evident in Fig. 4. There is the complication that mass 17 peak is a secondary peak for water and mass 18 peak is a secondary peak for ammonia so that they contribute to each other somewhat. The major loss corresponding to the decomposition of the oxalate ions occurs almost simultaneously precluding any clear distinction of intermediates.

The DTA curves, shown in Fig. 5 are consistent with the above explanation. There are multiple endothermic peaks in the 100–300°C region corresponding to the overlapping decompositions. Around 750°C there is a small exothermic peak which could correspond to the removal of the carbon or to the crystallization of the tantalum

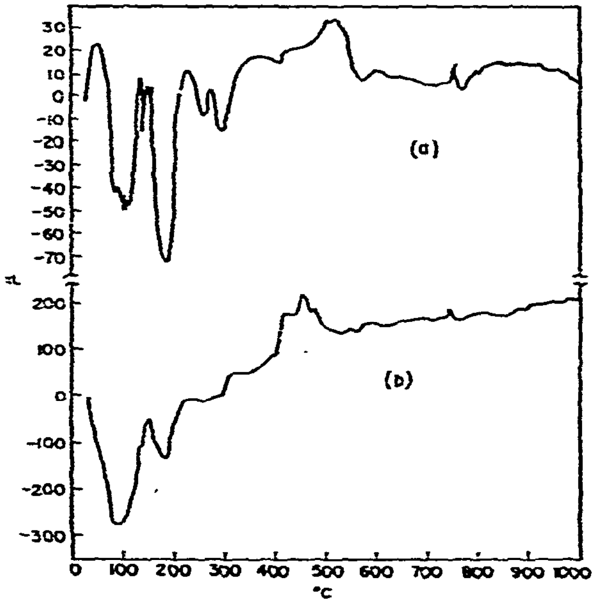


Fig. 5. DTA curves for $NH_4Ta(C_2O_4)_3 \cdot 2H_2O$; (*a*) in He, (*b*) in O_2.

oxide. This crystallization is evident from the X-ray patterns shown in Fig. 6. There is some structure in the freeze dried material itself but it is quickly destroyed during the decomposition process and as usual X-ray diffraction is of little help during the actual decomposition. The pattern appears to be that of an amorphous material even at 700°C; however, at 800°C the pattern of tantalum oxide is clear. It appears therefore that the initially formed oxide is amorphous and undergoes a sharp crystallization between 700 and 800°C. This process is exothermic and probably is responsible for the DTA peak around 750°C. The broadening and splitting of the X-ray peaks at high temperature indicate a different polymorph of tantalum oxide of some reduction brought about by the intermixed carbon.

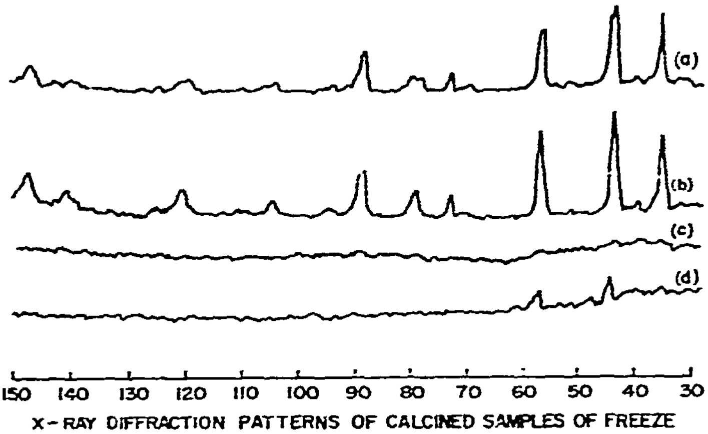


Fig. 6. X-ray diffraction patterns of $NH_4Ta(C_2O_4)_3 \cdot 2H_2O$; heated 30 min in air; (*a*) 1100°C, (*b*) 800°C, (*c*) 700°C, (*d*) uncalcined.

There is an interesting sidelight to this decomposition of tantalum oxalate. If the material which has been calcined to 500°C in air is then subjected to a high temperature firing (around 1200–1400°C) in hydrogen it will form a partially reduced oxide as anticipated. If, however, the decomposition is performed from the start in hydrogen, that is starting with freeze-dried oxalate, then tantalum carbide is obtained at 1200°C as indicated by the X-ray pattern. If a sample of this is subsequently fired in air there is a 14.5% gain which is in excellent agreement with the calculated value of 14.4% for conversion of TaC to Ta_2O_5. The carbon monoxide and dioxide normally formed during the decomposition is reduced and a residue of finely divided highly reactive carbon remains. This readily reacts with the oxide around 1200°C to form the carbide.

The differential thermogravimetric (DTG) plots for the lithium–niobium samples are shown in Fig. 7 for the two samples in oxygen. The results in nitrogen were similar. The overall weight loss observed at 1000°C was 66.1% for the oxalate and 13.1% for the mixed carbonate oxide. These compare well with the theoretical weight losses associated with:

$$Li_2C_2O_4 \cdot 2HNb(C_2O_4)_3 \rightarrow 2LiNbO_3 + H_2O + 7CO + 7CO_2[-67.5\%] \quad (1)$$

$$Li_2CO_3 + Nb_2O_5 \rightarrow 2LiNbO_3 + CO_2[-13.0\%] \quad (2)$$

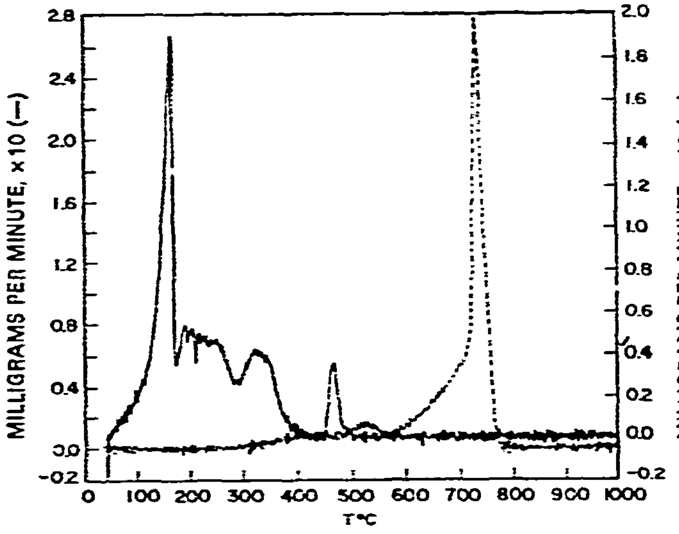


Fig. 7. DTG curves in O_2; $Li_2C_2O_4\cdot 2HNb(C_2O_4)_3$ (2.10 mg), $Li_2CO_3\cdot Nb_2O_5$(9.44 mg).

It may be that there is a partial hydroxide substitution for oxalate in the starting material or it may already have been slightly decomposed in the freeze-drier before the start of the thermogravimetric experiment. Either of these reasons would result in a smaller weight loss.

The composition of a mixed $Li_2C_2O_4\cdot 2HNb(C_2O_4)_3$, is reasonable for the freeze-dried product. The niobium oxalate solution contains excess oxalic acid to insure complete complexing action and the species is completely analogous, except for the hydrogen-ion substitution, to the corresponding tantalum compound prepared in this manner. The decomposition pattern in Fig. 7 is also directly comparable to Fig. 3 for tantalum oxalate. The only difference appears to be the decomposition of the lithium oxalate. The higher temperature peak around 450–500 °C is probably the decomposition of the finely divided reactive lithium carbonate formed during the prior decomposition of the oxalate. A more complete elucidation of the scheme for the decomposition would be difficult because, as in the case of tantalum oxalate, the low temperature decompositions overlap considerably.

The conventional lithium carbonate–niobium oxide mixture shows that the major loss of CO_2 occurs around 700 °C where it would be expected. Apparently there is some slight reaction at lower temperatures around 400 and 500 °C. This 1 or 2% weight loss that occurs in the conventional material before the major decomposition would seem to correlate with the observation of the low-temperature reaction of the reactive material. Probably the mixing and grinding process yield a few percent of thoroughly mixed small particle material which is capable of reacting at this low temperature in similar fashion to the freeze dried material.

Both the DTA and EGA results summarized in Figs. 8 and 9 are consistent with this interpretation. The DTA patterns indicate a similar differential, about 300 °C, between the final decomposition temperature of the freeze-dried and conventional material.

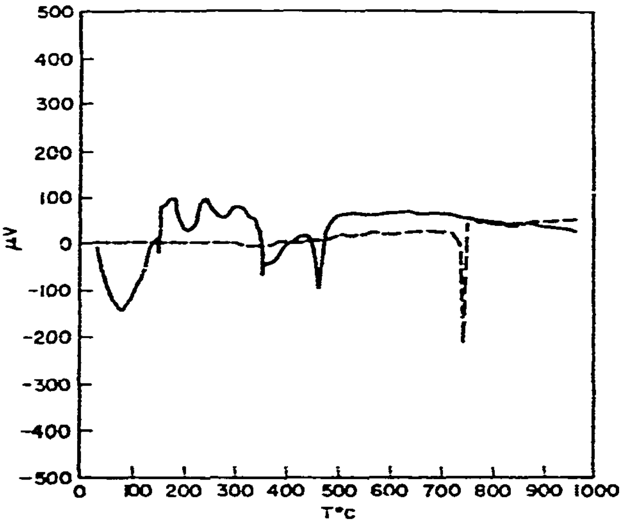


Fig. 8. DTA curves in O_2; $Li_2C_2O_4 \cdot 2HNb(C_2O_4)_3$, $Li_2CO_3 \cdot Nb_2O_5$.

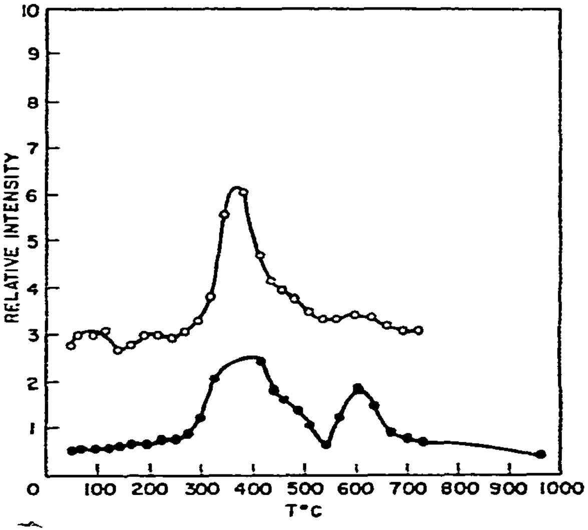


Fig. 9. EGA curves for $Li_2C_2O_4 \cdot 2HNb(C_2O_4)_3$; mass no. 28 ○, mass no. 44 ●.

In Fig. 9 there is a background of mass 28 peak due to the partial pressure of nitrogen in the system (total pressure about 1×10^{-5} torr). The evolution of carbon monoxide can clearly be distinguished, however. The secondary peak for nitrogen is 14 while that of carbon monoxide is 12. The mass 14 peak is essentially constant during the experiment while the mass 12 peak appears only during the 300–700°C range when there is carbon monoxide or dioxide present.

The broad X-ray diffraction pattern discernible for the sample calcined at 400°C is that of lithium niobate and this pattern sharpens for samples calcined at higher temperatures. X-ray patterns of similarly calcined samples of the mixed lithium carbonate plus niobium oxide do not show the lithium niobate pattern until 800°C and above.

The surface areas indicated in Fig. 10 have their peak values immediately following the decomposition as expected. The effects of higher temperatures upon particle growth are obvious in both the surface and X-ray results. It would seem that lithium niobate could be prepared in a range of particle sizes depending upon the choice of calcining conditions. If one assumes spherical particles and a density of 4.6 g/cm^3 for the resulting lithium niobate, then the average particle size would be in the range of 0.05 nm at 400°C to about 1.5 nm at 1000°C.

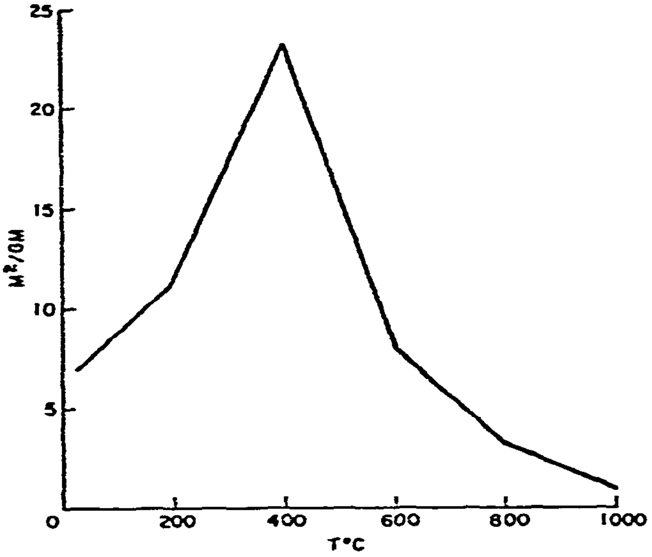


Fig. 10. Surface areas for samples of $Li_2C_2O_4 \cdot 2HNb(C_2O_4)_3$ calcined in air.

Fig. 11 is an electron micrograph of lithium niobate agglomerates formed by the decomposition of the freeze-dried material in oxygen at 500°C for 4 h. The marker represent 1μ so that the individual particle size appears to be a few tenths or so but they are severely agglomerated. These agglomerates, of course, are loosely held together in the much larger spherical agglomerates corresponding to the initial droplet size.

This technique does not have the built in control of stoichiometry that the precipitation of a unique compound has, *e.g.*, $BaTiO(C_2O_4)_2$[3] or $SmFe(CN)_6$[4], but the starting solutions are subject to accurate assay and, if used fresh, should yield a stoichiometric product. The purity indicated in Table I is indicative of what can be obtained without any purification steps and using readily available starting material.

CONCLUSIONS

(*1*) Commercially available solutions of tantalum(V) oxalate may be readily freeze-dried.

(*2*) Subsequent thermal decomposition yields finely divided spherical aggregates of tantalum(V) oxide.

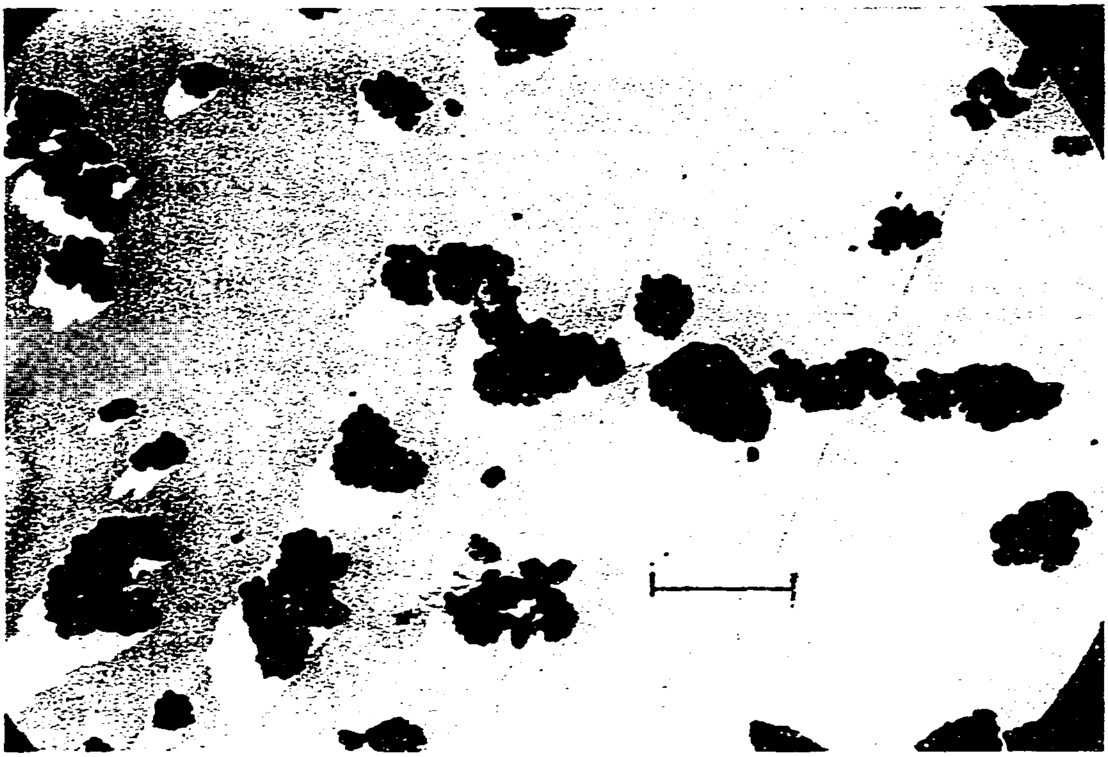


Fig. 11. Electron micrograph (replica) of freeze-dried lithium–niobium oxalate which has been heated in oxygen at 500 °C for 4 h; marker is 1 nm.

(*3*) Calculation based on weight loss suggest that the stable species after freeze-drying is $NH_4Ta(C_2O_4)_3 \cdot 2H_2O$.

(*4*) X-ray, DTA, TGA, and surface area all indicate that amorphous oxide, formed at low temperature, crystallizes between 700 and 800 °C.

(*5*) Decomposition of the oxalate in a reducing atmosphere yields an intimately mixed tantalum(V) oxide and carbon which subsequently reacts in a neutral or reducing atmosphere at temperatures greater than 1200 °C to form tantalum carbide, TaC. This type process may be useful for the formation of refractory carbides in general.

(*6*) The freeze-dried mixed oxalate is a suitable material for the preparation of lithium niobate powder. Its principal advantage is its lower temperature of conversion to the compound, around 500 compared to 800 °C for the conventional material. This results from increased reactivity and homogeneity which alleviates the need for high-temperature firing and offers a wider range of particle size and crystalline perfection. A second advantage is that the product preserves the dust free, free flowing, spherical agglomerate so convenient for subsequent handling and processing as either a feed powder for crystal growth or for use as a polycrystalline ceramic.

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