

Formation of niobium-tantalum pentoxide orthorhombic solid solutions under chlorine-bearing atmospheres

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This paper studies, by means of X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDXS), the structural changes suffered by amorphous hydrated Nb oxide and mixtures of amorphous and crystalline Nb and Ta oxides subjected to thermal treatments in air and chlorine atmospheres. The air heating of amorphous $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ leads to different crystalline phases depending on the working temperature. The hexagonal phase of Nb_2O_5 is obtained at 773 K and the monoclinic phase $\beta\text{-Nb}_2\text{O}_5$ is obtained at 1173 K. The thermal treatment of amorphous Nb oxide in chlorine atmosphere decreases the temperature at which phase $\gamma\text{-Nb}_2\text{O}_5$ appears and at 1173 K the stable monoclinic phase $\alpha\text{-Nb}_2\text{O}_5$ is obtained. Air calcination for 5 hours at temperatures between 973 and 1273 K of different amorphous $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ - $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ mixtures does not lead to solid solution of these oxides. Thermal treatment in chlorine atmosphere of amorphous Nb and Ta oxides leads to the formation of Nb_2O_5 and Ta_2O_5 orthorhombic solution in one hour at 973 K and in 24 hours at 1223 K, when starting from crystalline oxides. The effect of chlorine is due to the dissolution-recrystallization of the metallic chlorides and the oxygen formed, when the system evolves to chemical equilibrium between solid phases and gaseous chlorine. © 2001 Kluwer Academic Publishers

1. Introduction

Nb(V) and Ta(V) oxides can exhibit different crystalline structures [1, 2]. Tantalum oxide exhibits two stable structures: orthorhombic, $\beta\text{-Ta}_2\text{O}_5$, and tetragonal, $\alpha\text{-Ta}_2\text{O}_5$, for low and high temperatures, respectively, with reversible transition at 1633 K [1, 3]. Nb_2O_5 can exhibit various crystalline forms [2, 4], but unlike Ta_2O_5 , it has only one stable crystalline structure which corresponds to a monoclinic structure, $\alpha\text{-Nb}_2\text{O}_5$ [4, 5], also referred to in early works as $\text{H-Nb}_2\text{O}_5$ [6]. Amorphous Ta(V) and Nb(V) oxides are usually obtained by hydrolysis of their respective chlorides or organic complexes. Hydrated oxides form highly insoluble white gels, which, after being filtered and dried off at 423 K, retain between 5 and 15% of water, which is eliminated by heating at high temperatures [6–9].

It has been found that when amorphous Ta_2O_5 is air heated, an hexagonal structure ($\delta\text{-Ta}_2\text{O}_5$) appears before the formation of the orthorhombic phase $\beta\text{-Ta}_2\text{O}_5$. This structure is only stable at low temperatures and

irreversibly transforms to the orthorhombic form at higher temperatures [10, 11]. The formation of this hexagonal structure previous to the orthorhombic phase has also been reported for treatments of amorphous Ta_2O_5 films by heating [12].

When amorphous Nb_2O_5 is air heated, metastable intermediate phases are obtained before the appearance of the monoclinic structure $\alpha\text{-Nb}_2\text{O}_5$. Among these is the orthorhombic structure equivalent to that of $\beta\text{-Ta}_2\text{O}_5$, known as phase $\gamma\text{-Nb}_2\text{O}_5$ [4, 5] or $\text{T-Nb}_2\text{O}_5$ [6]. Further heating leads to monoclinic $\beta\text{-Nb}_2\text{O}_5$ [4, 5] or $\text{M-Nb}_2\text{O}_5$ [6]. Finally, at temperatures close to 1373 K, the stable monoclinic structure $\alpha\text{-Nb}_2\text{O}_5$ is irreversibly formed.

Isomorphism between Nb_2O_5 and Ta_2O_5 occurs between several of their phases. For example, the hexagonal phase of Nb_2O_5 and orthorhombic phase $\gamma\text{-Nb}_2\text{O}_5$ are isomorphic with the hexagonal and orthorhombic phases of Ta_2O_5 , with a slight variation of peak position and therefore of lattice parameters [13–16]. The

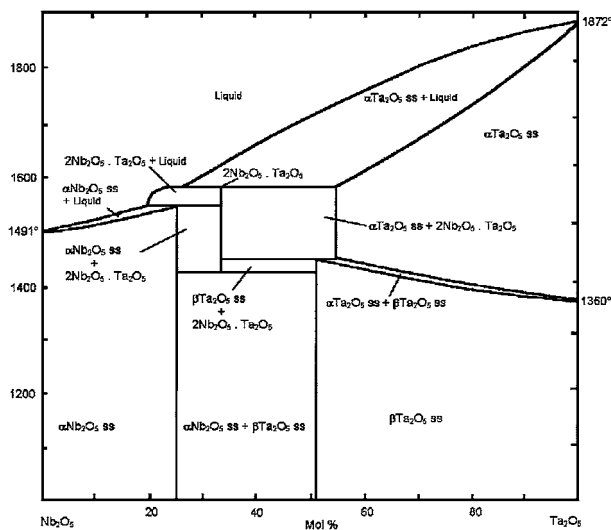


Figure 1 Phase diagram for the Nb_2O_5 - Ta_2O_5 system (from F. Holtzberg and A. Risman, J. Phys. Chem., 65, 1193 (1961).

formation of solid Nb and Ta solutions, according to the phase diagram in Fig. 1, indicates that the Nb_2O_5 - Ta_2O_5 solid solution of orthorhombic structure (β - Ta_2O_5 ss), which is of particular interest for this work, forms up to a composition close to 50% in moles of Nb and Ta [17].

However, it has been reported by Zafirir *et al.* [5] that the formation of solid $(\text{Nb}_x\text{Ta}_{1-x})_2\text{O}_5$ solutions in its orthorhombic phase can occur in all the composition of the binary mixture when starting from the amorphous oxides mixture obtained by joint hydrolysis and subsequent calcination at 873–1073 K for 24 h, since the Nb orthorhombic phase is metastable at temperatures under 1073 K [5].

It has recently been reported that thermal treatment of amorphous Ta_2O_5 in chlorine atmosphere affects and alters the sequence of transformation to phase β [18]. This has also been reported for other refractory oxides, such as ZrO_2 [19], TiO_2 [20] y Al_2O_3 [21]. In these oxides, it was observed that the acceleration of the phase transformations caused by Cl_2 is due to formation of nuclei in the stable phase from the reaction in gaseous phase between metallic chloride and oxygen, which are products of previous chlorination of the starting oxide.

On the basis of the above results and considering the work by Zafirir *et al.* [5], this paper reports a study on the influence of gaseous chlorine on the formation of solid solutions of Nb and Ta oxides from mixtures of pure amorphous and crystalline oxides of these elements. The structural and microstructural evolution of the products obtained by thermal treatment of the above mentioned oxides were investigated by X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDXS).

2. Experimental

2.1. Materials

Starting materials were pure Nb and Ta oxides (Fluka AG, CH-9470 Buchs) in their monoclinic phase, α - Nb_2O_5 , and orthorhombic phase, β - Ta_2O_5 , respec-

tively, and amorphous hydrated Nb and Ta oxides with particle size between 5 and 100 μm , obtained by fusion of the pure oxides. The methodology for preparation of the amorphous phases is described in [18].

Fig. 2 shows the morphology of the particles of pure oxides. The α - Nb_2O_5 particles exhibit long crystals of approximately 10–50 μm (Fig. 2a). The amorphous phase of $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ exhibits spherical particles with tiny grains under 1 μm (Fig. 2b). Orthorhombic Ta_2O_5 (Fig. 2c) exhibits spherical particles with grains of approximately 1 μm , which do not agglomerate uniformly. The amorphous $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ particles show an irregular morphology, which can be seen in [18].

The mixture of amorphous $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ - $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ was performed mechanically in a quartz crucible with a small stainless steel rod.

The gases used in the heating assays were chlorine (99.5%), nitrogen (99.99%) and air. All gases were conveniently dried before entering the reactor.

2.2. Equipment

A schematic diagram of the experimental system used for the thermal treatment of amorphous oxides is described in [18]. The flow of the different gases was controlled by flowmeters. The transformations produced in the samples were monitored with a Rigaku D-Max IIC diffractometer operated at 35 kV and 30 mA using $\text{Cu K}\alpha$ radiation, $\lambda = 0.15418$ nm with Ni filter. The samples subjected to different treatments were examined by scanning electron microscopy and energy-dispersive X-ray spectroscopy with a Philips Electronic Instruments SEM 515 microscope.

2.3. Procedure

Flow system: Samples of amorphous Nb_2O_5 or amorphous Nb_2O_5 - Ta_2O_5 mixtures were placed in a quartz crucible and heated in different atmospheres. Each sample was placed in a N_2 current until working conditions were reached. The nitrogen current was then stopped and a flow of air or chlorine at 50 $\text{cm}^3 \text{min}^{-1}$ was passed into the reactor at 1.013×10^5 Pa, for the time the experiment lasted. The system was purged with N_2 after each run. The times of purging and previous sample heating in N_2 were standardized. The samples were weighed after and before each run.

Encapsulated samples: Powders of α - Nb_2O_5 and β - Ta_2O_5 were mixed in molar ratio 1:1. The mixture was placed within the spherical capsule and held in vacuum (1.3×10^{-8} Pa) for 1 hour until it was degassed. Then, chlorine gas was injected and the capsule was sealed. The gas pressure was chosen so that a pressure of 0.021×10^{-3} Pa was obtained at room temperature. The encapsulated sample was then heated at 1223 K for 24 hours and finally quenched at room temperature.

After thermal treatment, the sample was examined by XRD, SEM and EDXS.

3. Results and discussion

3.1. Thermal treatment of amorphous $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ in air

In order to understand the effect of thermal treatment on the mixtures of amorphous and crystalline oxides

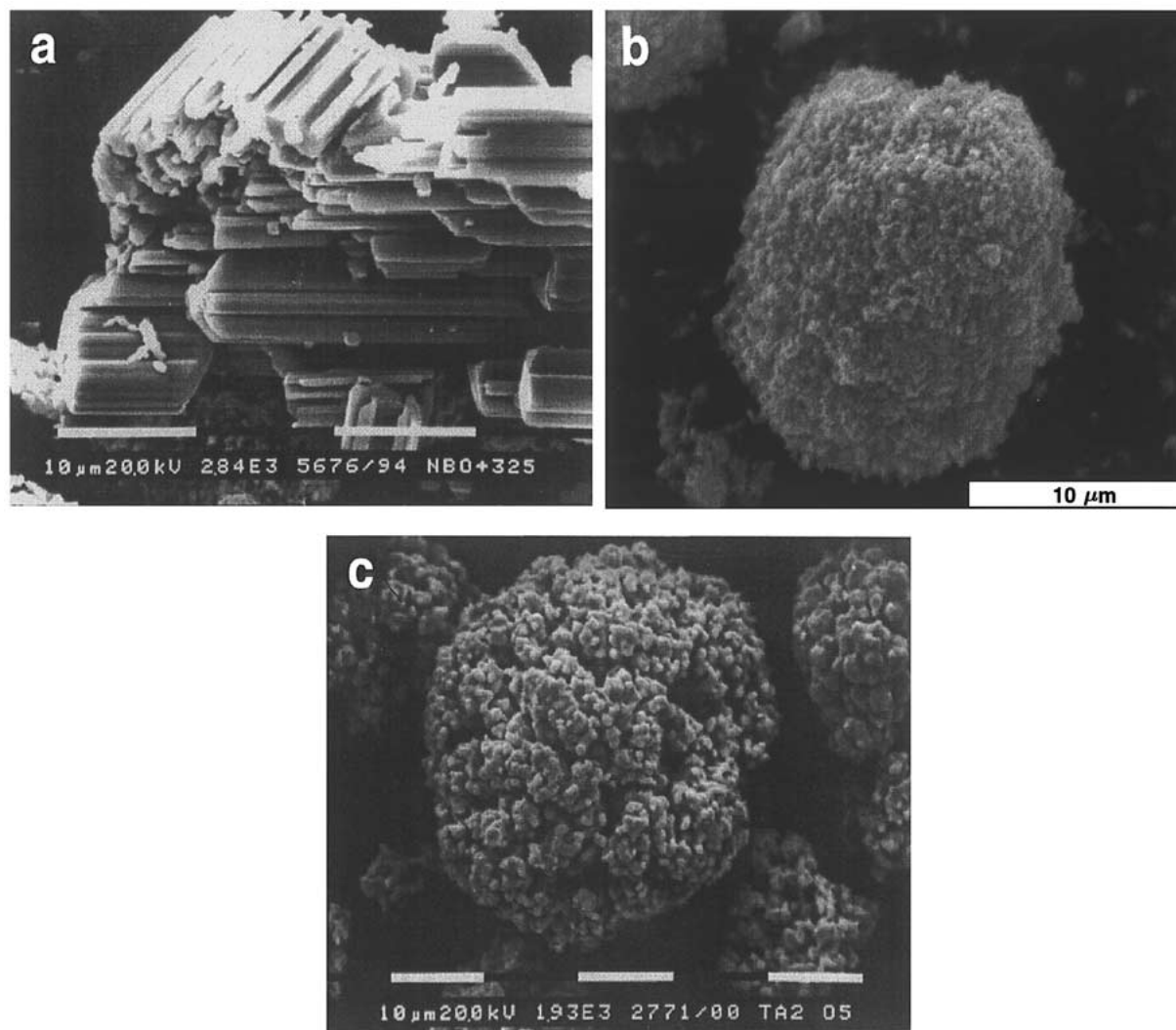


Figure 2 Micrographs of starting oxides. (a) conglomerate of monoclinic α - Nb_2O_5 particles; (b) amorphous $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ particle; (c) conglomerate of orthorhombic β - Ta_2O_5 particles.

under chlorine atmospheres, it is advisable to first determine the effect of chlorine on the crystallization of each of the oxides. In a previous study of the effect of chlorine on the crystallization of amorphous tantalum oxide [18] it was recently reported that heating in chlorine markedly decreases the crystallization temperature of the orthorhombic phase of Ta oxide as compared to identical treatments in air. It was also observed that, when heating the amorphous oxide, the first crystalline phase to appear is that corresponding to the γ - Ta_2O_5 .

In order to know the effect of chlorine on crystallization of amorphous $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ when heated in chlorine and for the purposes of comparison, the heating of amorphous hydrated Nb oxide under air current was first studied. The samples were treated at 773, 873, 973, 1073, 1173 and 1273 K for 5 hours. The mass losses due to dehydration of amorphous $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ upon heating increased with temperature from 8 to 15%, these values being higher than those observed for amorphous Ta_2O_5 [18]. Phase transformation undergone by the effect of air-heating are shown in Fig. 3.

Fig. 3 shows that amorphous $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ undergoes a series of phase transformation in air with increasing temperatures. Crystallization occurs at 773 K,

indicated by the appearance of diffraction lines at approximately 22.6, 28.6 and 36.8 degrees. At 873 K the above mentioned diffraction lines become more clearly defined, and at 973 K the formation of one or more crystalline phases becomes clear by a sharp, high-intensity line at $2\theta = 22.65$. Further heating to 1173 and 1273 K leads to disappearance of these diffraction lines and appearance of new set of lines, which can undoubtedly be interpreted as formation of a new phase.

The phase changes observed in Fig. 3 can be interpreted from the diffractograms (Fig. 4) simulated from the JCPDS files, which correspond to the hexagonal Nb_2O_5 [13], orthorhombic γ - Nb_2O_5 [14], monoclinic β - Nb_2O_5 and monoclinic α - Nb_2O_5 structures, respectively [22, 23]. From comparison between Figs 3 and 4, it results that air-heating for 5 hours leads to successive crystallization to several Nb_2O_5 phases. Under our working experimental conditions, the hexagonal and/or orthorhombic phases start to form at 773 K. Subsequently, at 873 K, the orthorhombic phase begins to define and remains up to 1073 K, temperature at which the monoclinic β - Nb_2O_5 phase appears. The stable monoclinic α - Nb_2O_5 structure does not form by air calcination under our experimental conditions.

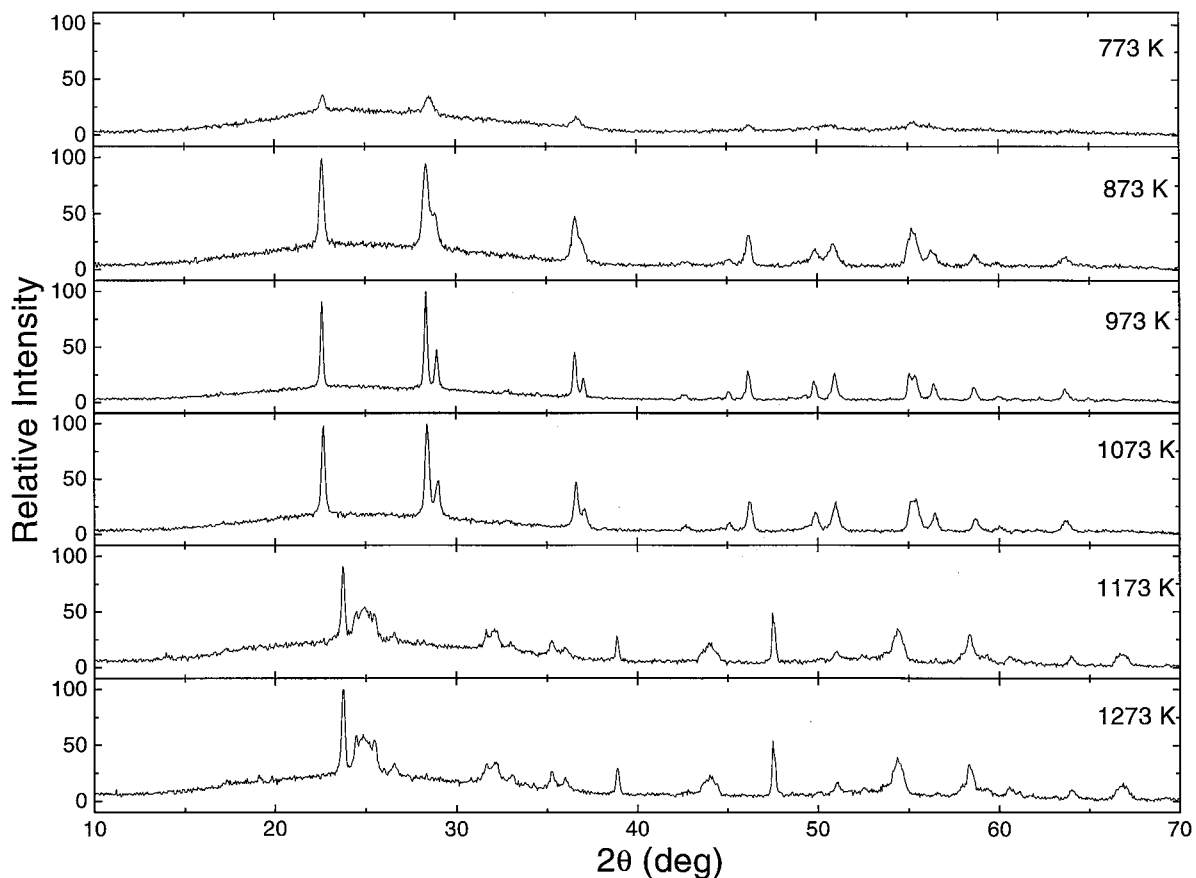


Figure 3 Diffractograms of the products obtained after calcination of amorphous $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ at different temperatures, in air current for 5 hours.

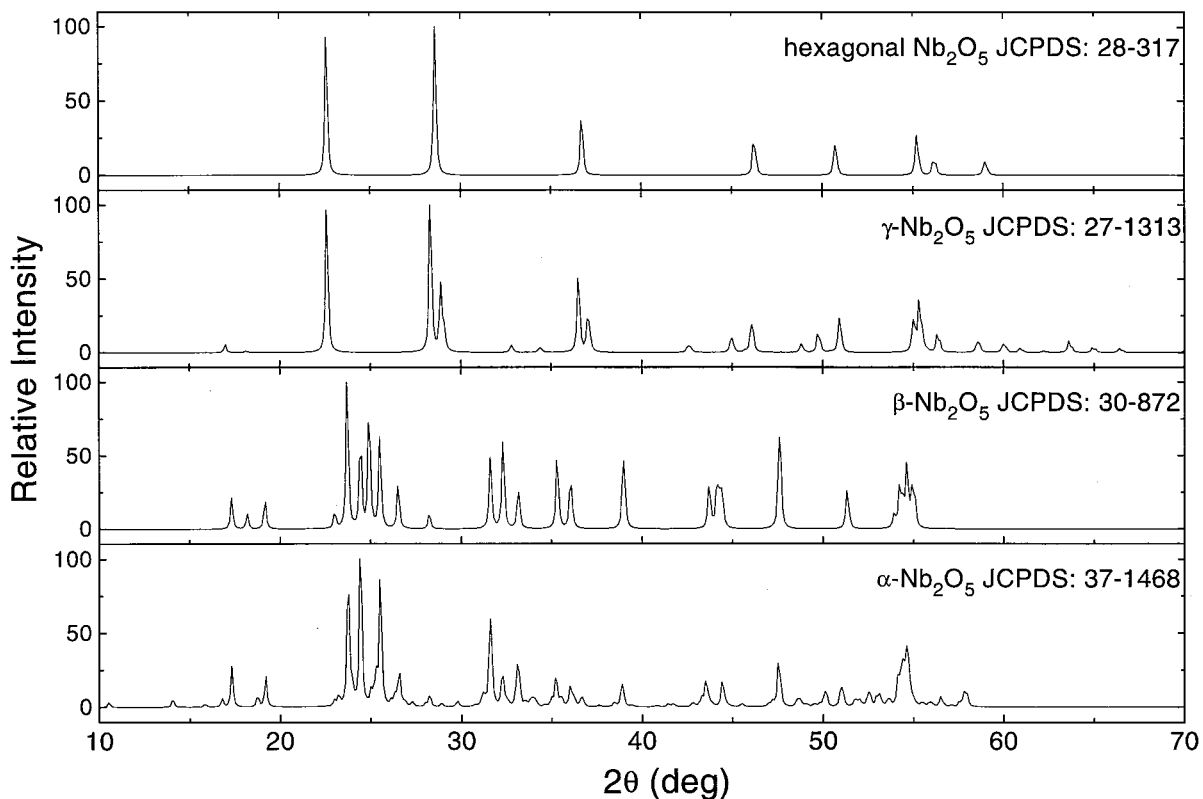


Figure 4 Diffractograms simulated from JCPDS files corresponding to the Nb_2O_5 phases.

SEM analysis of the air thermal treatment did not show appreciable changes in particle morphology as compared to the starting material. No marked changes were observed on particle surface when the hexagonal

and orthorhombic phases were obtained. The only variation detected was a slight increase and better definition of the crystalline grains when the sample transformed to the monoclinic phase $\beta\text{-Nb}_2\text{O}_5$ at 1173 K.

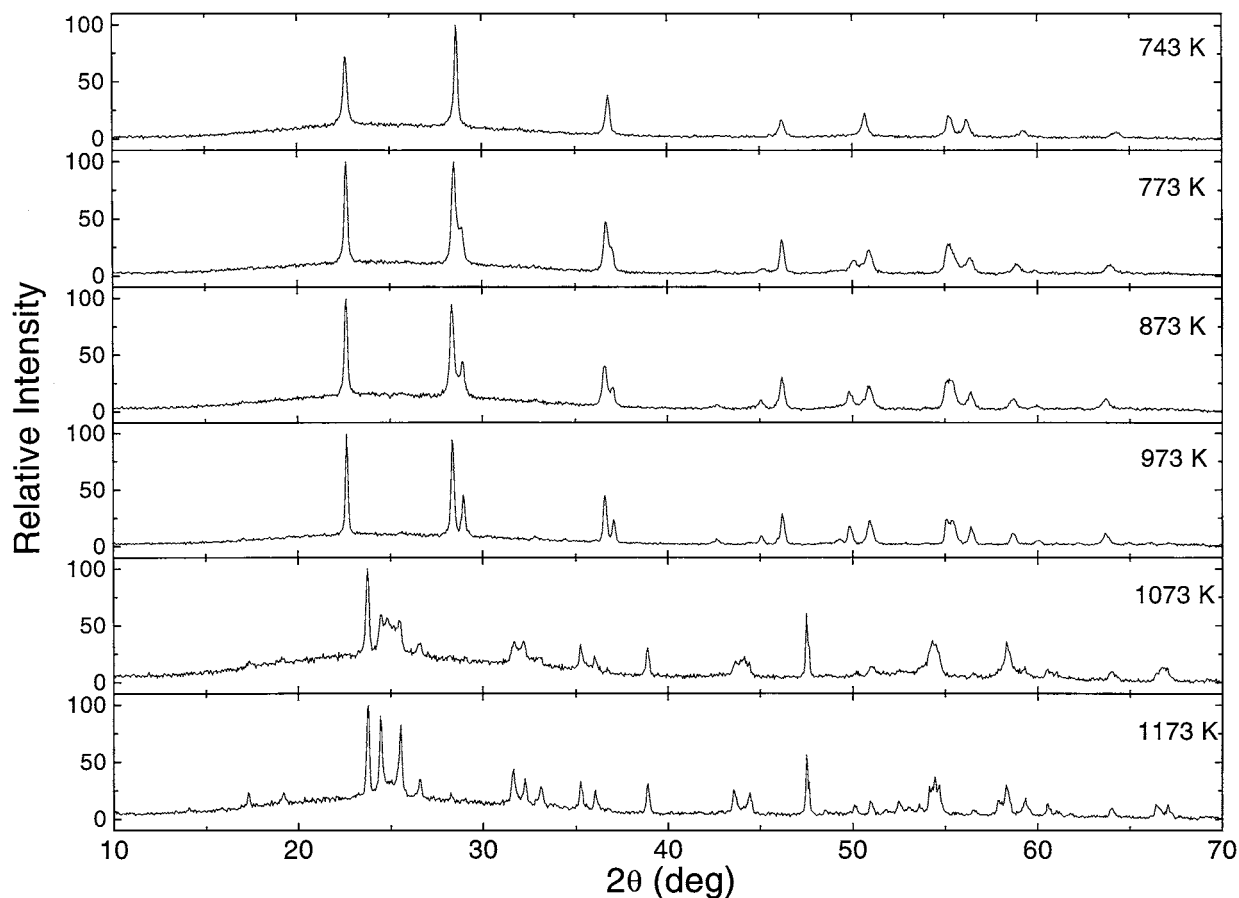


Figure 5 Diffraction patterns of the products obtained after calcination of amorphous $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ at different temperatures in Cl_2 current for 1 hour.

3.2. Thermal treatment of amorphous $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ in Cl_2 current

Fig. 5 shows the phase transformations undergone by $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ when calcined under Cl_2 for one hour.

It can be observed that thermal treatment in chlorine atmosphere, as in air, results in a series of crystalline phases which at low temperatures follow a sequence similar to that in Fig. 3. However, Fig. 5 shows that, as compared to air-calcination, crystalline phase formation begins at lower temperature and that the stable monoclinic structure $\alpha\text{-Nb}_2\text{O}_5$ crystallizes in the time the experiment lasted. In short, the hexagonal phase clearly appears at 743 K, and at 773 K the orthorhombic phase begins to form and remains up to 973 K. The monoclinic phase $\beta\text{-Nb}_2\text{O}_5$ appears at 1073 K, and the stable monoclinic $\alpha\text{-Nb}_2\text{O}_5$ structure is finally reached at 1173 K. It can be clearly concluded that the presence of chlorine markedly increases crystallization of the several Nb_2O_5 phases, which confirms observations for heating of amorphous tantalum oxide [18].

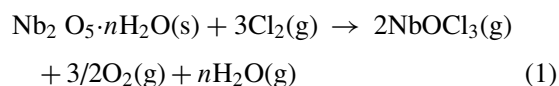
Mass losses suffered by amorphous Nb oxide under Cl_2 current were slightly higher than those observed for air heating treatment. This is due to greater water loss by the dehydrating effect of chlorine, as well as to a slight volatilization of $\text{NbCl}_5(\text{g})$ and $\text{NbOCl}_3(\text{g})$ in chlorine current at high temperatures [24, 25]. In order to minimize the volatilization of the formed Nb chlorides, heating in chlorine atmosphere was done for a lapse 5 times lower than that used in air treatments. Formation of $\text{NbCl}_5(\text{g})$ and $\text{NbOCl}_3(\text{g})$ will be discussed in detail below.

SEM analysis of some of the residues after thermal treatment in Cl_2 of amorphous $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ is shown in Fig. 6a and b.

Fig. 6a corresponds to the residue obtained at 973 K in Cl_2 , in which the orthorhombic phase was detected. This figure, together with Fig. 2b, shows that there is particle disintegration, probably caused by Cl_2 chemical attack, as well as slight growth of crystalline spherical grains that constitute the particle. The shape of these grains is similar to that observed in crystalline phases obtained from amorphous Ta oxide heated in chlorine atmosphere [18].

Fig. 6b corresponds to the 1173 K residues, where the monoclinic phase $\alpha\text{-Nb}_2\text{O}_5$ appears. The spherical particles cannot be distinguished because of the stronger Cl_2 attack at this temperature. It is to be noted here that recrystallization of $\alpha\text{-Nb}_2\text{O}_5$ leads to the formation of grains of greater size, which differ from those of the orthorhombic phase.

The mechanism by which chlorine favors the formation of Nb_2O_5 crystalline phases at lower temperature and shorter times than those required for crystallization in air is probably similar to that proposed for Ta_2O_5 [18]. This is a mechanism of dissolution-recrystallization through the gaseous phase, by means of volatile species in equilibrium with the oxide. In fact, when Nb_2O_5 is heated under chlorine atmosphere, the following reactions are expected:



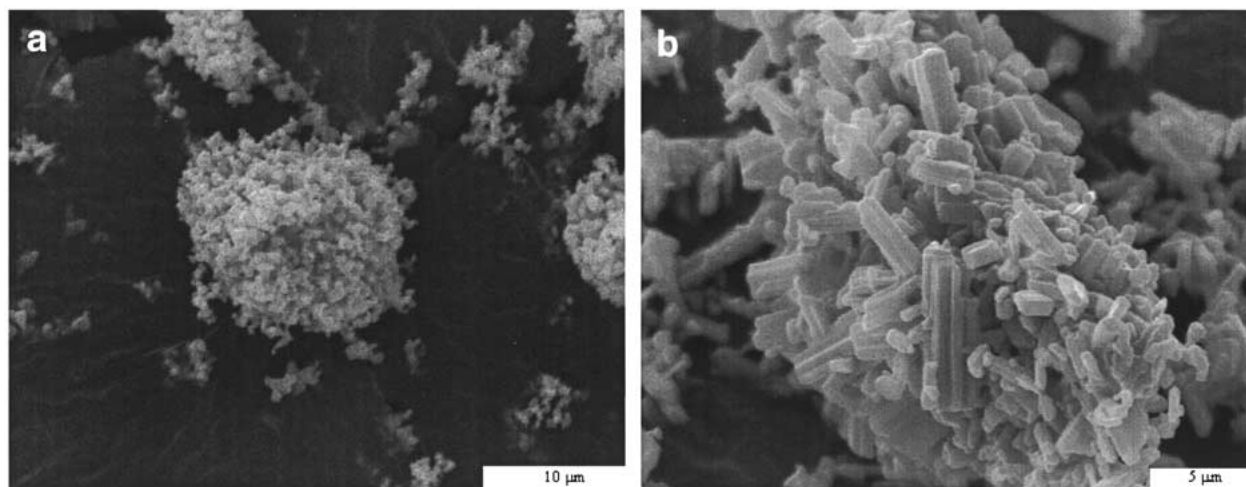
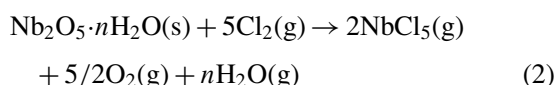
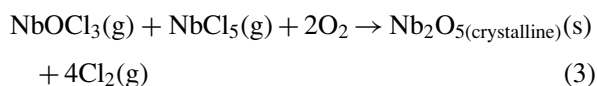


Figure 6 Micrograph of the products obtained after calcination of $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ in Cl_2 . (a) at 973 K for 1 hour, orthorhombic phase; (b) at 1173 K for 1 hours, monoclinic phase “ α ”.



At 973 K, and for chlorine partial pressure of 101, 223 Pa, equilibrium pressures of 135, 6.21×10^{-10} and 101 Pa, for NbOCl_3 , NbCl_5 , and O_2 , respectively are expected for a closed system. It can be assumed that the pressure reached in a flow open system such as the one used in this study, generates a partial pressure that, although lower than that of equilibrium, is enough to favor mass transport through the pores of the powder generated in recrystallization through reactions reverse to those above indicated. This is:



In short, we have: amorphous oxide + chlorine = crystalline oxide + chlorine, where chlorine acts as an intermediary to favor the formation of a crystalline phase, which is thermodynamically more stable than the amorphous phase. Therefore, the vapor pressures of the respective chlorides and of O_2 are enough to allow the formation of the new crystalline structures from the gaseous phase, and subsequently an increase of these crystals [18, 25]. This has also been reported for other refractory oxides in similar systems [18–20].

3.3. Thermal treatment of the $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ - $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ mixture in air

A mixture of amorphous oxides in a composition of approximately 25% of $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ and 75% of $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ in moles was treated in air current for 5 hours at 973 K. The residue was analyzed by XRD (Fig. 7a). Figs. 7b and c show the diffractograms of the residues of pure $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ and $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ thermal treatments, under the same conditions of the mixture. The orthorhombic and hexagonal phase were obtained, respectively, for $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ and $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$.

Comparison of the diffractograms in Fig. 7 shows that the diffraction lines corresponding to phases $\delta\text{-Ta}_2\text{O}_5$

and $\gamma\text{-Nb}_2\text{O}_5$ appear in the residue obtained from air calcination of the mixture at 973 K, with marked peaks at 2θ of 22.65, 22.95, 46.2, 46.9, 49.85, 50.45 and 50.95. In fact, the diffractogram of Fig. 7a is equal to the addition of the diffractograms in Fig. 7b and c, for our experimental conditions, as can be observed by projecting the corresponding non-overlapping lines of phases $\delta\text{-Ta}_2\text{O}_5$ and $\gamma\text{-Nb}_2\text{O}_5$ on the diffractogram of the air calcined mixture.

A more detailed view of the line combination of the Ta oxide hexagonal phase, $\delta\text{-Ta}_2\text{O}_5$, and the Nb oxide orthorhombic phase, $\gamma\text{-Nb}_2\text{O}_5$, can be seen by enlarging the area between 20 and 40 degrees, as shown in Fig. 8. Thermal treatment in air, therefore, does not lead to the formation of a solid solution of Nb and Ta oxides. Rather, each of them reorders in the crystalline phase corresponding to the treatment temperatures.

When the product calcined at 973 K suffered a subsequent heating to 1273 K for 5 hours, the $\gamma\text{-Nb}_2\text{O}_5$ phase transformed to monoclinic form $\beta\text{-Nb}_2\text{O}_5$ while hexagonal Ta_2O_5 crystallized in the orthorhombic structure. This can be seen in Fig. 9 and is coherent with the behavior expected for each separate phase.

As seen in Fig. 9, the position of the diffraction lines of the phases of each oxide show that there was no formation of solid solution. The diffractogram of the product obtained by air heating of the $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ - $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ mixture is the same as the one that would be obtained by addition of the diffractograms of the separately treated oxides, under the same conditions.

The results of air calcination experiments of mixtures with different compositions of $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ and $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ showed that, when starting from a mechanical mixture it is not possible to obtain solid solutions of these oxides, under our experimental conditions.

3.4. Thermal treatment of the $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ - $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ mixture in Cl_2 current

A $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ - $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ mixture with identical composition and mixed in the same way as that used for the air heating experiment was calcined in Cl_2 current at

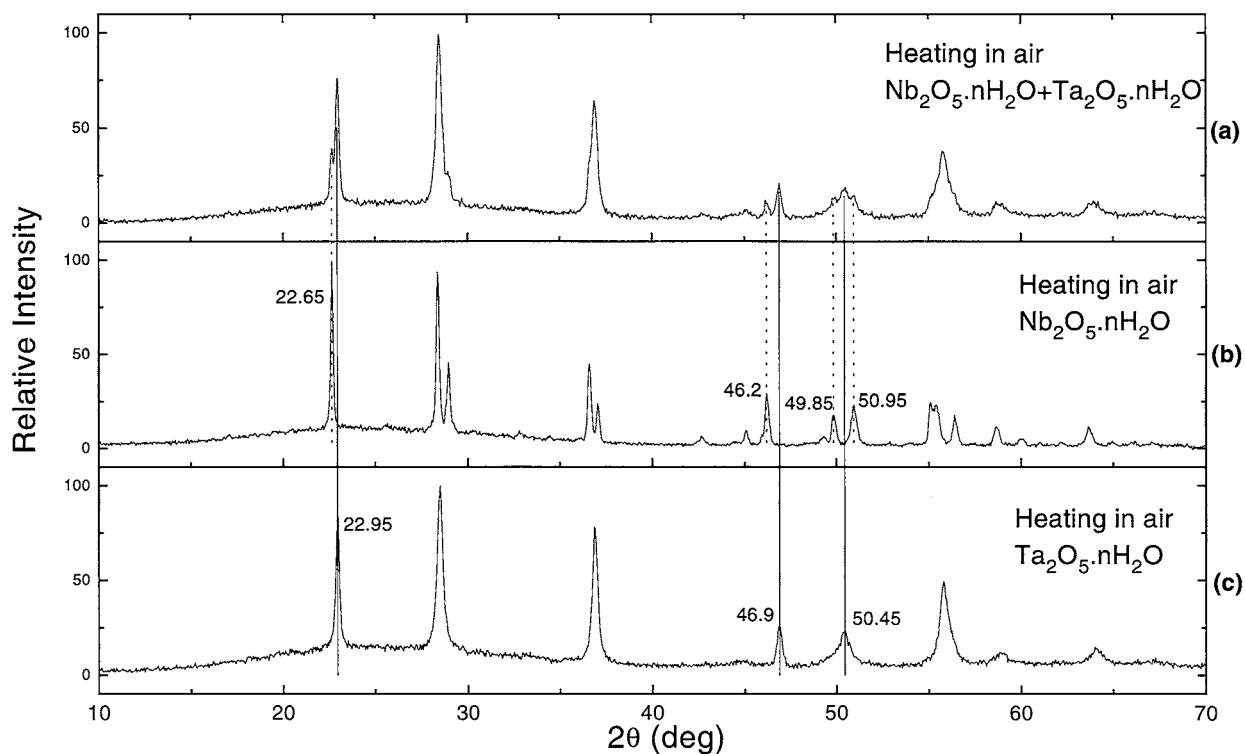


Figure 7 Diffraction of the products obtained after calcination in air current at 973 K, for 5 hours of (a) amorphous $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O} - \text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ mixture; (b) $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$; (c) $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$.

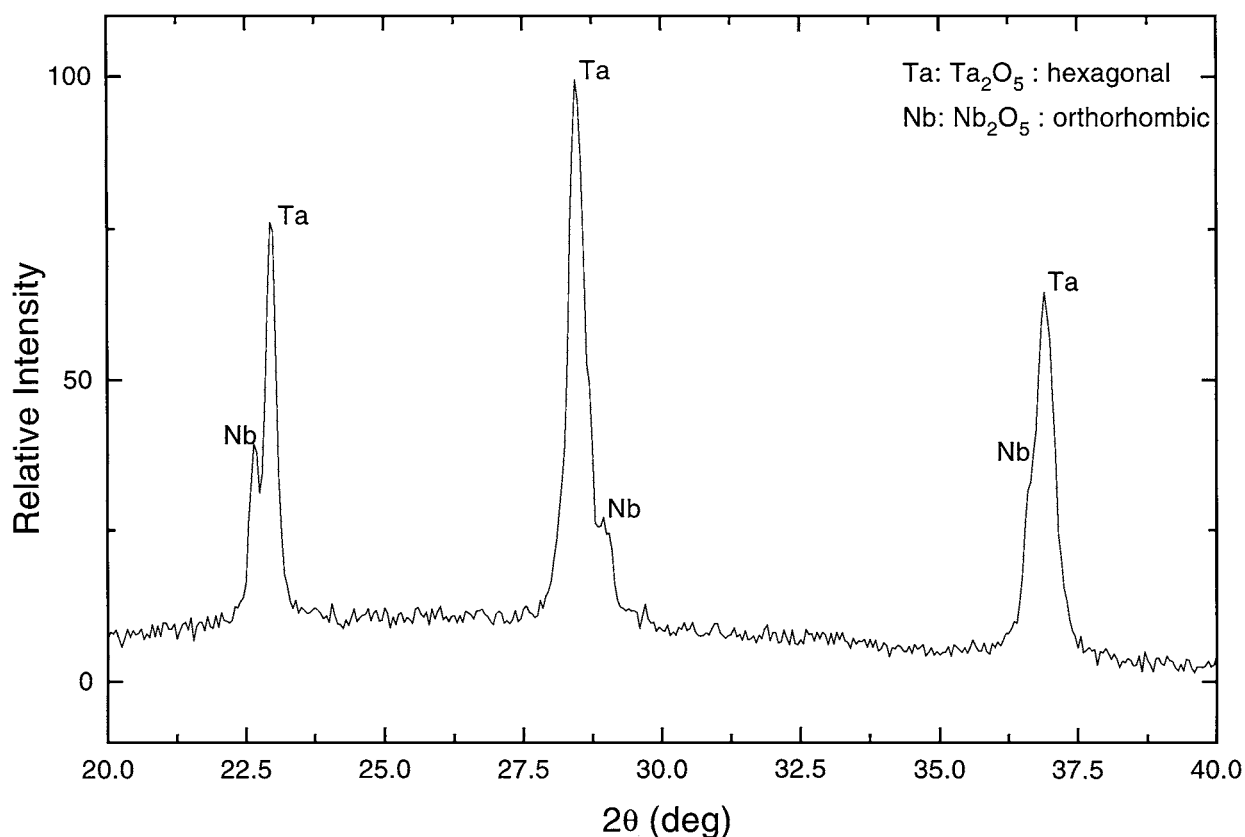


Figure 8 Diffraction lines between 20 and 40 degrees corresponding to Fig. 7.

973 K for one hour. The residue diffractogram, between 20 and 40 degrees, is shown in Fig. 10a.

Comparison between diffractograms in Figs 10a and 9 reveals that chlorine treatment generates a crystalline phase different from the phase mixture obtained by air heating of the amorphous oxide mixture.

The diffractogram shown in Fig. 10a corresponds to the orthorhombic structure for which phases $\gamma\text{-Nb}_2\text{O}_5$ and $\beta\text{-Ta}_2\text{O}_5$ are isomorphic. In this figure, the diffraction lines typical of the orthorhombic phase, which for pure Nb_2O_5 appear at 22.65, 28.3, 28.9, 36.5 and 37.0 degrees, are slightly shifted.

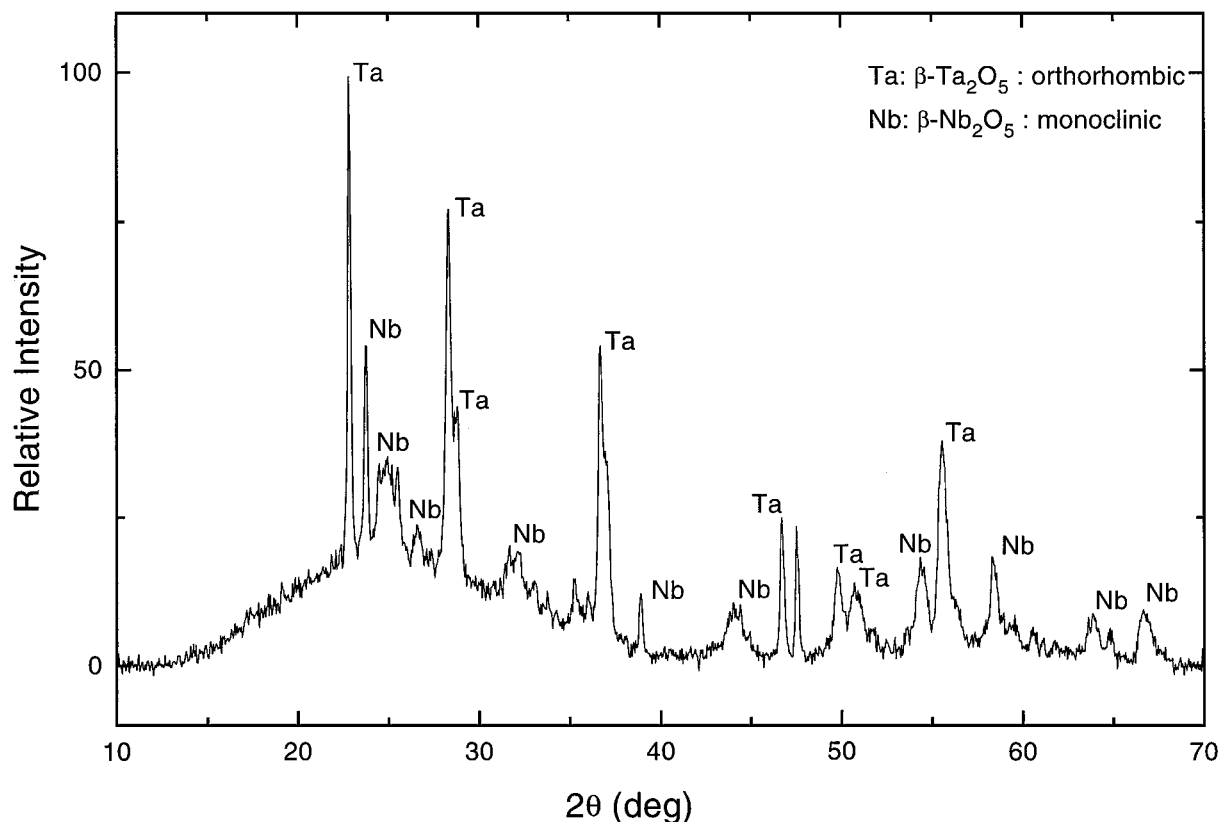


Figure 9 Diffraction pattern of the products obtained after calcination of the amorphous $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ - $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ mixture in air current at 1273 K for 5 hours.

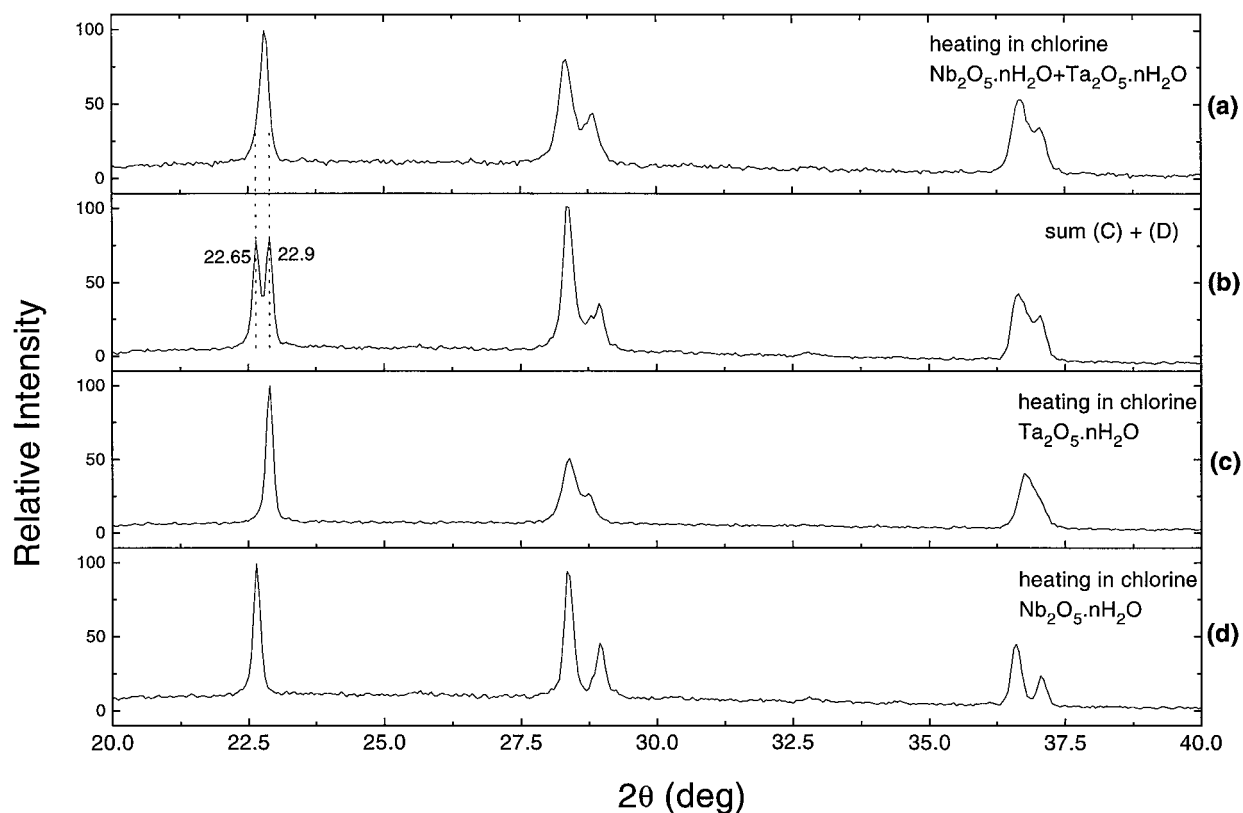


Figure 10 Diffraction pattern of the products obtained after calcination of the 25% $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ - 75% $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ Mixture at 973 K and the pure oxides, in Cl_2 for 1 hour.

The formation of a single orthorhombic structure phase matches the individual phases obtained from each of the amorphous oxides when treated at 973 K under chlorine atmosphere, as already discussed for Fig. 5 and in a previous report [18]. Comparison of

the diffraction pattern in Fig. 10a with that in 10b, which in turn results from overlapping the independent phases of the orthorhombic structures of $\gamma\text{-Nb}_2\text{O}_5$ and $\beta\text{-Ta}_2\text{O}_5$, shows that diffraction pattern 10a is not a simple overlapping of both separate phases. In fact, the presence of a

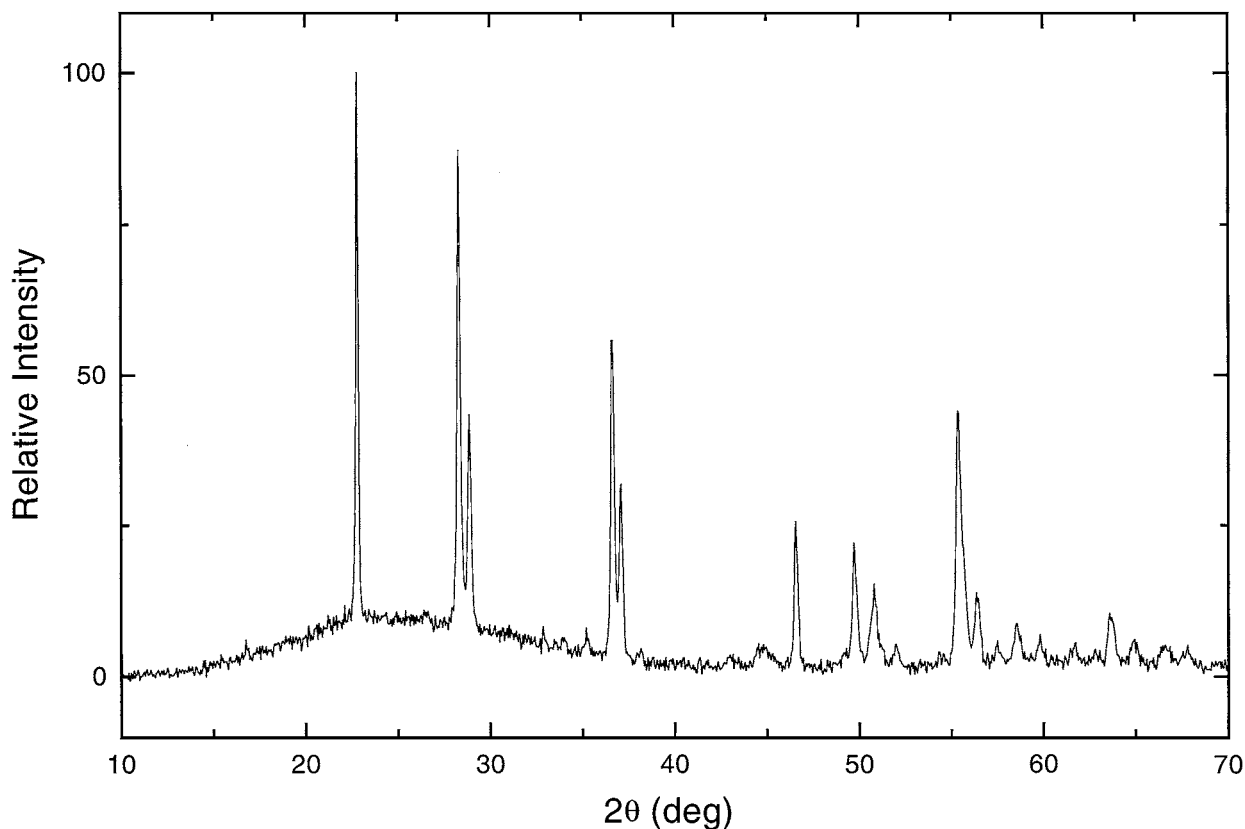


Figure 11 Diffractogram of the products obtained after calcination of the residue of Fig. 13 in air current at 1273 K for 5 hours.

single peak for the set of 001 planes in an intermediary position indicates the formation of a solid solution in the orthorhombic phase.

It is to be noted that mass loss by dehydration and volatilization of the Nb and Ta chlorides did not lead to important variations in the Nb and Ta concentrations in the solid, as compared to the starting composition. It was experimentally determined that, at 973 K in Cl_2 current, the mass loss by metallic chlorides volatilization is under 5%.

SEM analysis of the residues of this chlorination showed the presence of spherical microcrystals on the particles, similar to those observed in the thermal treatment residues of pure oxides, under the same working conditions (Fig. 6a). EDXS analysis of these microcrystals showed the presence of Nb and Ta in all of them, in proportions similar to that of the starting mixture.

Subsequent air calcination at 1273 K of the same residue did not lead to appearance of the monoclinic phase $\beta\text{-Nb}_2\text{O}_5$ observed in Fig. 9. On the contrary, more crystallinity of the orthorhombic phase was achieved, as shown in Fig. 11. This result matches the phase diagram of Fig. 1. It is evident that a solid solution of orthorhombic structure is thermodynamically stable for composition of 75% Ta and 25% Nb.

Similar results, with a small shift of the diffraction lines with respect to the orthorhombic phase of Nb_2O_5 , were obtained with a mixture richer in Nb_2O_5 : 50% of amorphous $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ and $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$.

Further increment of Nb concentration, 75% of $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ - 25% of $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ in moles, also led to the orthorhombic solid solution shown in Fig. 12a upon calcination under Cl_2 atmosphere. In this figure,

it can be observed that peak 001 is split up (22.6 for pure Nb_2O_5). However, when this same residue is subsequently calcined in air at 1273 K for 5 hours, the orthorhombic solid solution together with the monoclinic phase $\beta\text{-Nb}_2\text{O}_5$ are obtained, as shown in Fig. 12b.

The segregation of the thermodynamically metastable monoclinic phase $\beta\text{-Nb}_2\text{O}_5$ matches the phase diagram in Fig. 1. In effect, for compositions of 75% Nb_2O_5 and 25% Ta_2O_5 , the existence of a single phase is not possible. The phase diagram shows that the orthorhombic solid solution exists as a single phase in compositions close to 50% Nb_2O_5 and that, for higher compositions, the stable α -monoclinic phase precipitates. The obtention of phase $\beta\text{-Nb}_2\text{O}_5$ instead of the stable monoclinic phase is also coherent with the results observed in Fig. 3 at 1273 K.

3.5. Effect of composition on lattice parameters

The linear variation with composition of the lattice parameters a and c of the orthorhombic solid solutions of $(\text{Nb}_x\text{Ta}_{1-x})_2\text{O}_5$ constitutes an approximate analytic method to determine the composition of this type of compounds [5]. Even though a study of the effect of composition on the linear variation of the lattice parameters of Nb-Ta solid solutions is beyond the scope of this work, it is possible to perform an estimate of these parameters from the results here obtained. In fact, the shift of the diffraction line with composition is revealed by the variation of position of line 001 ($2\theta = 22.65$ for pure Nb_2O_5) with the composition of the solid solution, as shown in Fig. 13.

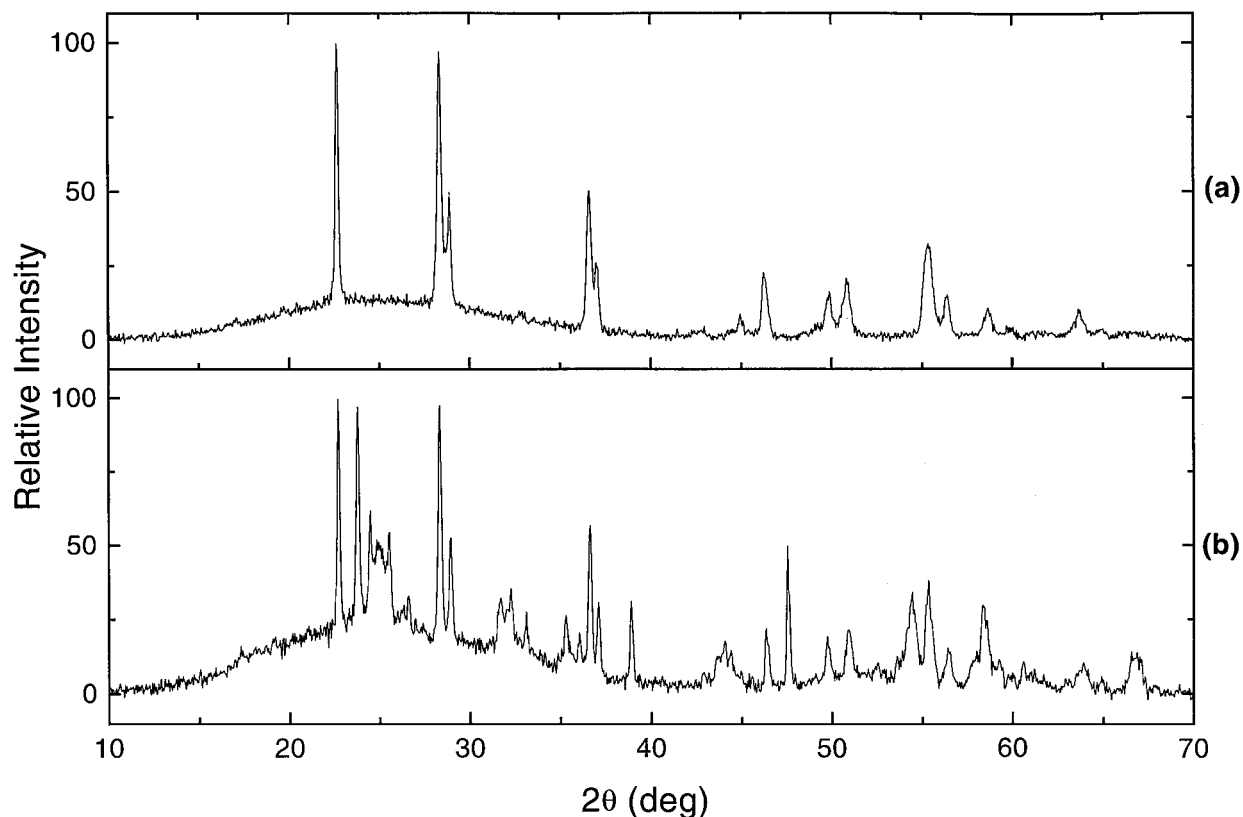


Figure 12 Diffraction patterns of the products obtained after calcination of the 75% $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ - 25% $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ mixture: (a) in Cl_2 current at 973 K for one hour; (b) in air current at 1273 K for 5 hours of the residue obtained in (a).

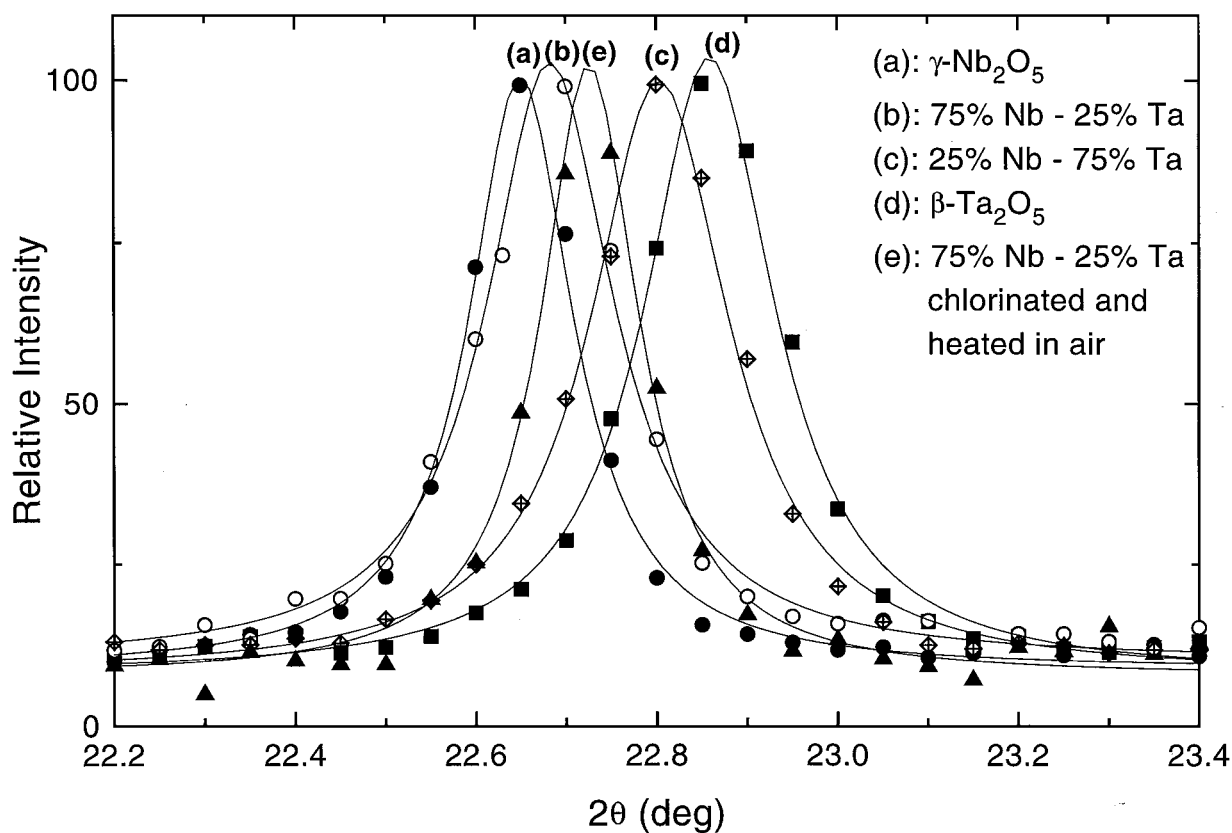


Figure 13 Variation of peak 001 position with solid solution composition.

The position of peak 001 shows that phase $\gamma\text{-Nb}_2\text{O}_5$ (a) corresponds to the lower values of 2θ (close to 22.6), while phase $\beta\text{-Ta}_2\text{O}_5$ (d) corresponds to the higher value (close to 22.9). Intermediate peaks correspond

to the solid solutions of 75% Nb_2O_5 - 25% Ta_2O_5 (b) and 25% Nb_2O_5 - 75% Ta_2O_5 (c). Peak (e) corresponds to the residue of the solid solution in Fig. 12b. The shift in peak (b) after residue calcination is due to the fact

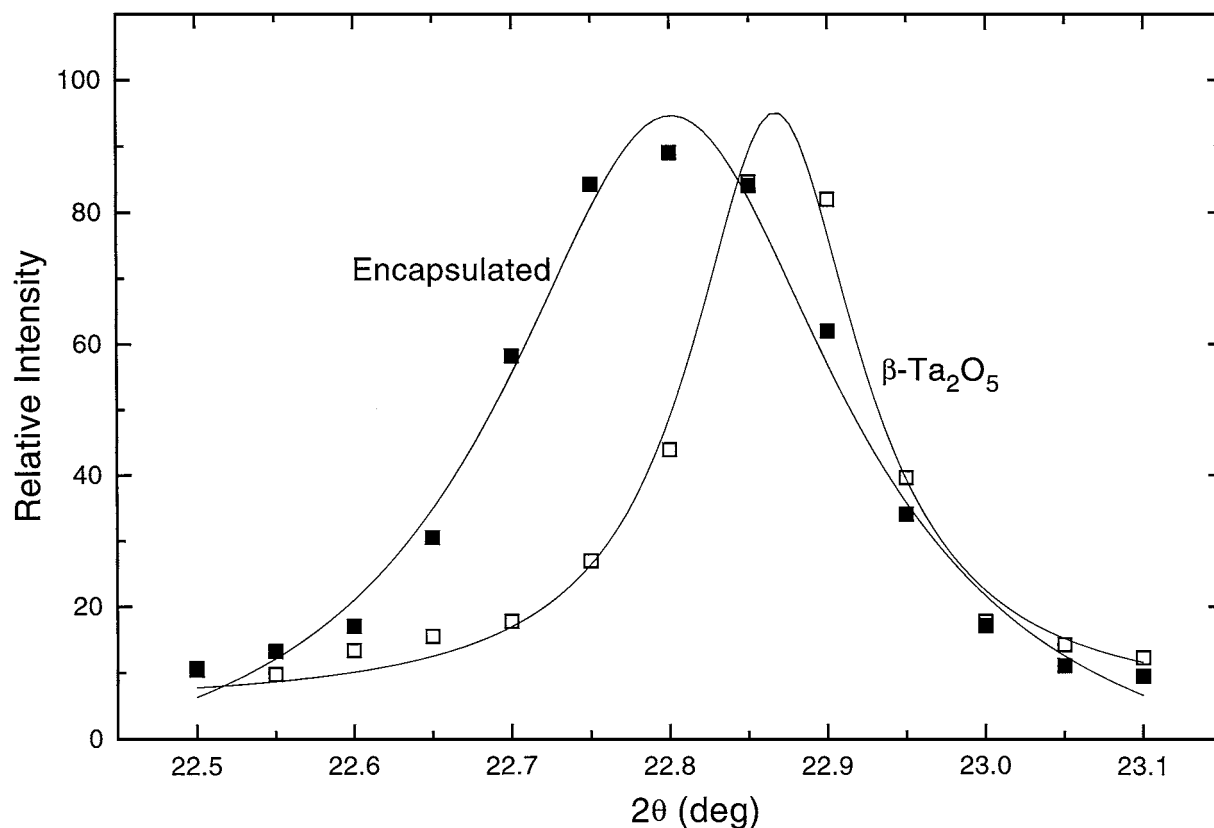


Figure 14 Variation of line 001 position by formation of solid solution $(\text{Nb}_x\text{Ta}_{1-x})_2\text{O}_5$ in the orthorhombic phase.

that part of the Nb_2O_5 transformed to the monoclinic structure $\beta\text{-Nb}_2\text{O}_5$, therefore, the Nb and Ta oxide solution in orthorhombic phase contains lower Nb concentration.

3.6. Thermal treatment of $\alpha\text{-Nb}_2\text{O}_5$ - $\beta\text{-Ta}_2\text{O}_5$ mixture in Cl_2 atmosphere

Thermal treatment under Cl_2 atmosphere of the mixture of the stable crystalline phases of both oxides was done in order to study the behavior of these oxides when they are in the stable crystalline phases. Calcination in Cl_2 atmosphere showed that for the formation of solid solutions in the orthorhombic phase more severe working conditions than those here used for amorphous oxides are needed. Obtention of solid solutions from stable crystalline phases was possible at longer reaction times

(24 hours in Cl_2 atmosphere) and higher temperatures (1223 K). To achieve this, it became necessary to work in encapsulated systems so as to prevent volatilization of the respective chlorides.

The formation of solid solutions in the orthorhombic phase in this system can be verified by the shift of peak 001 ($2\theta = 22.6$ for pure Nb_2O_5), as shown in Fig. 14.

Fig. 15a and b show micrographs of the residue of the $\alpha\text{-Nb}_2\text{O}_5$ and $\beta\text{-Ta}_2\text{O}_5$ mixture after calcination for 24 hours in Cl_2 atmosphere.

Fig. 15a shows a particle initially corresponding to $\alpha\text{-Nb}_2\text{O}_5$. Comparison with Fig. 2a shows that the $\alpha\text{-Nb}_2\text{O}_5$ particles suffer a severe Cl_2 attack.

Fig. 15b shows a particle initially corresponding to $\beta\text{-Ta}_2\text{O}_5$, like the one shown in Fig. 2c. These crystals exhibited growth and EDXS analysis showed the

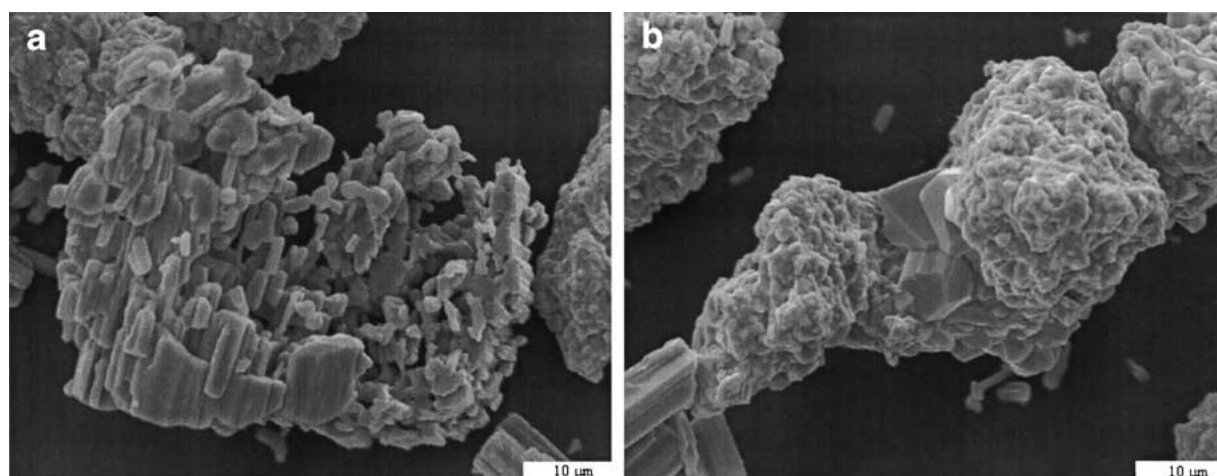


Figure 15 Micrographs of the products obtained after calcination of $\alpha\text{-Nb}_2\text{O}_5$ and $\beta\text{-Ta}_2\text{O}_5$ mixture for 24 hours in Cl_2 atmosphere. (a) particle initially corresponding to $\alpha\text{-Nb}_2\text{O}_5$; (b) particle initially corresponding to $\beta\text{-Ta}_2\text{O}_5$.

presence of Nb and Ta with concentrations up to 50% in Nb moles.

The results of α -Nb₂O₅ and β -Ta₂O₅ heating in chlorine atmosphere for long times show that Cl₂ attack takes place especially on Nb₂O₅ particles and that recrystallization of the solid solution occurs especially on the original β -Ta₂O₅ particles. The former phenomenon is due to the facts that Nb₂O₅ is more reactive than Ta₂O₅ [25, 26], and that, upon chlorination, tantalum oxide gives only TaCl₅. On the contrary, the chlorination of Nb₂O₅ can produce NbCl₅ and NbOCl₃, as reported by different authors [27, 28], being the formation of the latter the most thermodynamically favored [25]. The fact that recrystallization of the new phase occurs on the original Ta₂O₅ particles can be attributed to the fact that Ta₂O₅ is in the orthorhombic phase, which is stable for this oxide, and therefore the solid solution will form on this phase. Great crystal size in the orthorhombic phase (Fig. 15b) might be due to higher working temperature and longer time under chlorine atmosphere in encapsulated systems. However, when treating pure β -Ta₂O₅ samples under similar conditions, crystalline growth was not so marked. It could therefore be inferred that the presence of Nb favors crystal growth in the orthorhombic phase.

4. Conclusions

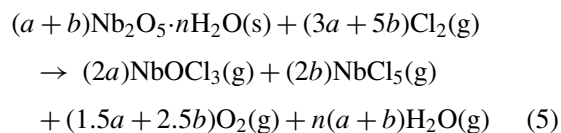
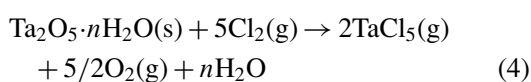
Thermal treatment of amorphous or crystalline Nb and Ta oxides under Cl₂ atmosphere favor phase transformation of these oxides and the formation of the orthorhombic solid solution of Nb₂O₅ and Ta₂O₅ at low temperatures.

Air calcination of a mixture of the amorphous oxides obtained mechanically at different temperatures and longer times than those employed for chlorine thermal treatment did not lead to solid solutions between both oxides. The formation of the solid solution is faster when amorphous oxides are used instead of the α and β phases of the Nb and Ta oxides, respectively. This is probably a consequence of the lower thermodynamic stability of amorphous phases as compared to the crystalline phases of the respective oxides, which are thermodynamically stable.

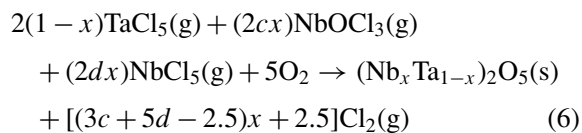
The effect of chlorine is accounted for by the phenomenon of dissolution-recrystallization occurring between the small amounts of the metallic chlorides and oxygen formed, when the system evolves to chemical equilibrium between the solid phases and the gaseous chlorine. Evidence of the role of mass transport through the gaseous phase results from observation of higher size crystals in chlorine atmosphere, which are typical of oxides recrystallized from gaseous metallic chlorides, as has been observed in various comparable systems [18–21].

The effect of Cl₂ on the phase transformations of the Nb and Ta amorphous oxides and the formation of solid solutions at temperatures under 1073 K can be summarized by the following reactions:

(a) *Stage of chlorination of the amorphous or crystalline oxides:*

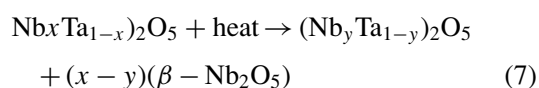


(b) *Recrystallization of the orthorhombic solid solution in all its composition at temperatures under 1073 K:*



where $0 \leq x \leq 1$, link: $c + d = 1$

At high temperatures the solid solution (Nb_xTa_{1-x})₂O₅ with $x > 0.5$ is unstable, so air calcination at 1273 K causes segregation of monoclinic phase β -Nb₂O₅, and a residue with lower Nb content is obtained, according to the following reaction:



where $y < x$ and $y \leq 0.5$

The behavior of crystalline oxides when heated at high temperatures in chlorine atmosphere shows that the formation of solid solution in the orthorhombic phase also takes place. In this system, as expected according to the phase diagram in Fig. 1, a solid solution was formed at temperatures above 1073 K, the crystals of which exhibited at all times niobium concentrations under 50%.

Acknowledgements

The authors J. González and M. del C. Ruiz wish to thank Consejo Nacional de Investigaciones Científicas y Técnicas, Agencia Nacional de Promoción Científica y Tecnológica and Universidad Nacional de San Luis, Argentina, for financial support for this study

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*Received 28 December 1999
and accepted 4 October 2000*