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Chemical and structural aspects of a layered acid niobium (V) phosphate

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Some experimental parameters that influence in the preparation of the layered niobium phosphate were investigated, among them the molar ratio P/Nb in the reaction system and the time of reaction. Starting from that research, it was obtained, through simple stages, the acid layered niobium phosphate with the representative chemical formula $NbOPO_4{\cdot}0.4H_3PO_4{\cdot}1.0H_2O$. It was verified that the phosphoric acid in the interlayer space causes distortions to the angles of the lattice parameters. The thermal treatment of the compound up to 1000°C promoted several chemical and physical alterations, such as phase transitions, that occurred with the preservation of the crystallographic *ab* plane. At the temperature of 1000°C, was formed only a structurally well defined tetragonal system α-$NbOPO_4$. *© 2005 Springer Science + Business Media, Inc.*

1. Introduction

Potential application of lamellar materials as catalyst, ion exchanger or selective adsorber makes these compounds of increasing interest for researchers, particularly because one can easily performed structural changes on those materials by intercalation with different chemicals for specific intended use. Included in this category are the hydrated niobium phosphates [1–5], such as $NbOPO_4 \cdot nH_2O$. The interlayer space for n equal to 3 is 8.04Å and this spacing proportionally changes as water is eliminated by heat until the formation of the anhydrous niobium phosphate. The three-dimensional structure has tetragonal symmetry, with *a* and *c* parameters of 6.3873(10) and 4.1037(8) Å respectively for the α-$NbOPO_4$ phase [6]. The lamellar niobium phosphate when intercalated with amines and alcohols swells along *c* direction [3, 4]. Beneke and Lagaly [3] have prepared niobium phosphates containing interlayer acidic phosphate groups, which water leaching eliminates the acidic phosphate: $NbOPO_4 2H_3PO_4 \cdot 5H_2O$, with interlayer spacing of 11-11.2 Å, and $Nb_2O_5 1.5P_2O_5{\cdot}5.9H_2O$, probably contains $\{Nb_2(OH)_2(HPO_4)(PO_4)_2\}$ layers and more reactive in the amines intercalation of the one that $NbOPO_4{\cdot}3H_2O$. A acid niobium phosphate with P/Nb ratio = 1.5, $HNb_2(OH)_2(PO_4)_3 \cdot H_2O$, having lattice constants a = 6.485(2) Å, b = 6.415(3) Å, c = 16.18(2) Å, α = 90.11(7)°, β = 95.91(5)° and γ = 90.95(5)° in the triclinic system, and $NaNb_2(OH)_2(PO_4)_3 \cdot 2.5H_2O$ with a = 6.488(2) Å and c = 16.286(5) Å in the tetragonal system were prepared by Kinomura and Kumada [8]. These two compounds have a three-dimensional structural framework composed of $NbO(H_2O)PO_4$ layers combined with PO_4 groups. The PO_4 group that links the layers one another is removed upon ion exchange with certain ions and intercalation with definite amines, transforming the three-dimensional structure in a layered structure. The acid niobium phosphate can intercalate *n*-alkylamines in its cavities in the case of short alkyl chains and in the interlayer spaces when the chain is long.

The present paper reports the influence of the P/Nb ratio, reaction time and thermal treatment on the chemical and structural aspects of the layered acid niobium phosphate. The synthesis of this compound and its characterization by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), X-Ray Fluorescence (XRF), X-ray Photoelectron Spectroscopy (XPS), X-Ray Diffractometry (XRD), Infrared (IR) and Raman spectroscopies, Thermogravimetry (TG) and Differential Thermal Analysis (DTA), and Nuclear Magnetic Resonance (NMR) techniques are described.

2. Experimental

2.1. Preparation

Layered acid niobium phosphate was prepared by the reaction of orthophosphoric acid with potassium niobate AD-1148 from CBMM (Metallurgy and Mining Brazilian Co.), with 44% of niobium after heating at 120°C for 30 min. The products were obtained by adding the 12.5% (g/mL) potassium niobate solution

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to an orthophosphoric acid (85.%-wt) at 70°C, with the P/Nb ratio between 2 and 20, under stirring. After the addition, the mixture was refluxed for 24 h. The resulting solid was washed with water until pH 4.0, air-dried and heated at different temperatures for 2 h.

2.2. Characterization

XPS measurements were carried out on the Escalab-MK2 spectrometer with an Al Kα excitation source (1486.6 eV) for determination of the surface composition of samples heated up to 600°C. The binding energies were referenced to C1s (set at 284.6 eV). Chemical composition of products heated at 120°C was determined by ICP-AES, using Perkin-Elmer plasma 1000 instrument. The composition of samples heated at 1000°C was analyzed by XRF on a Philips PW-1480 spectrometer. XRD patterns were recorded using a Seifert diffractometer with Cu Kα radiation at a rate of 1.5°/min of 2θ. IR spectra were obtained on a Nicolet 60 SXR-FTIR spectrophotometer using KBr pellet technique. Raman spectra were measured with a Nicolet RAMAN 950 spectrometer using self-supported wafer of the samples. The light source was 1064 nm radiation from a Nd-YAG laser. NMR spectra for ^{31}P with magic angle spinning (^{31}P MAS) were recorded at 121.4 MHz on a Varian unity inova-300 spectrometer using H_3PO_4 (85wt.-%) as a standard. TG and DTA analyses were performed with a Rigaku 8150 thermoanalyzer where the samples were heated from room temperature up to 900°C at 10°C/min rate under N_2/O_2 atmosphere.

3. Results and discussion

The P/Nb molar ratio obtained by ICP-AES, as well as the binding energy, the width of the spectral lines P 2p, Nb 3d and O ls, and the P/Nb atomic ratio revealed by XPS analyses for the samples prepared with 2 to 20 P/Nb ratio in the reaction system are shown in Tables I and II. From now on the samples will be designated by its P/Nb molar ratio in the reaction system like PNb2, PNb5, PNb10 and PNb20. The results indicate that the sample prepared with a higher P/Nb ratio have a more uniform P/Nb distribution than the one with the 2 P/Nb ratio. In this last sample, the phosphorus appears to concentrate on the surface, probably due to phosphate adsorption during sample preparation. No significant binding energy variation was observed in the samples. Chemical analysis by XRF gives P/Nb ratio equal to 1.2 for the PNb20 sample heated at 1000°C for 2 h. The result indicates phosphorus excess in the calcined sample, possibly because of some occluded phosphate [9]. It was also noticed that the potassium contamination decreases as the P/Nb ratio increases. This is probably related to the high hydrogen ion concentration in the reaction system. Earlier studies of amorphous niobium phosphate revealed that most of the non-lattice phosphate groups are eliminated by thermal treatment and have also demonstrated that potassium affects the acidity but not the surface area [9]. Okasaki and Wada also observed the effect of potassium on amorphous niobium phosphate [10].

TABLE I P/Nb molar ratio obtained by ICP-AES of samples heated at 120°C

Sample designation	P/Nb molar ratio	
	In the reaction system	In the product
PNb2	2	1.18
PNb5	5	1.13
PNb10	10	1.36
PNb20	20	1.38

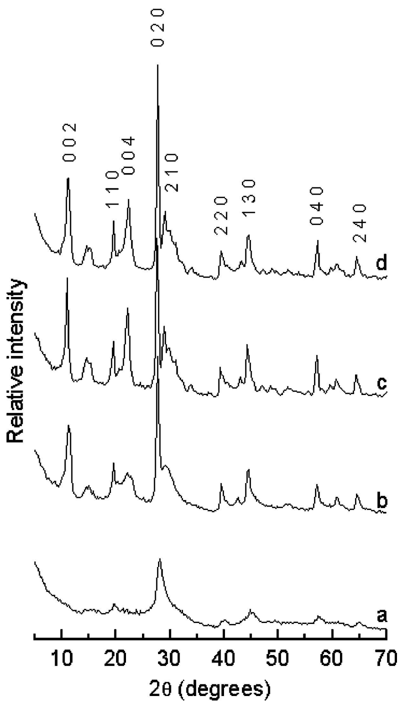

Figure 1 XRD patterns of samples at 120°C: (a) PNb2, (b) PNb5, (c) PNb10, and (d) PNb20.

The XRD patterns of samples heated to 120°C (see Fig. 1) shows that the organization of the layers along the *c* axis increases as the P/Nb ratio increases in the

TABLE II XPS data for samples heated at different temperatures

Sample designation	Temperature (°C)	Binding energy/eV[a]			P/Nb atomic ratio
		P 2p	Nb 3d	O 1s	
PNb2	400	134.0 (2.0)	208.0 (2.0)	531.7 (2.4)	1.56
PNb10	400	133.9 (2.2)	208.0 (1.8)	531.7 (2.2)	1.68
PNb20	400	134.0 (2.0)	208.1 (1.8)	531.8 (2.2)	1.53
PNb20	600	134.1 (2.2)	208.3 (1.8)	531.8 (2.2)	1.54

[a]The corresponding line width is in brackets.

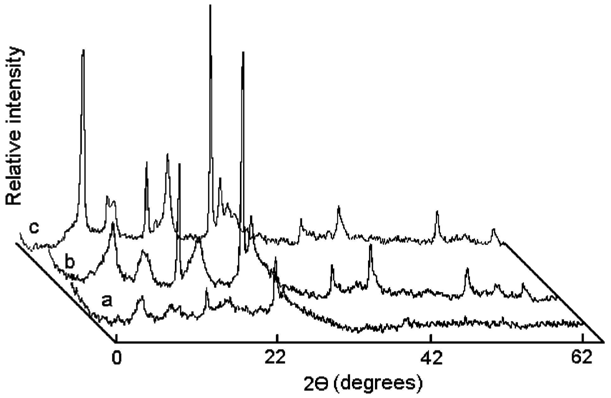

Figure 2 XRD patterns of the PNb20 sample obtained with different times of reaction: (a) 30 min, (b) 90 min, and (c) 24 h.

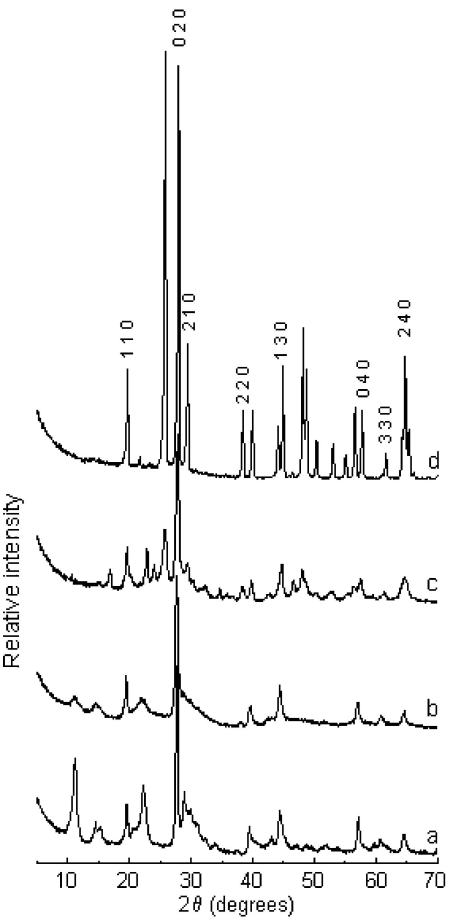

Figure 3 XRD patterns of the PNb20 sample at (a) 120°C, (b) 400°C, (c) 600°C, and (d) 1000°C.

reaction system. It was also observed that the reflux time applied during preparation directly affects the properties of the product, increasing the peak height of the interlayer distance d_{002} and showing better resolution for other broad peaks, as seen in Fig. 2.

Fig. 3 shows the XRD patterns of the PNb20 sample heated at 120, 400, 600 and 1000°C. The McMaille [11] program was used for indexing powder patterns of this sample heated at 1000°C. The results agrees with the tetragonal crystalline system, with parameters: $a = 6.3753$ Å and $c = 4.1013$ Å ($R_p = 0.069$). These results and those obtained from the powder diffraction data by least-squares refinement with the program

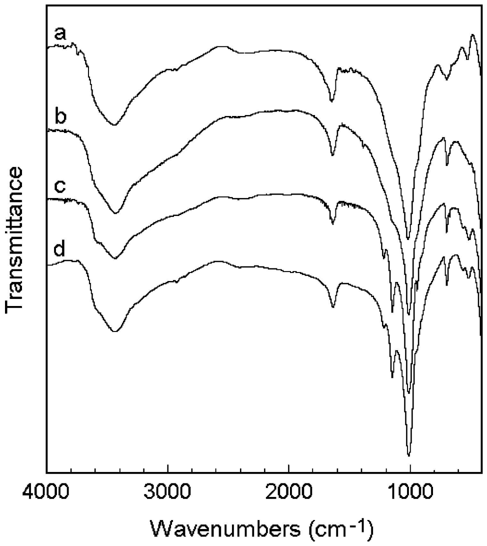

Figure 4 IR spectra of samples at 120°C: (a) PNb2, (b) PNb5, (c) PNb10, and (d) PNb20.

PULVER91 [12] were used to evaluate the influence of the temperature in the structure of the PNb20 sample heated at 120, 400, 600 and 1000°C. It was observed that at temperatures of 400 and 600°C, the interlayer distance d_{002} decreases significantly as the structure collapses, increasing the symmetry from triclinic crystalline system and at 1000°C the crystalline system changes resulting in tetragonal structure. The results perfectly agree with the α-$NbOPO_4$ single-phase [7]. The XRD pattern of the PNb10 sample heated at 1000°C also indicates the formation of the α-$NbOPO_4$ phase, similar to the PNb20 sample. Nevertheless, that was not so evident for the PNb2 sample heated at same temperature, where non-identified low intensity peaks were observed.

The IR spectra of the samples heated to 120°C are shown in Fig. 4. The PNb20 sample shows absorption bands at 1135 and 1010 cm^{-1}, related to stretching vibration of phosphate groups. For the PNb2 and PNb5 samples this absorption is not so evident. This is an indication that the experimental condition strongly affects the resulting material. The Fig. 5 shows significant changes in the infrared spectrum when the PNb20 sample is heated at 1000°C. The vibration bands associated to phosphate group appear broaden and the intensity of the 1633 cm^{-1} band is reduced. The absorption bands at 897 and 630 cm^{-1} are probably related to Nb—O stretching vibrations. Those bands appear when the structure collapses along the axial direction of the octahedral NbO_6 groups at 400–600°C to form the α-$NbOPO_4$ phase as observed in the sample heated at 1000°C.

Fig. 6a shows Raman spectra for the PNb2 sample heated at 120°C. The band at 236 cm^{-1} appears broadened, compared to the one in Fig. 6b for the PNb20 sample under the same conditions. It indicates a more diverse chemical environment in the vicinity of the octahedral NbO_6 group, and could be associated to less phosphoric acid content in the reactional system. The same was observed for $NbOPO_4 \cdot nH_2O$ sample, where it seems to occur compression along the c axis at low

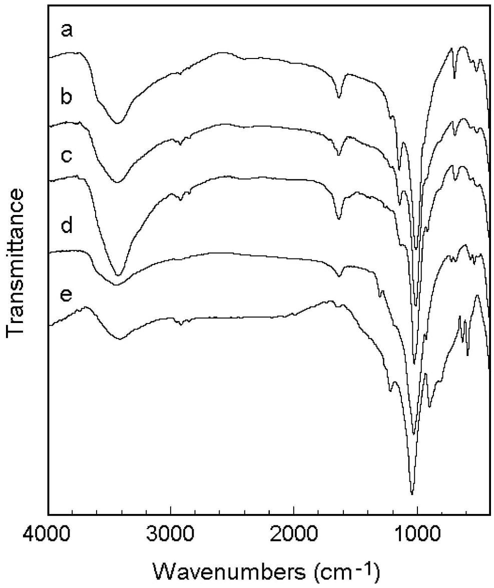

Figure 5 IR spectra of the PNb20 sample at (a) 120°C, (b) 300°C, (c) 400°C, (d) 600°C, and (e) 1000°C.

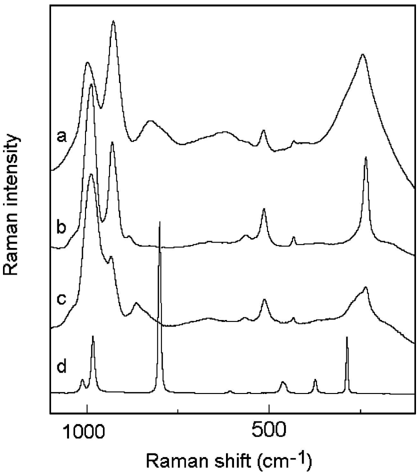

Figure 6 Raman spectra of (a) PNb2 at 120°C, (b) PNb20 at 120°C, (c) PNb20 at 400°C, and (d) PNb20 at 1000°C.

TABLE III Raman stretching frequencies of Nb—O bonds, bond distances (*R*) and calculated valency of Nb—O bond (*s*) for the PNb20 sample at 1000°C

Frequency (cm^{-1})	*R* (Å)	*s*	Nb—O bond	Reference *R* (Å)[a]	 s^{b}
801	1.814	1.25	1 × (axial)	1.783	1.40
608	1.958	0.85	4 × (equatorial)	1.969	0.85
287	2.349	0.34	1 × (axial)	2.321	0.37

[a] Single crystal XRD results for α-$NbOPO_4$ by Longo and Kierkegaard [7];

[b] Hardcastle and Wachs [14].

temperature [1, 2]. This effect can be observed for the PNb20 sample heated at 400°C as well (see Fig. 6c), and it is coincident with the layer collapsing observed at 400–600°C, when the interlayer water molecules are removed. The broad bands at 826 and 866 cm^{-1} for the PNb2 and PNb20 samples heated at 120 and 400°C, respectively, could be related to a double bonding Nb = O. The bands at 984 and 1013 cm^{-1} shown in Fig. 6d for the PNb20 sample heated at 1000°C are typical of stretching vibrations of phosphate group. Those bands are slightly shifted, as water molecules are removed by the thermal treatment at 1000°C. Consequently, the *ab* crystal plane suffers only a small alteration after collapsing of the structure, resulting in a short and stronger axial Nb—O bond, indicated by the presence of the band at 801 cm^{-1}.

The interpretation of the spectra was based on studies performed by Stranford and Condrate [13] for thermal treatment of niobium phosphate hydrates with P/Nb = 1. Additionally to Raman spectroscopy, the evaluation of the Nb—O bond length (*R*) was based on the Hardcastle and Wachs [14] empirical equations: $\nu(\text{cm}^{-1}) = 25\,922\exp(-1.9168\,R)$; $s(\text{Nb—O}) = 653\,[\ln(25\,922/\nu)]^{-5.0}$, where ν is the Nb—O stretching frequency and s is the bond valence. Table III lists the results for the PNb20 sample heated at 1000°C which agree with those for α-$NbOPO_4$ [7, 12], assumed as reference for the evaluations made herein for PNb20 sample heated at 120°C. For the PNb20 sample heated at 120°C, the Nb—O distance in the equatorial plane (566 cm^{-1}, $R = 1.995$ Å, $s = 0.80$) showed smaller difference than in the axial direction (236 cm^{-1}, $R = 2.452$ Å, $s = 0.29$). This result is probably due to the removal of the water molecules axially bonded to the octahedral NbO_6 groups during heated at 1000°C to form the α-$NbOPO_4$ phase.

Fig. 7a shows the MAS NMR spectra for the PNb20 sample heated at 120°C, where ^{31}P resonance peaks can be observed at −1.8 ppm (54%) and −3.6 ppm (46%), indicating two different chemical environments for the phosphate groups, as result of the presence of interlayer weakly bonded phosphate groups other than those of the crystalline structure. The above reasoning is consistent with the disappearance of the peak at −1.8 ppm at 400°C (see Fig. 7b). In the spectrum of the PNb20 sample heated at 600°C (see Fig. 7c), the broad band at −6.7 ppm indicates a diverse chemical environment with change of symmetry as suggested by IR and XRD analyses. Heating the PNb20 sample to 1000°C caused a negative peak shifting to −23.1 ppm (76%) and −10.0 ppm (24%) as can be seen in Fig. 7d. The results obtained by ^{31}P MAS NMR, XRF, IR and XRD indicate the presence of non-crystalline phosphate groups in the PNb20 sample heated at 1000°C. The ^{31}P MAS NMR spectrum for the PNb10 sample is similar to the PNb20. However, the PNb2 sample heated at 120°C (see Fig. 7f) showed a broad peak at −2.2 ppm (74%), −8.0 ppm (26%), as result of structural disorder.

The TG-DTA curves indicate a gradual removal of water as the sample is heated up to 200°C. For the PNb20 sample, the endothermic effects with 7.4% mass loss up to 400°C, and 2.6% at 600°C is probably also associated to water removal. Beyond 600°C, no significant mass loss was observed. The peak at 806°C can be related to the formation of the α-$NbOPO_4$ phase, as suggested by IR, XRD and Raman analyses. Similar results were also observed for the PNb10 sample. However, in the Fig. 8c a distinct crystalline phase formation for the PNb2 sample is not clearly observed.

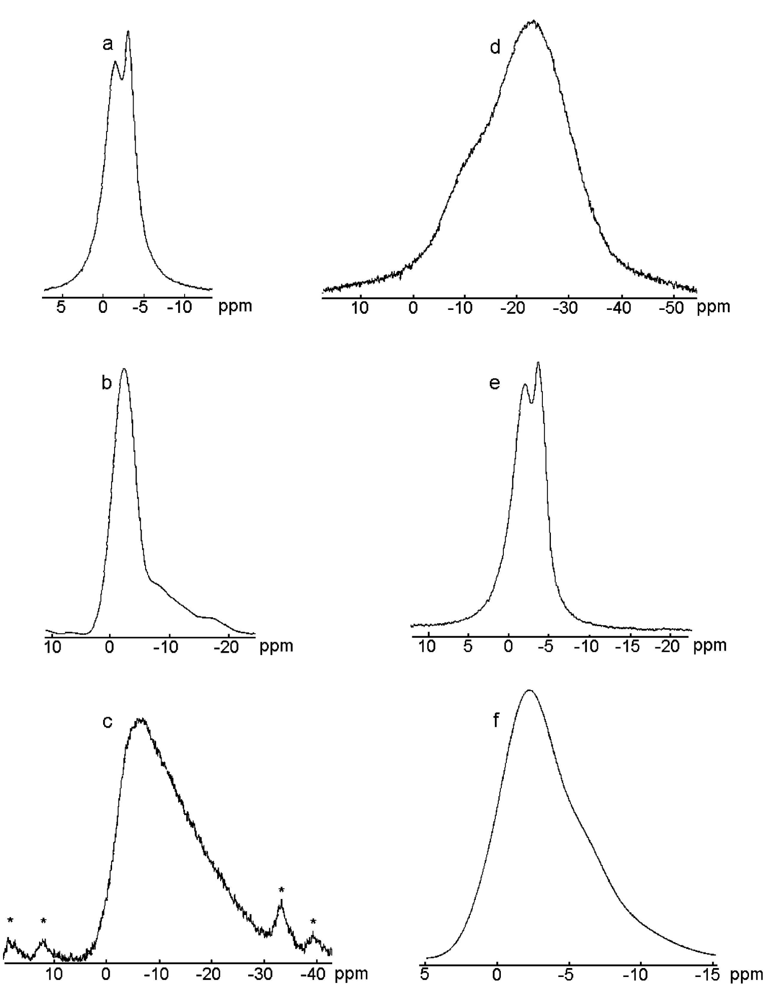

Figure 7 ^{31}P MAS NMR spectra of (a) PNb20 at 120°C, (b) PNb20 at 400°C, (c) PNb20 at 600°C, (d) PNb20 at 1000°C, (e) PNb10 at 120°C, and (f) PNb2 at 120°C. Peaks marked with an asterisk are spinning sidebands.

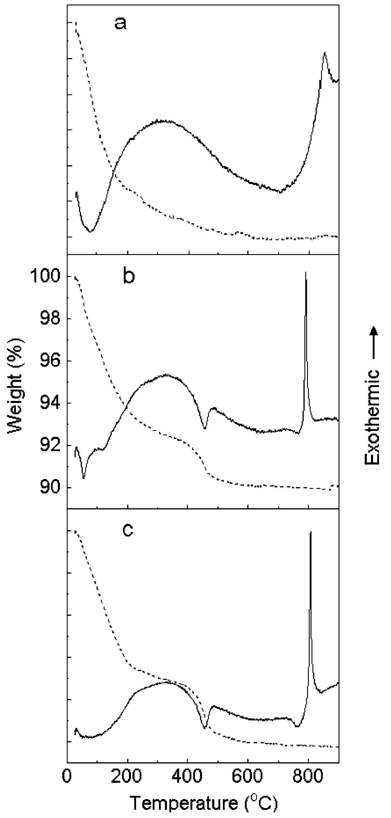

Figure 8 TG (dots) and DTA curves of (a) PNb2, (b) PNb10, and (c) PNb20.

Based on the ICP-AES and TG results, the empirical chemical formulae for the PNb10 and PNb20 samples heated at 120°C were established as it follows: $NbOPO_4 \cdot 0.36H_3PO_4 \cdot 0.94H_2O$ and $NbOPO_4 \cdot 0.38H_3PO_4 \cdot 1.00H_2O$, respectively. The remaining water is removed by treatment at 600°C as indicated by the TG curve and observed in niobium phosphate hydrate studies [2], and it seems to be related to the non-crystalline phosphate content. According to XRD patterns of the PNb20 sample heated at different temperatures, no significant peak shift occurred to the peaks associated to *hk0* Miller index. Nevertheless, those peaks associated to *00l* Miller index showed lower intensity and greater 2θ values consistent with a closer layer structure. The intense decreasing of the interlayer distance d_{002}, observed when the sample is heated from 120 to 600°C, agrees with the mass loss observed in the TG curve and suggests that the structure collapses when a complete dehydroxylation in the interlayer space is achieved.

4. Conclusion

The structural and thermal results indicate that increasing the P/Nb ratio from 2 to 20 enhances the formation of the crystalline niobium phosphate phase containing interlayer phosphate groups. During sample preparation and thermal treatment, most of the structural changes occur along the axial *c* direction, rather than in the equatorial *ab* plane. Interlayer hydrogen bonds involving acidic phosphate groups are probably responsible for the angle distortions observed on the triclinic structure. The potassium content is inversely associated to the P/Nb ratio and controls the acidity. As the compound heated up, the lattice angle gradually approaches 90° and the structure changes from the triclinic structure to the tetragonal α-$NbOPO_4$. The formation of the α-$NbOPO_4$ phase occurs as an irreversible process between 760 and 840°C after complete dehydroxylation and collapse of the layer structure. The empirical chemical formulae suggest the ratio of three niobium atoms to one interlayer phosphate group.

Acknowledgments

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