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# Desorption of carbon dioxide from small potassium niobate particles induced by the particles' ferroelectric transition

E. Ramos-Moore, J.A. Baier-Saip, A.L. Cabrera \*

Pontificia Universidad Católica de Chile, Facultad de Física, Casilla 306, Santiago 22, Chile

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#### Abstract

The aim of this work is to understand surface properties of ferroelectric crystals related to gas adsorption. Various ferroelectric crystals involved in these studies readily adsorb carbon dioxide, thus our studies were centered on adsorption studies of this molecule. It has been claimed that a dipole moment is induced on carbon dioxide molecules that are near an oxide surface. Our experiments explored the possibility of a dipole–dipole interaction between the gas molecule and the ferroelectric oxide surface in order to explain its adsorption. We characterized the samples with scanning electron microscopy, X-ray diffraction and Raman spectroscopy. We determined the ferroelectric nature of the particles and studied the temperature-dependent phase transitions in small particles of KNbO<sub>3</sub> using Raman spectroscopy. We were able to correlate desorption of  $CO_2$  from one surface state of KNbO<sub>3</sub> with the occurrence of the orthorhombic to tetragonal transition in KNbO<sub>3</sub> in particles of 1  $\mu$ m size. This CO<sub>2</sub> surface site was not observed in KTaO<sub>3</sub>, which does not show ferroelectricity at room temperature.

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## 1. Introduction

Ferroelectric oxides such as BaTiO<sub>3</sub> and KNbO<sub>3</sub> undergo several crystallographic phase transitions within a temperature range of 150–700 K.

These oxides which have a perovskite structure undergo crystallographic transitions with increasing temperature. These transitions go from rhombohedral to orthorhombic, then to tetragonal and finally cubic. When they become cubic the ferroelectricity is lost. In the ferroelectric state, the polarization vector points along a preferential direction determined by the break in the symmetry of the structure. All these transitions occur below room temperature for KTaO<sub>3</sub>. In the case of BaTiO<sub>3</sub> the first two transitions occur below 273 K. The transition from tetragonal to cubic (ferroelectric to paraelectric) is the only one that remains above room temperature ( $T_c = 393$  K). In the case of KNbO<sub>3</sub>, the last two transitions remaining occur above room temperature: from orthorhombic to tetragonal occurs around 473 K. This crystal loses its ferroelectricity at  $T_c = 723$  K (tetragonal to cubic). KTaO<sub>3</sub> is a non-ferroelectric oxide at room temperature [1].

One would expect KNbO<sub>3</sub> and KTaO<sub>3</sub> to have similar chemisorption properties for the adsorption of oxygencontaining molecules such as NO, CO and CO<sub>2</sub> [2] from a chemical point of view, but they differ in physical properties at room temperature: KNbO<sub>3</sub> is ferroelectric and KTaO<sub>3</sub> is not. If we observe differences in adsorption properties, this must be related to the differences in the ferroelectric state of the crystals.

In prior work, we have studied the adsorption properties of many of these ferroelectric oxides [3,4] – with the exception of KTaO<sub>3</sub> – in search of an effect on the adsorption of simple molecules by their ferroelectric surfaces. The effect has remained elusive. All of these oxides readily adsorbed CO<sub>2</sub> at room temperature, but not CO, N<sub>2</sub>, or H<sub>2</sub>, and

<sup>\*</sup> Corresponding author. Tel.: +56 2 354 4478; fax: +56 2 553 6468. *E-mail address:* acabrera@uc.cl (A.L. Cabrera).

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for this reason we have concentrated our studies on the adsorption of  $CO_2$ .

These adsorption studies were conceived after studying the description of the Hedvall effect for ferromagnetic materials [5] related to the adsorption of molecules around the transition temperature of the substrate. The effect is described as a change in the reaction rate of a surface reaction, above and below the phase transition of the substrate. A change in the reaction rate might be related to the surface ability to adsorb the reactants in the different phases. Many examples of these effects were discussed by Voorhoeve [5] and a theoretical explanation was proposed by Suhl [6]. In the case of ferroelectric materials, very few reports of anomalies found in reaction rates are found in the literature [7,8].

An initial naïve explanation proposed for a possible effect on adsorption of  $CO_2$  was that the dipole moment of a polar molecule (or induced dipole moment, as is the case of  $CO_2$  adsorbed on barium titanate) [8] interacts with the electric polarization of some ferroelectric domains on the surface. This interaction would then increase the strength of the molecular adsorption on the surface of the substrate with increasing value of their spontaneous polarization ( $P_s$ ). We have pursued studies in the past, trying to demonstrate this [3,4,9].

In this study, we exposed powder of the different oxides to a  $CO_2$  atmosphere under controlled conditions and measured the desorption of the gas as a function of the temperature. This procedure is called Thermal Programmed Desorption or TPD. We could also determine the nitrogen BET (Brunauer, Emmett and Teller) area. Using Micro-Raman spectroscopy, we were able to ascertain the ferroelectric state or the absence of ferroelectricity for both crystals.

## 2. Experimental

Potassium niobate (KNbO<sub>3</sub>) and potassium tantalate (KTaO<sub>3</sub>) powder with a mean particle size of  $1\mu m$  and 99.98% pure was obtained from Alfa Caesar, Inc.

The surface area of the powder was determined from N<sub>2</sub> adsorption according to the BET model [10]. The BET model explains that breaks in the adsorption isotherms of gases at temperatures near their condensation points correspond to the formation of multi-molecular adsorbed layers. The BET areas of adsorbed N2 and the TPD of desorbed CO<sub>2</sub> on the powder samples were measured with a Quantasorb instrument (Quantachrome Corp.). This instrument is capable of measuring the N<sub>2</sub> adsorption by a solid material at different N2 partial pressures. Single-point BET refers to the use of only one N<sub>2</sub> partial pressure. High-purity (99.999% pure) He and N<sub>2</sub> and CO<sub>2</sub> (99.9% pure) were used in all the experiments. A modification to the Quantasorb instrument was made in order to measure desorption of  $CO_2$  from the powder samples. Because  $CO_2$  is chemisorbed by the samples, desorption must be induced by heating the samples well above room temperature (a typical

TPD experiment). A special glass cell was built that allowed the powder sample to be introduced in an electrical tube furnace. The samples were typically heated up to 700 K during desorption, and their temperature was monitored by a chromel–alumel thermocouple, which was in close contact with the sample but outside the glass cell [11].

Raman spectroscopy was performed with a LabRam 010 instrument from ISA using 5.5 mW in a He–Ne-LASER (632.8 nm). The Raman microscope is operated in a back-scattering geometry, where the incident beam is linearly polarized and the spectral detection is unpolarized. We used an Olympus MPlan  $10 \times$  (NA 0.25) objective lens. We must consider that these ferroelectric materials have a high refractive index (n > 2) and therefore the effective NA within the probed crystallites is much smaller [12].

The powder sample was located in a LINKAM THMS 600 sample stage controlled by the TMS 94. This stage allows sample cooling to liquid nitrogen temperature and sample heating up to 600 °C with a precision of  $\pm 0.1$  °C. The samples were inspected in situ by micro-Raman spectroscopy as a function of the temperature.

X-ray diffraction (XRD) was performed with a Bruxer D8 Advance diffractometer in the standard  $\theta$ -2 $\theta$  geometry (Bragg Brentano configuration) using Cu K<sub> $\alpha$ </sub> radiation ( $\lambda = 0.154$  nm). A typical spectrum, at room temperature, was taken for 2 $\theta$  in the range of 20–90° with step size of 0.01° every 2 s.

Scanning electron microscopy (SEM) was performed with a Leo 1400 VP microscope, using 10 keV electrons, 100  $\mu$ A beam current and a working distance of 6 mm. The microscope was operated at high vacuum ( $\sim 10^{-6}$  mbar).

## 3. Results and discussion

#### 3.1. Potassium niobate

The XRD spectrum of the KNbO<sub>3</sub> powder displays strong (111), (110) and (200) and (311) reflection and the relative intensities correspond to the intensities listed in the standard powder diffraction reference for this material [13]. Small quantities of other phases are also observed (KNb<sub>3</sub>O<sub>8</sub> and Nb<sub>2</sub>O<sub>5</sub>).

SEM photograph of this same sample was obtained and displayed in Fig. 1a. At this magnification, one can observe small cubic-shape crystallites of 5  $\mu$ m size, indicating that strong agglomeration occurs. The surface of these crystallites is quite smooth.

Surface area was obtained for a series of ferroelectric powder samples and displayed in Table 1. Powder of 1  $\mu$ m size potassium niobate shows a smaller surface area than potassium tantalate in agreement with the observation by SEM micrographs.

Carbon dioxide desorption curves from potassium niobate powder with main particle size of 1  $\mu$ m are displayed in Fig. 2a. The orthorhombic to tetragonal transition for potassium niobate is also indicated by an arrow drawn at



Fig. 1a. SEM photograph of KNbO<sub>3</sub> powder used in adsorption measurements. At this magnification, one can observe small crystallites with a cubic shape with sizes of 5  $\mu$ m, indicating that strong agglomeration occurs.



Fig. 1b. SEM photograph of  $KTaO_3$  powder used in adsorption measurements.

Table 1 Adsorption volume of  $N_2$  and  $CO_2$  expressed as  $m^2/g$  by samples of KTaO<sub>3</sub>, and KNbO<sub>3</sub> with different mean particle sizes

Material $P_s$ (C/m <sup>2</sup> ) [17,18] Size ( $\mu$ m)	BaTiO <sub>3</sub> 0.26 Area (m <sup>2</sup> /g)		KNbO <sub>3</sub> 0.30		KTaO <sub>3</sub>	
	N <sub>2</sub>	CO <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>
1	1.400	0.174	0.590	0.088	0.900	0.203
59	0.169	0.021	0.101	0.015	_	_
111	0.060	0.012	0.015	0.004	_	_
223	0.029	0.009	0.009	_	_	_
551	0.015	0.005	0.008	_	_	_
1015	0.009	_	0.005	_	_	_

BaTiO<sub>3</sub> is displayed as a comparison. The N<sub>2</sub> adsorption is measured at liquid nitrogen temperature. The CO<sub>2</sub> adsorption is performed around 300 K and the CO<sub>2</sub> desorption determined from TPD. The area is calculated assuming that a N<sub>2</sub> molecule occupies 0.162 nm<sup>2</sup> at the surface of the substrate.

a temperature  $T_2 = 498$  K in the figure. The desorption was measured using three heating rates: 4.3, 11.3 and 15.0 K/min.



Fig. 2a. Carbon dioxide desorption curves for powder of  $KNbO_3$  at three different heating rates. Indicated by an arrow is the phase transition for the oxide.



Fig. 2b. Carbon dioxide desorption curves for powder of  $KTaO_3$  at two different heating rates.

One can see in Fig. 2a two  $CO_2$  desorption peaks. The first peak, corresponding to a lower energy state, shifts with the temperature as predicted by the rate equation. Using the simplified Redhead's formula [14] – shown in Eq. (1) – one can estimate the energy of desorption, resulting in  $10.2 \pm 0.5$  Kcal/mol. This value is in agreement with prior work [3]:

$$E = RT_p\{\ln(v_n T_p/\beta) - 3.35\}\tag{1}$$

In Eq. (1),  $v_n$  is a pre-exponential factor, R is the gas constant  $T_p$  is the temperature corresponding to the maximum of the desorption curve,  $\beta$  is the heating rate and E is the activation energy. The pre-exponential factor  $v_n$  was assumed to be  $10^3 \text{ s}^{-1}$ .

The abrupt desorption which peaks at 580 K appears to follow the crystallographic transition which occurs at 498 K. This desorption peak remained in the same position independent of heating rate. In prior work we estimated the energy of desorption at this site being around 20 Kcal/mol. Potassium niobate has the same perovskite structure as  $BaTiO_3$ , but at room temperature the crystals have an orthorhombic rather than a tetragonal structure.

We looked at particles of different sizes and obtained Raman spectra of them [3]. The Raman spectrum of this crystal is composed of three main Raman peaks: at 276 (with a peak in the shoulder at 300), a double peak around 600 and a single peak at 833 cm<sup>-1</sup>. This spectrum is similar to that of the BaTiO<sub>3</sub>, but differs somewhat (double peak around 600) in that the structure of KNbO<sub>3</sub> is orthorhombic and not tetragonal. The crystallographic transition can be detected by the shifting of the peak at 600 cm<sup>-1</sup>. Fig. 3 displays the position of the 600 cm<sup>-1</sup> Raman peak as a function of temperature for a cluster formed by several micron-size particles. We can obtain good Raman spectra of particles as small as 17 µm in diameter.

We can clearly observe the orthorhombic to tetragonal transition occurring around 473 K in agreement with the bulk-reported transition for this crystal.

The tetragonal to cubic transition is observed around 673 K, 50 K below the bulk  $T_c$  transition (723 K). This observation is subject to an independent research effort and is not relevant to this work.

## 3.2. Potassium tantalate

The XRD spectrum for  $KTaO_3$  powder displays strong (110), (100) and (210) and (211) reflection and the relative intensities correspond to the intensities listed in the standard powder diffraction reference for this material [13]. No other phases are observed indicating that the crystalline part of this material is 100% potassium tantalate.

SEM photograph of this same sample was obtained and displayed in Fig. 1b. At this magnification, one can observe small aggregates of 1  $\mu$ m particles that homogeneously cover the surface; the surface looks porous and rough.

The surface area of this sample (1  $\mu$ m particle size) was also obtained and is displayed in Table 1.



Fig. 3. Position of a KNbO<sub>3</sub> Raman peak as a function of temperature. The Raman spectra were taken of a cluster formed by several 1  $\mu$ m particles. The crystallographic transition can be detected by the shifting of a characteristic Raman peak at 600 cm<sup>-1</sup>.

Carbon dioxide desorption curves from potassium tantalate powder with main particle size of 1  $\mu$ m are displayed in Fig. 2b. Only one CO<sub>2</sub> desorption peak was observed. The desorption was measured using two heating rates: 4.2, and 14.1 K/min. The peak of desorption shifts with the temperature as predicted by the rate equation. The desorption peaks at 361 K when the heating rate is 4.2 K/ min and then the peak shifts to 423 K when the heating rate is increased to 14.1 K/min.

Using the simplified Redhead's formula, Eq. (1), we estimated a desorption energy of  $9.0 \pm 0.5$  Kcal/mol, very similar to that corresponding to the first peak of KNbO<sub>3</sub>.

### 3.3. Potassium niobate versus potassium tantalate

These two Perovskites are compounds of the formula  $A^+B^{5+}O_3$  [1] but at room temperature the structure of KNbO<sub>3</sub> is orthorhombic while the structure of KTaO<sub>3</sub> is cubic. A simplified description, according to Herbert [18], of how the structure of KNbO<sub>3</sub> a changes when it undergoes the transition orthorhombic–tetragonal is the following: A movement of the Nb<sup>5+</sup> ion towards the center of the oxygen octahedra in the (110) direction is accompanied by an orthorhombic lattice distortion; a movement of the Nb<sup>5+</sup> ion towards the center of the Nb<sup>5+</sup> ion towards the center of the oxygen in the (100) direction is accompanied by a tetragonal lattice distortion.

Surface termination of any of the two compounds must be either  $K^+$  ions surrounded by oxygen ions or Nb<sup>5+</sup> (in the case of KNbO<sub>3</sub>) surrounded by oxygen ions. In the case of fine powder of the material, the surface termination must be a combination of both. Since KNbO<sub>3</sub> is the only compound that undergoes a transition around 473 K, the displacement of the Nb<sup>5+</sup> on the surface must be related to the desorption of carbon dioxide right above this temperature.

On the other hand, Pacchione [15,16] discussed in detail the adsorption of carbon dioxide on an oxide surface (especially in the case of MgO). He concluded – after computer simulation and comparison with spectroscopic data – that carbon dioxide adsorbed weakly on the metal ions "endon-linear" with a desorption energy of about 9.2 Kcal/ mol. He also found another possible adsorption structure in which the CO<sub>2</sub> molecule lays down on the surface and the oxygen atoms on both ends are coordinated with two adjacent surface metal ions. A third and final likely adsorption of the CO<sub>2</sub> molecule on the oxide surface takes place by forming surface carbonates on step sites with activation energies of the order of 23 Kcal/mol.

Potassium tantalate of main particle size of  $1 \mu m$  has more surface area than potassium niobate and clearly adsorbed proportionally more carbon dioxide (see Table 1). Thus the CO<sub>2</sub> desorption peak observed below 498 K (for both compounds) must be related to the weak "endon-linear" adsorption described by Pacchione. The second CO<sub>2</sub> desorption peak, observed only in the case of KNbO<sub>3</sub>, and correlated with its crystallographic transition, must be  $CO_2$  adsorbed on edge site. This analysis is based on the estimated energy of desorption which is larger than the energy of desorption of the first site. A possible explanation for the correlation of  $CO_2$  desorption with crystallographic transition of the substrate is the loss of many step sites due to the crystal distortion when undergoing the transition. Another possibility is the increase of inter-atomic distances between two adjacent Nb<sup>5+</sup> ions which share the adsorption of a  $CO_2$  molecule when the transition occurs. These explanations remain speculative for the moment and clearly more experiments are needed.

## 4. Conclusions

Samples of KNbO<sub>3</sub> with different particle sizes yield desorption of CO<sub>2</sub> corresponding to a weaker state of adsorption that peaks at 398 K (with a heating rate =  $4.3 \,^{\circ}$ C/min). The activation energy for desorption for this state, being around 10 Kcal/mol, is similar in the cases of KNbO<sub>3</sub> and KTaO<sub>3</sub>. Thus this CO<sub>2</sub> desorption peak observed for both compounds must be related to the weak "end-on-linear" adsorption on top of Nb or Ta ions located at the oxide surface.

The second  $CO_2$  desorption peak (peaks at 580 K), observed only in the case of KNbO<sub>3</sub>, and occurring after its crystallographic transition, might be  $CO_2$  adsorbed on edge sites, from desorption energy considerations. The Raman data show that the micron-size particles of KNbO<sub>3</sub> undergo the orthorhombic to tetragonal transition at 497 K as expected in bulk material.

From these results, it seems that the local electrostatic potential produced by the configuration of the surface ions of the oxide and directly related to the oxide ability for adsorbing  $CO_2$  are modified when an oxide undergoes a bulk crystallographic transition. One interesting property of the ferroelectric oxides is that the crystal structure can be manipulated with external electric fields since ferroelectricity and structure are intimately related. Changes in structure produce changes in surface orientation and consequently changes in adsorption properties take place, as observed in these experiments.

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