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

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Received 13 February 2006; accepted for publication 26 June 2006
Available online 20 July 2006

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 KNbO₃ using Raman spectroscopy. We were able to correlate desorption of CO₂ from one surface state of KNbO₃ with the occurrence of the orthorhombic to tetragonal transition in KNbO₃ in particles of 1 μm size. This CO₂ surface site was not observed in KTaO₃, which does not show ferroelectricity at room temperature.

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Keywords: Ferroelectricity; Induced desorption; Carbon dioxide desorption; Chemisorption; Perovskite structures; Phase transitions

1. Introduction

Ferroelectric oxides such as BaTiO₃ and KNbO₃ 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 KTaO₃. In the case of BaTiO₃ 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 \( T_c = 393 \text{ K} \). In the case of KNbO₃, the last two transitions remaining occur above room temperature: from orthorhombic to tetragonal occurs around 473 K. This crystal loses its ferroelectricity at \( T_c = 723 \text{ K} \) (tetragonal to cubic). KTaO₃ is a non-ferroelectric oxide at room temperature [1].

One would expect KNbO₃ and KTaO₃ to have similar chemisorption properties for the adsorption of oxygen-containing molecules such as NO, CO and CO₂ [2] from a chemical point of view, but they differ in physical properties at room temperature: KNbO₃ is ferroelectric and KTaO₃ 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 KTaO₃ – 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 CO₂ at room temperature, but not CO, N₂, or H₂, and
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 naı́ve 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 it 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$_3$) and potassium tantalate (KTaO$_3$) powder with a mean particle size of 1 μm and 99.98% pure was obtained from Alfa Caesar, Inc.

The surface area of the powder was determined from N$_2$ 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 N$_2$ and the TPD of desorbed CO$_2$ on the powder samples were measured with a Quantachrome instrument (Quantochrome Corp.). This instrument is capable of measuring the N$_2$ adsorption by a solid material at different N$_2$ partial pressures. Single-point BET refers to the use of only one N$_2$ partial pressure. High-purity (99.999% pure) He and N$_2$ and CO$_2$ (99.9% pure) were used in all the experiments. A modification to the Quantachrome 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× (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 ±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 Bruker D8 Advance diffractometer in the standard 0–2θ geometry (Bragg Brentano configuration) using Cu K$_\alpha$ radiation ($\lambda = 0.154$ nm). A typical spectrum, at room temperature, was taken for 20 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 μA beam current and a working distance of 6 mm. The microscope was operated at high vacuum (~10$^{-6}$ mbar).

3. Results and discussion

3.1. Potassium niobate

The XRD spectrum of the KNbO$_3$ 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$_5$O$_{14}$ and Nb$_2$O$_5$).

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 μm 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 μm 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 μm are displayed in Fig. 2a. The orthorhombic to tetragonal transition for potassium niobate is also indicated by an arrow drawn at