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PROTON NUCLEAR MAGNETIC RELAXATION STUDY OF HYDRATED Na- $\beta''$ -ALUMINA

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Beta aluminas are well known as prominent  $\text{Na}^+$  superionic conductors ( $\sigma \sim 0.8 (\Omega\text{cm})^{-1}$  at 550 K)<sup>(1)</sup>. It is also known that the presence of absorbed water affects this conductivity<sup>(2)</sup>. Recently Kuhns et al. a  $^1\text{H}$  NMR study of the orientation of water in hydrated Na- $\beta''$ -alumina<sup>(3)</sup>. According to them, when exposed to moisture, water molecules are absorbed and can diffuse, by translation, into the conduction plane, making a "chimpanzee swing" motion. We have measured the temperature dependence of the proton magnetic relaxation time,  $T_1$  and  $T_2$ , in pure and iron doped samples of hydrated Na- $\beta''$ -alumina, in order to study the water motion and to examine the influence of iron on the proton motion.

Na- $\beta''$ -alumina was prepared by calcining a mixture of  $\text{Na}_2\text{CO}_3$ ,  $\text{Li}_2\text{CO}_3$  and alumina by heating at 1260 °C for some hours. The composition of the product was 8.85%  $\text{Na}_2\text{O}$  + 0.75%  $\text{Li}_2\text{O}$  + 90.4%  $\text{Al}_2\text{O}_3$ <sup>(4)</sup>. Three polycrystalline powder samples, with particle diameter size of 150 - 250  $\mu\text{m}$ , were selected for NMR measurements: (1) a pure sample, (2) a iron doped sample (500 ppm nominal), and (3) a almost pure sample. A RPE analysis was made in order to determine the presence of paramagnetic ions. Water was introduced into the sample by exposing them to atmosphere of saturated salt solutions. The hydration was controlled to 19%  $\text{H}_2\text{O}$  of powder's dry weight.

The proton  $T_1$  measurements were performed at 24.4 MHz in the temperature range 255 - 430 K. A  $T_1$  maximum was observed around 385 K in sample (1). When temperature decreases,  $T_1$  decreases and seems to reach a minimum for 288 K. This  $T_1$  maximum appears to move to lower temperature with lower hydration levels. Activation energies for proton motion may be obtained from the slope of the  $\ln(T_1)^{-1}$  vs  $T^{-1}$  curve, giving  $E(1) = 0.21$  eV. This result is in agreement with the value estimated from the temperature dependence of both the  $^1\text{H}$  linewidth in hydrated Na- $\beta''$ -alumina ( $0.18 \pm 0.03$  eV)<sup>(3)</sup> and the  $^1\text{H}$   $T_1$  in  $\text{H}_2\text{O}$   $\beta''$ -alumina (0.20 eV)<sup>(5)</sup>.

The results of samples (2) and (3) show that magnetic impurities, (mainly Fe and Mn) affect considerably the temperature dependence of the proton relaxation times. The data also display a maximum around 330 K, but the variation of  $T_1$  with the temperature was very weakly. Now, the activation energy for the proton motion were  $E(2) \approx E(3) \approx 0.1$  eV. Motional narrowing was apparent at 267 K for the pure sample leading to an activation energy of 0.25 eV but a constant  $T_2$  was observed in the doped sample in the temperature range 260 - 360 K, decreasing above 370 K.

The NMR relaxation rate behaviours are not fully understood yet and further investigation are under course. (This work has been partially supported by CNPq and FINEP (Brazil)).

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