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Anelastic and Dielectric Relaxation Measurements in the Protonic Conductor $\text{Ba}_3(\text{Ca}_{1.18}\text{Nb}_{1.82})\text{O}_{9-\delta}$

S. Bausch, H.G. Bohn and W. Schilling

Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

Abstract. In order to study the local proton motion in complex perovskite-type protonic conductors anelastic and dielectric relaxation measurements have been carried out at the compound $\text{Ba}_3(\text{Ca}_{1.18}\text{Nb}_{1.82})\text{O}_{9-\delta}$. Both techniques show spectra depending on the proton concentration. From the dielectric measurements an activation energy of $E_a \approx 0.5$ eV for the local reorientation of a proton-related defect can be derived. The observed anelastic spectra support the assumption that the same type of defect gives rise to an anelastic relaxation peak. Partial desorption experiments of proton charged samples reveal a rather complex defect behavior.

1. INTRODUCTION

High temperature proton conductors are candidate materials as electrolytes in applications like fuel cells, steam electrolyzers or hydrogen sensors. The compound $\text{Ba}_3(\text{Ca}_{1.18}\text{Nb}_{1.82})\text{O}_{9-\delta}$ belongs to a group of complex perovskites of general type $\text{A}_3(\text{B}'_{1+x}\text{B}''_{1-x})\text{O}_{9-\delta}$ where B' and B'' are divalent and pentavalent, respectively. The deviation (e. g. $x = 0.18$) from exact stoichiometry leads to the formation of oxygen vacancies due to charge conservation. This turns out to be a prerequisite for water absorption and subsequent incorporation of protons into the compound. Water uptake is commonly described in Kröger-Vink notation by:

The complex perovskites were recently introduced as proton conductors by Nowick et al. [1]. After exposure to water vapor at elevated temperatures they show proton conductivities which were found to be comparable or superior to the widely studied simple perovskites of general type ABO_3 [2]. In the Zr- or Ce- based simple perovskites like SrZrO_3 or BaCeO_3 the formation of oxygen vacancies is achieved by doping with trivalent rare earth metals like Yb or Nd.

In order to study the underlying microscopic transport mechanisms of proton conductivity we have carried out measurements of anelastic and dielectric relaxation spectroscopy. Both techniques give information about the local reorientation of anisotropic defects carrying an elastic and/or electric dipole moment. Relaxation spectroscopy has proven to give valuable information about defect kinetics in the simple perovskites. In these compounds mechanical relaxation peaks were observed which can be attributed to defect clusters containing both protons and dopant ions [3,4]. Dielectric measurements can be applied to gain additional information of the defect kinetics. The combination of both techniques has been applied successfully in oxides like ZrO_2 or CeO_2 [5]. The purpose of the present work was to investigate whether relaxation peaks can be observed in the complex perovskites mentioned above and if so, to derive kinetic parameters of the local reorientation of defects.

2. EXPERIMENTAL METHODS

Anelastic relaxation (also termed "internal friction" or "mechanical relaxation") in general measures the dissipation of elastic energy (damping Q^{-1}) and dielectric relaxation the loss angle ($\tan \delta$) due to the field induced reorientation of defects. If this reorientation is recoverable and thermally activated a relaxation peak shows up when Q^{-1} or $\tan \delta$ are measured as a function of temperature T . The peak position is given by the condition $2\pi f \tau = 1$ where f denotes the frequency of the experiment. τ describes some characteristic time of the underlying microscopic mechanism and is given by an Arrhenius-law $\tau = \tau_0 \exp(E_a/kT)$ where E_a is the activation energy of the local reorientation, τ_0 a preexponential factor and k Boltzmann's constant. The kinetic parameters E_a and τ_0 can be determined by carrying out the experiments at various frequencies [6].

The damping Q^{-1} was determined from the free decay of a resonant vibrating reed (typical measurement frequency 300 Hz) while the dielectric loss was measured by means of a LCR-meter operating at four different frequencies in the range of 120 Hz - 100 kHz. The experimental setup allows one to apply both relaxation methods simultaneously during one temperature run. In order to reduce background damping the setup was placed in a high vacuum environment. The possible change of the proton concentration due to degassing of the samples during the measurements was monitored by quadrupole mass spectroscopy.

3. SAMPLES

The ceramic samples were prepared by solid state mixing, calcining in two steps at 1000°C and 1050°C for 10h and cold pressing of rectangular reeds (40x5x0.5mm) or pellets ($\varnothing=14$ mm) with a pressure of 200 MPa. The subsequent sintering was done at 1400°C or 1600°C for 14h which leads to a final density of 70-90% of the theoretical value (TD). Electrodes were made by painted platinum paste heated at 950°C in wet air. After this preparation routine the samples contain a proton concentration in the range of 2-3 mol%. Additional charging was done in well-defined Ar-O₂ atmospheres with water partial pressure of 4×10^3 Pa. The proton-free state was obtained by heating at 600°C in a high vacuum system for several hours.

4. EXPERIMENTAL RESULTS

Fig. 1. shows the anelastic relaxation spectra for Ba₃(Ca_{1.18}Nb_{1.82})O_{9.8} in the charged and in the proton-free state. The water-containing samples show a peak which vanishes after degassing. The water-free samples reveal a peak at higher temperatures. In case of the dielectric measurements a similar behavior was found (Fig. 2 and Fig. 3). From the observed peak shift an activation energy of the local reorientation jumps of $E_a = 0.5$ eV and $E_a = 0.9$ eV can be derived for the defects in the proton-charged and proton-free state. Samples sintered at 1600°C and thus having a higher density reveal in both relaxation techniques the same behaviour. From this it is concluded that the situation do not depend on microstructural properties.

Fig. 1. Anelastic relaxation spectra for the charged and the proton-free state of Ba₃(Ca_{1.18}Nb_{1.82})O_{9.8}.

Fig. 2. Dielectric relaxation spectra for the charged state. The proton concentration c_H monitored by mass spectroscopy remains stable up to 270°C.

Fig. 3. Dielectric relaxation spectra for the proton-free state after degassing at 600°C.

Fig. 4. Selection of dielectric relaxation spectra during a partial desorption sequence. Each step included heating for 5 min at the final measuring temperature.

Fig. 5. Arrhenius diagram for the first four steps in the partial desorption sequence. Measurement 4 corresponds to the second spectrum shown in Fig. 4.

In order to prove a simple defect model where clusters containing protons or, respectively, oxygen vacancies are responsible for the relaxation process, we investigated the transition from the charged to the proton-free state. This was carried out by a sequence of dielectric measurements after each of several heating steps where partial water desorption took place. Fig. 4 show the results for a pellet charged at 300°C for 20h in a wet atmosphere with a final proton concentration of 7.6 mol% at the beginning of the sequence. The observed continuous change of the spectrum is in contrast to a simple model where the height of a proton-related peak should decrease with decreasing proton concentration. The change in the kinetic parameters describing the peak shift due to degassing is demonstrated in Fig. 5. During the first four steps of the desorption sequence which were carried out after heating at 350°C for 5 min the activation energy E_a remains constant whereas the preexponential factor τ_0 increases more than one order of magnitude.

5. DISCUSSION

The first results showing different spectra for the water-containing and for the water-free samples may indicate some analogies with the simple perovskites where it is commonly accepted that defect clusters involving dopant atoms give rise to reorientational jumps. In contrast to the simple perovskites there are no considerable numbers of doping atoms present in the complex perovskites because the oxygen vacancies are induced by deviations from the stoichiometric B'/B'' ratio. Nevertheless charge centers may arise from the off-stoichiometric composition of the B'/B'' sublattice. If a divalent B' atom occupies a regular site of a pentavalent B'' atom (e. g. Ca^{2+} on a Nb^{5+} site) an effective charge center is created which can form clusters with opposite charged OH^+ groups or oxygen vacancies.

The kinetic parameters derived from the dielectric relaxation measurements are in good agreement with the peak positions observed in the anelastic spectra. This leads to the assumption that both techniques detect the same type of local defect motion. The continuous change in the dielectric spectra with the peak shift during the partial desorption sequence is somewhat contradictory to the simple defect model. A mechanical relaxation peak shifting as the sample becomes drier was also noted in Nd-doped BaCeO_3 but not investigated systematically [4]. To elucidate the rather complex situation regarding proton-related defects in these compounds further information is required. If the derived activation energy $E_a \approx 0.5$ eV describes the local motion of a proton-related defect it can be compared to the mean value $E_\sigma = 0.55$ eV obtained from long-range conductivity [1]. The difference between these activation energies may be interpreted as a binding energy of the proton to the charge center. For a more detailed atomic picture of proton conductivity more structural information providing a sophisticated defect model would be helpful.

6. CONCLUSIONS

Both relaxation techniques show proton related peaks in $\text{Ba}_3(\text{Ca}_{1.18}\text{Nb}_{1.82})\text{O}_{9.6}$. The kinetic parameters obtained indicate local reorientation of defect dipoles. The spectra depend on proton concentration but no simple correlation between relaxation strength and proton content can be found.

References

- [1] Liang K. C., Du Y. and Nowick A. S., *Solid State Ionics* **69** (1994) p. 117-120
- [2] Nowick A. S. and Du Y., *Solid State Ionics* **77** (1995) p. 137-146
- [3] Zimmermann L., Bohn H. G., Schilling W. and Syskakis E., *Solid State Ionics* **77** (1995) p. 163-166
- [4] Du Y., *J. Phys. Chem. Solids* Vol. 55, No. 12, pp 1485-1490, 1994
- [5] Weller M., *J. Mater. Educ.*, Vol. 17, p. 33, 1995
- [6] Nowick A. S. and Berry B. S., *Anelastic Relaxation in Crystalline Solids*, Academic, New York, 1972