JOURNAL OF MATERIALS SCIENCE **34** (1999) 2183–2188

Conductivity in human tooth enamel

J. REYES-GASGA, R. GARCÍA G.
Instituto de Física, UNAM, Apdo. Postal 20-364, 01000 México. D.F., Mexico
E-mail: jose@jreyes.ifisicacu.unam.mx

O. ALVAREZ-FREGOSO, J. A. CHÁVEZ-CARVAYAR
Instituto de Investigaciones en Materiales, UNAM, Circuito Exterior Cd. Universitaria, Coyoacan 04510, México. D.F., Mexico

L. E. VARGAS-ULLOA
Facultad de Odontología, División de Estudios de Posgrado, UNAM, Circuito Exterior, Cd. Universitaria, Coyoacan 04510, México. D.F., Mexico

When human tooth enamel is heated either in vacuum or air it presents drastic changes in electrical susceptibility, conductivity and structural properties. In this paper we report an insulator-conductive transition which is observed in air around 350 °C where enamel conductivity changes drastically and its electrical resistance decreases from 10^{15} to 10^5 Ω; that is, it goes from an insulator to a super-ionic ceramic behavior. This transition, first evidenced in vacuum by electron microscopy observations, is now completely determined by a.c. impedance spectroscopy technique and its characterization was carried out as a function of the frequency and temperature. X-ray *in situ* heating diffraction experiments show that there is no structural phase transition during a wide range of temperature including the one where the conductivity transition occurs.

1. Introduction

Tooth enamel is the most mineralized tissue of the human body. It can be considered as a composite material consisting of 96% inorganic material and 4% organic material and water. The inorganic material is mainly composed of a calcium phosphate named hydroxyapatite, $Ca_{10}(PO_4)_6(OH_4)_2$. The enamel structure is in such a way that the (impure) hydroxyapatite cylindrical crystals are tightly patched in an organic matrix.

Enamel has been always observed as a non electrical conductive material; it is in fact an insulator at room temperature. However ex-situ heating experiments in enamel have reported very interesting behaviors. For example, after heating, enamel presents reduced surface dissolution when it is exposed to acid solution to simulate the caries process suggesting that in the range from 100 to 650 °C there are some structural modifications and poor crystal packing due to void formation [1–3]. A significant increase in its structural order has been reported in a more detailed experimental procedure in the range from 270 to 400 °C [4]. There have also been some reports on the changes in sign of the enamel birefringence (from negative to positive) and alteration in the enamel crystal morphology in the range from 300 to 400 °C [4]. It is logical to assume that all these behaviors are results of the same phenomenon which appears when enamel is thermally treated. In this paper we report for the first time ever the ionic conductivity in enamel observed after it is passed through a insulator-conductor thermal transition caused by heating. The first indication of this behavior was deduced from some Transmission Electron Microscopy (TEM) work carried out on this material during an in-situ heating experiment [5] when it was possible to observe enamel samples commonly showing some charge effects.

Electrical signals are very important in the development of the human body and tooth enamel is not the exception [6]. The electrical response of polycrystalline solids, like enamel, is modified by a complicated microstructure, the size of the grains (about 200 nm), the grain boundary (which is unknown) and the charge carriers among other factors [7]. In earlier studies, Leicerster [8] and Björn [9] found that the resistance of the tooth enamel is high but coexists with low resistance zones, due to hypermineralizations. Later, Pincus [10] suggested to study the electrical conduction of the tooth enamel to detect dental caries. Murakami *et al*. [11] observed that the human tooth enamel is very resistant to electric conduction whilst the dentine has a constant resistance independent of the position in the tooth. Williams *et al*. [12] concluded that the resistance is sensitive to biomaterial defects, in which there is an increment in the ionic conduction. Aoki [13] measured the human tooth enamel impedance using an oscilloscope to find the amplitude of these changes, the frequency range was 7.14–3.22 KHz. In this work, electrical properties of the human tooth enamel were determined by using a.c. impedance spectroscopy technique during an

in-situ heating experiment carried out in air and the existance of a insulator-conductor transition is shown around 350 °C. Any structural change in the enamel samples around this temperature was studied by *in-situ* heating X-ray diffraction analyses. The results show that this conductivity is of ionic type.

2. Experimental procedure

The electrical properties of tooth enamel as function of temperature were measured by a.c. impedance spectroscopy, in the frequency range from 5 Hz to 13 MHz, using a Hewlett-Packard 4192A impedance analyzer. Impedance spectroscopy responses can be correlated with dielectric properties, defects, microstructure and compositional influences on the conductivity of solids. The a.c. theory, performed over a wide range of frequencies, is a powerful technique for characterizing electrical properties of heterogeneous materials, like enamel, where the overall behavior is usually determined by a number of strongly coupled processes. Under favorable conditions, by using a.c. methods it is possible to identify the characteristic response of each region (grain and grains boundaries) in the test system.

For the impedance spectroscopy measurements, enamel from teeth where denting was previously removed was sectioned with a diamond wheel to produce 0.3×0.3 cm slices of 250 to 500 μm thick. Electrodes were attached on their surface by coating pellet faces with a silver layer; samples were heated for 2 h at 200 °C to decompose the organic solvents and harden the electrodes. Afterwards the sample was mounted in a conductivity jig which was inserted in a vertical tube furnace, controlled to ± 3 °C by a home made temperature controller. The temperature was registered using a digital multimeter via a Pt-Pt (Rh 10%) thermocouple placed in contact with the sample. Conductivities were measured during heating cycles over a temperature range 25–550 °C, increasing the temperature in steps of $\sim$20 °C. At each temperature, at least one hour was allowed before measurements to ensure thermal equilibration of the sample.

For TEM observance the 0.3×0.3 cm slices were polished to a thickness of 60 μm. Afterwards a concavity was produced in the center with a FISHIONE dimpler until a thickness of less than 10 μm was obtained. The final polish was produced with a GATAN-600 ion mill. The ion polish was stopped when a small hole appeared in the center of the concavity. TEM observation and heating experiment of these samples were carried out with a JEOL-100CX electron microscopy using a heating holder.

To analyze the enamel structure during heating, mainly in the temperature range of interest, *in-situ* heating X-ray diffracton studies were carried out in enamel powder. For this analysis a SIEMENS D-5000 diffractometer with *in-situ* heating facilities was used. The powder was packed in a standard aluminum sample support with dimensions of 3 cm in diameter and 2 mm thick. The analysis was carried out using a CuK_α radiation with a 2θ scan range from 2 to 65°. The temperature range was from room temperature (approximately 20 °C) to 1000 °C, with an increment rate of 10 °C/min and 1 h of stabilization before take the X-ray diffractogram in each case.

3. Results

Recently electron microscopy *in-situ* heating observations have indicated the existence of a conductivity transition from insulator to conductive states [5]. In that case these observations were carried out in a 10^{-7} Torr vacuum and the change in conductivity was registered around 200 °C. Note that this evidenced-electron-microscopy conductivity is produced by electrons because before 200 °C, when the electron beam streaks a dielectric enamel, the absorbed electrons do not find a easy way to ground as in a conductive enamel (above 200 °C) and many charge effects are presented. Fig. 10 in reference [5] shows how the contrast of a enamel sample changes when the charge related phenomena disappear around 200 °C during *in-situ* heating experiments.

Electron diffraction patterns show that no structural phase transition occurs in the enamel samples although they were heated in vacuum up to 700 °C. X-ray diffractograms taken in air at different temperatures in *in-situ*-heating experiments also support the non occurrence of a phase transition during the insulator-conductive transition temperature of 350 °C. Fig. 1 shows the diffractograms for room temperature (Fig. 1a), 350 °C (Fig. 1b) and 500 °C (Fig. 1c); the peaks agree very well with the hexagonal hydroxyapatite structure. Fig. 1 shows that there is no appearance of new peaks and those already presented at room temperature remain in their same position even at 500 °C. The only difference observed is changes in intensity of some peaks, mainly those corresponding to (211), (300), (310) and (222). In fact, the only phase transition observed during this type of experiments was at 1100 °C, where peaks corresponding to tri-calcium phosphate began to appear such as reported everywhere [14].

The impedance results (Fig. 2) shows the enamel electrical response as a function of temperature and the reversible electrical bi-stability from insulator ceramic compound to ionic conductor at a critical temperature of 350 $\pm$ 10 °C. From the observed semicircles in this plot, resistance values showed a large change in magnitude, from the insulating state (state 0) with $\sim 10^{15}\ \Omega$ at $\sim$25 °C (extrapolated value) to a "low resistance" regime of $\sim 10^{5}\ \Omega$ (called "the conductive state or state 1") at 350 °C. This transition appears only as function of temperature and not with frequency or voltage. The calculated magnitude of capacitance C was approximately 10^{-12} F.

The Arrhenius plot constructed from the reciprocal values of resistances is shown in Fig. 3. The activation energy determined for both states where: for "state 0" ($T < 350$ °C) $E_a = 1.2$ eV (typical value of ceramic compound) whilst for "state 1" ($T > 350$ °C) $E_a = 126$ meV (typical value of an ionic conductor). Impedance results also indicate that the resistivity of enamel at room temperature is approximately $10^{17}\ \Omega$ cm, a typical value for an excellent insulator; at 350 °C

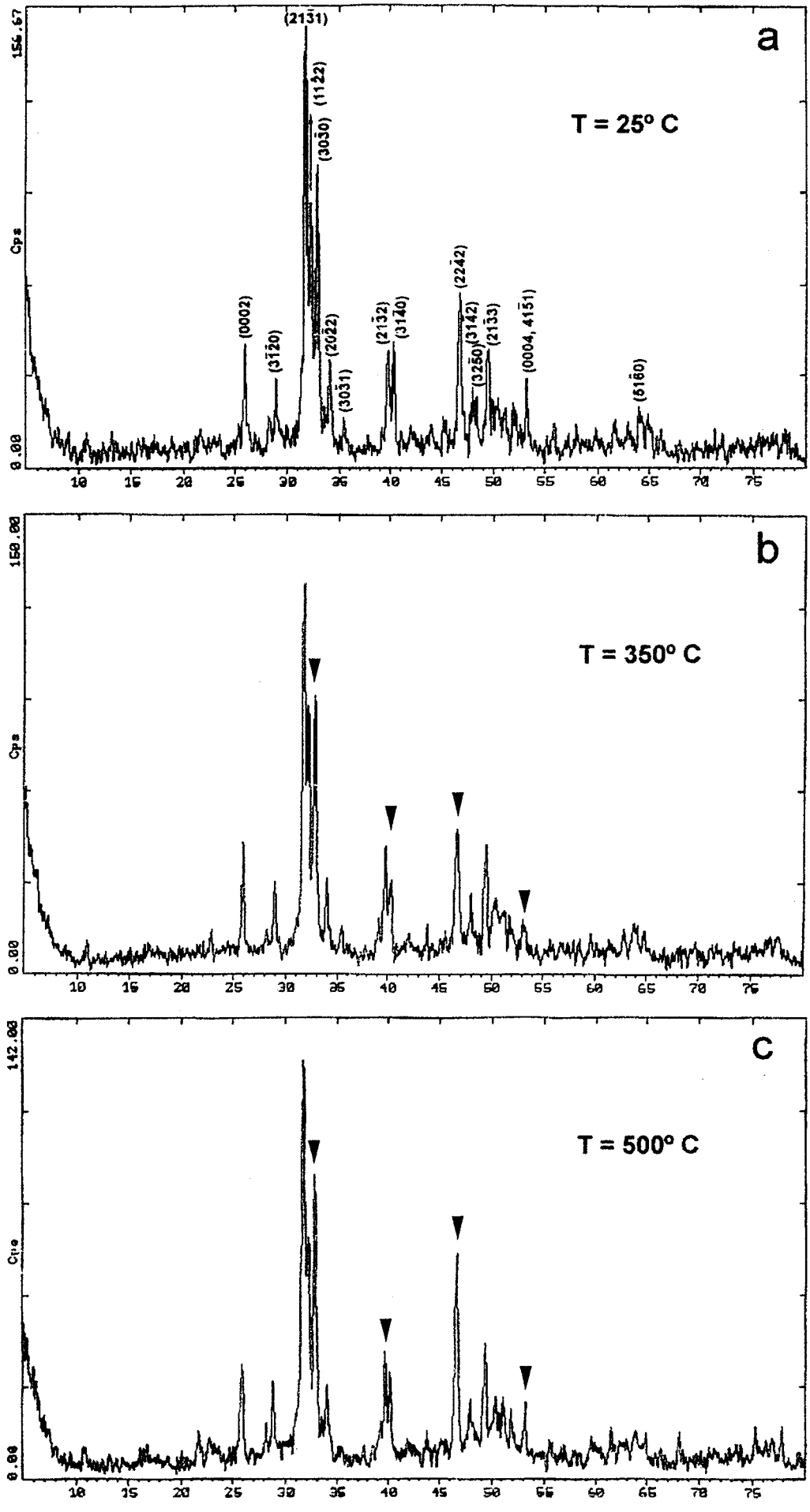

Figure 1 X-ray diffractograms from the *in situ* heating experiments in air of a powder enamel sample: (a) at room temperature, (b) at 350 °C, and (c) at 500 °C. The indexation fit very well with the hexagonal structure of hydroxyapatite. Note that the only difference is the change in intensity of some peaks, mainly those marked.

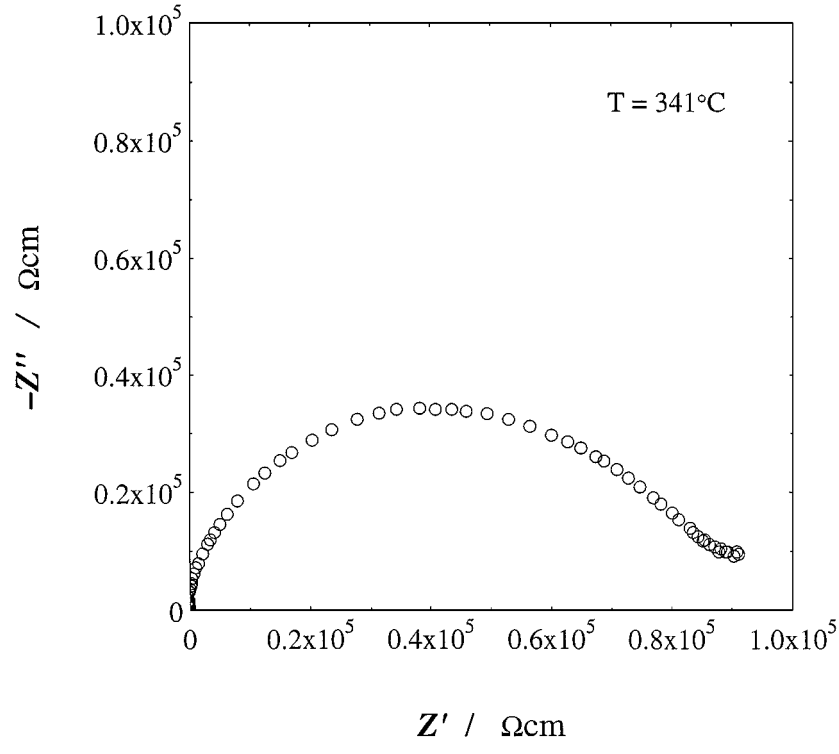

Figure 2 Impedance plot of the enamel sample for $T = 341\,^{\circ}\mathrm{C}$.

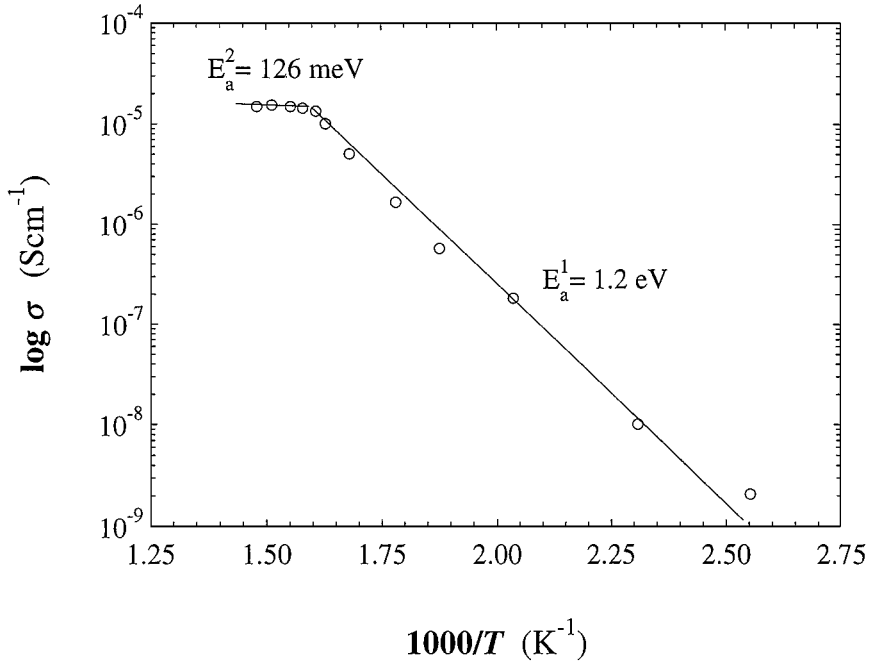

Figure 3 Arrhenius plot obtained from the reciprocal values of resistances. The transition temperature is observed at 350 °C.

this resistivity decreases to $10^5\,\Omega\,\mathrm{cm}$, a typical value for a super-ionic ceramic. Therefore, around 350 °C human tooth enamel presents an insulator-super ionic transition without any apparent change of structure.

The electrical properties of most materials may be described by an appropriate equivalent circuit based on a combination of RLC elements in a series and/or parallel arrangement [15]. These components represent the macroscopic processes involved in the charge transport due to inhomogeneities in the structure and the effect of electrode/solid interfaces of the measuring system. The electrical response registered from the enamel sample was modeled by an equivalent circuit using the Boukamp PC software; this circuit and its response are shown in Fig. 4. In Fig. 4b the open circles show the same experimental response data from enamel as shown in Fig. 2 and the simulated data obtained with the circuit shown in Fig. 4a are plotted as "+"; both plots fit quite well.

The sample will maintain its "state 1" whenever the sample changes are within the range from 350 to 410 °C. The sample can recover its original "state 0" by lowering the temperature below 350 °C. Generally, the stable and repeated electrical switching property in

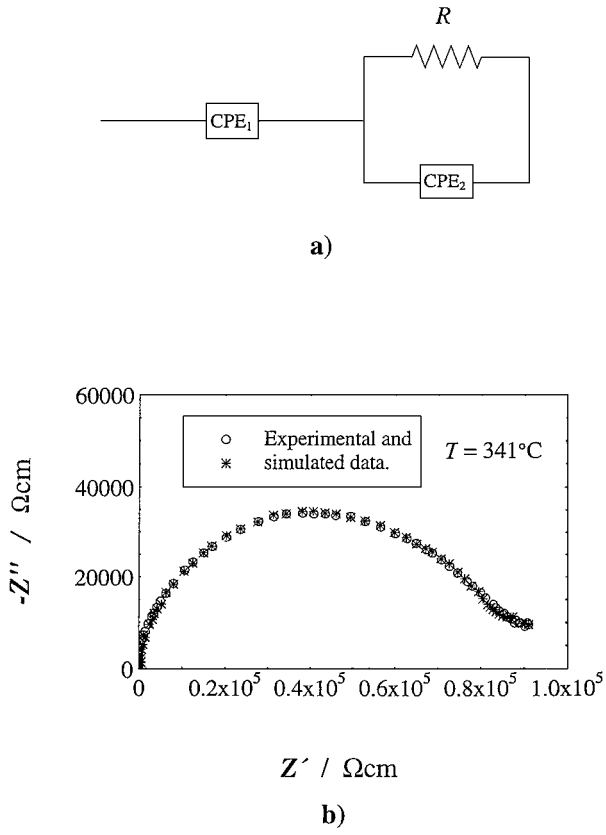

Figure 4 (a) Equivalent RC circuit for the experimental enamel response. (b) Adjusted impedance plot comparing the impedance plot shown in Fig. 2 for the experimental data (open circles) and the response ("+" signs) of the RC circuit shown in (a).

enamel remains in the range of temperature from 350 to 360 °C. This electrical bistability can be repeated several times using the same procedure. However, if the temperature is increased above 450 °C, although a large increase in ionic current is produced, a degradation mechanism is induced.

As it was reported earlier [5], after repeating the cycle of heating in vacuum up to 800 °C and cooling down to room temperature several times, the tooth enamel begins to show some nanometric sized holes in the TEM images. In the air heating experiments, for example the enamel sample used in the impedance experiments became so weak that it was easy to powder even with a fingers pressure. Electron diffraction patterns from this last sample (Fig. 5b) show that the enamel unit cell (hydroxyapatite) (Fig. 5a) has lost almost all the oxygen ions and that its diffraction rings have been weakened. The most intense ring in Fig. 5b represents a distance of 0.26 nm, which give us an idea that the hydroxyapatite enamel unit cell has changed to a calcium phosphide (CaP) unit cell. The presence of the mentioned holes in the many-times-heated enamel sample indicates the existence of a diffusional ionic process in the enamel sample produced by these heating cycles.

4. Discussion

This paper reports the transition in the electrical properties of human tooth enamel whose conductivity becomes ionic above 350 °C in air and 250 °C in vacuum. According with the above mentioned results there are some processes which have to be enhanced when the tooth enamel is heated in the range from 20 to 700 °C:

1. Vacuum *in-situ* heating experiments in TEM of enamel samples indicate that the conductor state appears at 200 °C; it is evidenced when the electron beam impinges into the surface of the sample and the image

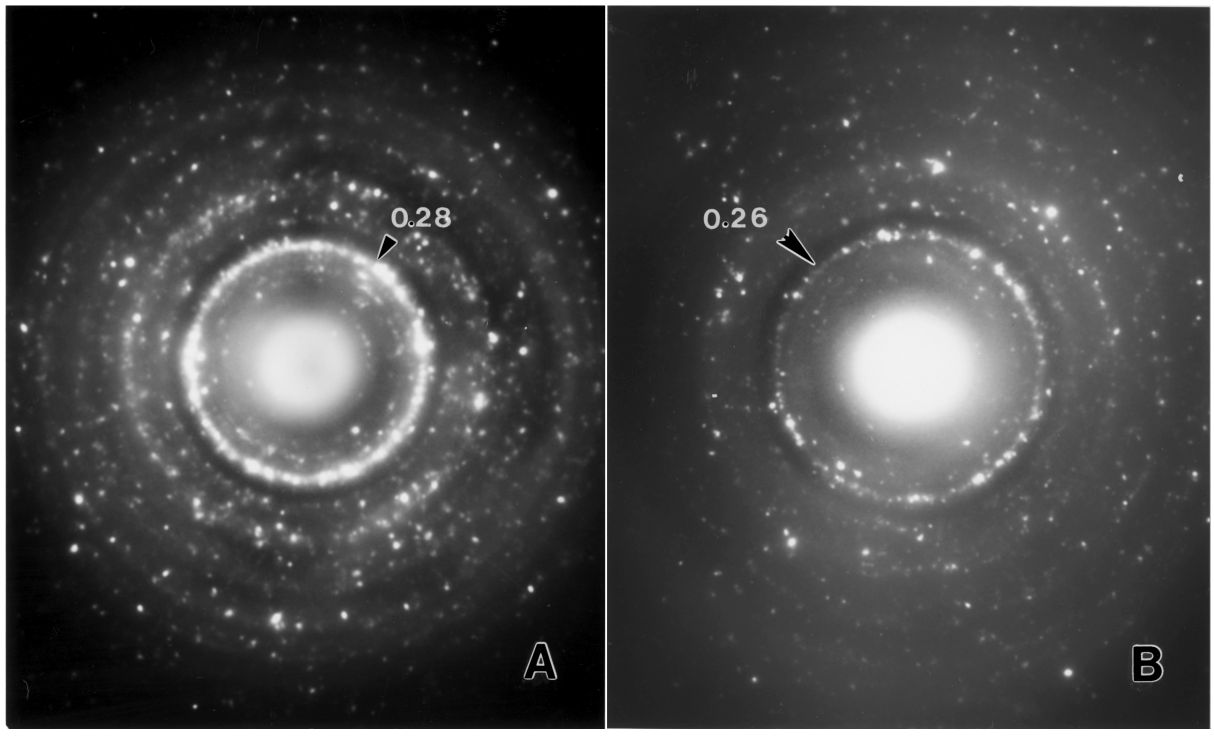

Figure 5 Comparison between the electron diffraction pattern from the enamel samples: (a) from the sample before any heating experiment; (b) from the sample showing degradation after several heating-cooling cycles. Note that the most intense ring in these diffraction patterns have changed from 0.28 to 0.26 nm.

is observed without any electronic charge effect. In this case the conductivity is produced with assistance of electrons and temperature.

2. The impedance spectroscopy results show that in air the insulator-conductor transition is observed at 350 °C and that in this case the response is produced by ionic conductivity across the grains and grain boundaries when enamel is heated.

3. In both cases, TEM and impedance spectroscopy, the insulator-conductor transition is reversible, although after several cycles of heating and cooling degradation of the enamel sample occurs due to the electron beam and ion displacement during conduction.

4. Electron and X-ray diffraction analyses show that no changes in the structure occur, only accommodation of some planes in the enamel unit cell (hydroxyapatite). Although the degraded enamel sample has changed it unit cell to a calcium phosphide (CaP) unit cell.

Conduction in ceramics is produced by ionic movement via material defects. The change from insulator, at room temperature, to ionic conductor observed in enamel is due to oxygen ion movement, the main cations present in hydroxyapatite. This ionic movement also allows us to explain the TEM *in-situ* heating results in a very easy way: under the conductor condition (above 200 °C in vacuum), TEM observations may be easily carried out since this conductive state avoids the electron charge accumulation in the sample.

From the experimental results, it is clear that XRD and TEM measurements can not detect directly the changes in the organic matrix at 200° but indirect evidence of this consists in a reduction of the intensities of XRD peaks and the clearly TEM observation of the enamel grains at this temperature. In a.c. impedance experiments, we observed a very cutting insulator-conductor transition that must be produced for the degradation of the organic matrix with almost any effect on the HPA. This organic matrix degradation process induce an increment in ionic population which increase the ionic current, so that we observed a conductivity transition. As it is known, synthetic HPA is made up of agglomerates of granular crystallites without any organic matrix, so the a.c. conductivity experiments should not show any drastic insulator-conductor transition because the organic matrix does not exist; in this case the behavior must be continuos as in ceramic materials.

Taking in account both TEM and impedance results it is easy to observe that the insulator-conductor transition temperature also depends on the pressure of the environment: in atmosphere pressure the transition is observed at 350 °C, but at 10^{-7} Torr this transition temperature is reduced to 200 °C. It should be also noted that in TEM this process is electron beam assisted whereas in impedance spectroscopy it is by the voltage apply; but both techniques are equivalent because they show the same effect on enamel samples. In any case, the transition temperature reported in both situations is well above any biologically relevant temperature, at least at this moment. With the laser technique used in some dental surgery it could be possible to get this range of temperature in very localized points and might signify the possibility of some application. Much more research must be done in this field before we have any idea on this and another possible application of the conductivity herein described for enamel; and the implications for hydroxyapatite, the main component of enamel, and its applications besides those it already has [16].

Acknowledgments

We would like to thank R. Hernández, L. Rendón, C. Zorrilla, S. Tehuacanero, P. Mexia, J. Cañetas, C. Flores, F. Solorio, A. Reyes, H. Esparza, E. Martínez, M. García and A. Sánchez for technical help.

References

1. R. H. STERN and R. F. SOGNNAES, *J. Amer. Dental Assoc.* **85** (1972) 1087.
2. H. YAMAMOTO and K. SATO, *J. Dental Res.* **59** (1980) 2171.
3. D. G. A. NELSON, M. SHARIATI, R. GLENA, C. SHIELDS and J. D. B. FEATHERSTONE, *Caries Res.* **20** (1986) 289.
4. J. PALAMARA, P. P. PHAKEY, W. A. RACHINGER and H. J. ORAMS, *J. Dental Res.* **66** (1987) 1742.
5. J. REYES-GASGA, R. GARCÍA and L. VARGAS-ULLOA, *Phil. Mag.* **A75** (1997) 1023.
6. A. B. MANSSON and T. BOSH, *Adv. Dent. Res.* **7** (1993) 70.
7. R. W. POWERS and S. P. MITTOF, 1975 *Electrochem. Sci. Tech.* **122** (1975) 226.
8. H. M. LEICERSTER, "Biochemistry of Tooth" (Mosby Co., St. Louis. C.V., 1941), p. 93.
9. H. BJÖRN, *Svensk Tandläk Tijdsk* **39** (1946) 625.
10. P. PINCUS, *J. Physiol.* **113** (1951) 13.
11. T. MURAKAMI, E. ABE, K. KATSUNUMA and T. KOBAYASHI, *Odont.* **59** (1971) 84.
12. D. L. WILLIAMS, A. TSAMTSOURI and G. E. WHITE, *J. Dent. Res.* **57** (1978) 195.
13. E. AOKI, *Shigaku* **72** (1985) 1338.
14. R. Z. LE GEROS, in "Calcium Phosphates in Oral Biology and Medicine," edited by H. M. Myers (Karger, San Francisco, California, 1991).
15. J. MACDONALD ROSS, "Impedance Spectroscopy, Emphasizing Solid Materials" (John Wiley & Sons, 1987)
16. D. E. C. CORBRIDGE, "Phosphorous: An Outline of its Chemistry Biochemistry and Technology in Studies in Inorganic Chemistry," 4th ed. (Elsevier Science Publishers, New York, 1990) Vol. 10.

Received 2 December 1997
and accepted 29 October 1998