Synthesis of $ZrTiO_4$ and $Ta_2Zr_6O_{17}$ Films by Composition-Combinatorial Approach through Surface Sol-Gel Method and Their Dielectric Properties

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Single phases of multi-component oxides films, $ZrTiO_4$ and $Ta_2Zr_6O_{17}$, could be synthesized by using the combinatorial approach through surface sol-gel route, coating the appropriate mole ratio of 100 mM zirconium butoxide, tantalum butoxide and titanium butoxide precursors on Pt/Ti/SiO_2/Si (100) substrate, following pyrolysis at 450 °C, and annealing them at 770 °C. Both the films and bulks of $ZrTiO_4$ and $Ta_2Zr_6O_{17}$ showed very stable dielectric properties in temperature range, −140 to 60 °C, and frequency range, 100 Hz to 1 MHz, promising their applications in wide range of temperatures and frequencies. The dielectric constants of the films were lower and a little more dependent on frequency than those of the bulks. The reduction of dielectric property in the film was mainly due to the interfacial effects that worked as series and parallel-connected capacitances toward the substantial film capacitance.

Key Words : Combinatorial approach, Surface sol-gel process, $ZrTiO_4$ and $Ta_2Zr_6O_{17}$ films, Dielectric constant

Introduction

Since biomolecules with desired properties were synthesized as large collections or libraries,[1] the application of molecular libraries generated by combining a large number of precursors, has been studied extensively in order to discover new superconducting,[2] or electrical[3a] materials using RF magnetron sputtering deposition. The "combinatorial approach" is useful and effective for discovering new materials because it can control the precise compositions of reactants in wide variations and can attempt to fabricate all desired compositions once.

In this work, the discovery of multi-component oxide dielectrics in ZrO_2-TiO_2-Ta_2O_5 system was tried out by using the combinatorial approach via surface sol-gel process[4,5] because the process was convenient in the application of film capacitors. By the surface sol-gel method, a large coating area can be obtained once, and the designed multi-compositions are controlled easily with low cost. In addition, the surface sol-gel route is more attractive than the conventional bulk sol-gel route, in which the surface metal alkoxide group adhered to the substrate is hydrolyzed partially in the air and the group is useful for the next linkage with another alkoxide group coming to the surface subsequently.[6] The liquid film adhered to substrate surface solidifies rapidly through the evaporation of the solvent. If the adhesion rate of each precursor on substrate is not quite different, multi-component oxides can be synthesized on the surface of substrate through decompositions of reactants at much lower temperature than usual reaction temperature of solid metal oxides.

The fabrication of binary oxide, $ZrTiO_4$ film with zirconium butoxide and titanium butoxide was reported by the same author.[7] Although its dielectric property was dependent on the thickness of the film as other material films, the dielectric stabilities of the $ZrTiO_4$ films/bulk in wide range of frequency could be a meaningful topic to continue the study. In addition, ZrO_2-TiO_2 mixed oxide[8] and $ZrTiO_4$ nanoparticles prepared by sol-gel method[9] have recently been studied for their high surface areas, humidity susceptibilities, and photocatalytic activities.

For another capacitive component that forms the basis of the memory device, Ta_2O_5 has been considered[10,11] and known to form high-quality thin film. The improved dielectric property of Ta_2O_5 through the addition of TiO_2 has been achieved by the standard ceramic processing method.[12] Although tantalum zirconates are rare, the synthesis of $Ta_2Zr_6O_{17}$ from tantalum ethoxide and zirconium acetylacetonate for a potential microwave dielectric material has been reported.[13] As a different research, ternary ZrO_2-SnO_2-TiO_2 system has been studied to obtain the high dielectric constant and a high breakdown field.[3a] Humidity sensing properties of binary TiO_2-SnO_2 also has been reported.[3b]

It is worthwhile to develop materials of single phase efficiently from the studies described above, using the combinatorial approach on the new ternary oxide system, TiO_2-ZrO_2-Ta_2O_5, and to investigate the properties of the dielectrics with their stabilities in the range of temperature/frequency. For this purpose, the substrate was directly used as one side electrode by the deposition of Pt on its surface before the sol-gel route proceeded.

Experimental Section

Pt substrate (1 cm × 1 cm) was purchased from the Inostek Corp. as a Pt film (1500 Å) grown on the Ti adhesion layer (100 Å)-SiO_2 adhesion layer (3000 Å)-Si wafer (100). The Pt on substrate worked as one side electrode when the dielectric property was measured. The substrate was primed with hydroxide layer of 5 wt% 2-mercaptoethanol (98%, Aldrich)/anhydrous ethanol solution. 100 mM of zirconium butoxide (98%), titanium butoxide (98%), and tantalum

butoxide (98%) solutions (Aldrich) were prepared separately in anhydrous ethanol and toluene solvent in the ratio of 3:1 in volume and the next steps proceeded in a dried nitrogen atmosphere box. The 40 compositions in ternary diagram, ZrO_2-TiO_2-Ta_2O_5, were selected and the volume of each precursor in accordance with its mole ratio was taken using micropipettes into 5 mL covered chalet, and mixed quickly. The mixture was dropped on the hydroxyl terminated substrate and spun with wafer spin processor (Laurell, WS-400-6NPP) for 2 minutes (3000 rpm/min.), followed by pyrolysis at 450 °C for 20 minutes after 2-4 coating cycles, and annealed at 770 °C for 15 minutes to complete the reaction. The process was repeated until the 10-16 multi-layer films were grown for the measurements of properties. The pyrolysis temperature was chosen by DTA analyses (TG/DTA 220, Seiko Inst.) of the three precursors that were decomposed at 390-450 °C. Although the surface sol-gel process is suitable for preparing ceramic films of a large coating area, cracks are likely to occur as the pyrolysis proceeds. In order to avoid these cracks and possible electric short circuit during measurement, it was necessary to fabricate multi-layer films by repeating the coating.

The phase of each product was confirmed by x-ray diffractometer (Philips X'Pert MPD) equipped with mono-chromatized Cu Kα radiation. To calculate the dielectric constant, thickness of the film was measured by α-step (Utencor Instr., 250) with the scanning length of 2000 μm. The cross-section of the film in single phase was obtained using SEM (Jeol Corp., JSM-6300). For the measurements of dielectric properties, gold was deposited on each film using the designed mask to have several electrode holes of 300 μm in diameter size, which allowed the measurements to be repeated.

To compare the dielectric properties of single phase films with the corresponding bulk materials, bulk samples were fabricated by heating the mixture of TiO_2 (99.9+%, Aldrich), $ZrOCl_2 \cdot 8H_2O$ (98%, Aldrich) and Ta_2O_5 (99.9%, Sigma) in appropriate molar ratio between 1400 and 1500 °C for 20 hours with the intermediate grinding. To decrease the reaction temperature, $ZrOCl_2 \cdot 8H_2O$ instead of ZrO_2 was used as a reactant because Cl_2 from $ZrOCl_2$ was dissociated at 324 °C after each $4H_2O$ was separated at 98 °C and 154 °C.[14] Then the powder sample was pressed into cylindrical pellet (1.3 cm in diameter) under a pressure of 400 kg/cm^2 and annealed at 1400 °C for 2 hours again. Gold was deposited on both sides of the pellet as electrodes.

The measurements of capacitances were performed between 100 Hz to 1 MHz using HP 4284A LCR meter at room temperature for the film/bulk. Measurements in temperature range −140 to 60 °C were carried out for the pellet-shaped bulks using the liquid nitrogen and temperature controller (Lakeshore Cryotronic, Inc. Mo. 321). The dielectric constant, k, was estimated from the capacitance data, using the equation

$$k = Cd/(k_0 A), \quad (1)$$

where k_0 is permittivity of free space, 8.854×10^{-12} F/m, C(Farad) is capacitance, d(m) is thickness of the pellet or film, and A(m^2) is the area of gold electrode.

Results and Discussion

Two single phases, $ZrTiO_4$ and $Ta_2Zr_6O_{17}$, could be obtained near 1 TiO_2:1 ZrO_2 and 1 Ta_2O_5:4 to 6 ZrO_2 of binary systems by the composition-combinatorial approach through surface sol-gel process among the selected 40 compositions. According to the x-ray analyses, the other compositions showed mainly amorphous phases in ternary system. Except for regions of $ZrTiO_4$ and $Ta_2Zr_6O_{17}$, the traces of multi-phases appeared near the binary systems. Figure 1 shows the region of $ZrTiO_4$ and $Ta_2Zr_6O_{17}$ phases in the three metal oxides system.

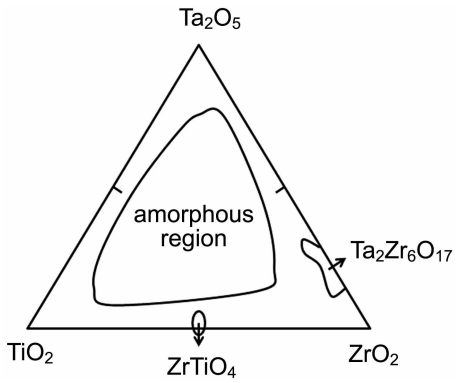

Figure 1. Ternary phase system of ZrO_2-TiO_2-Ta_2O_5.

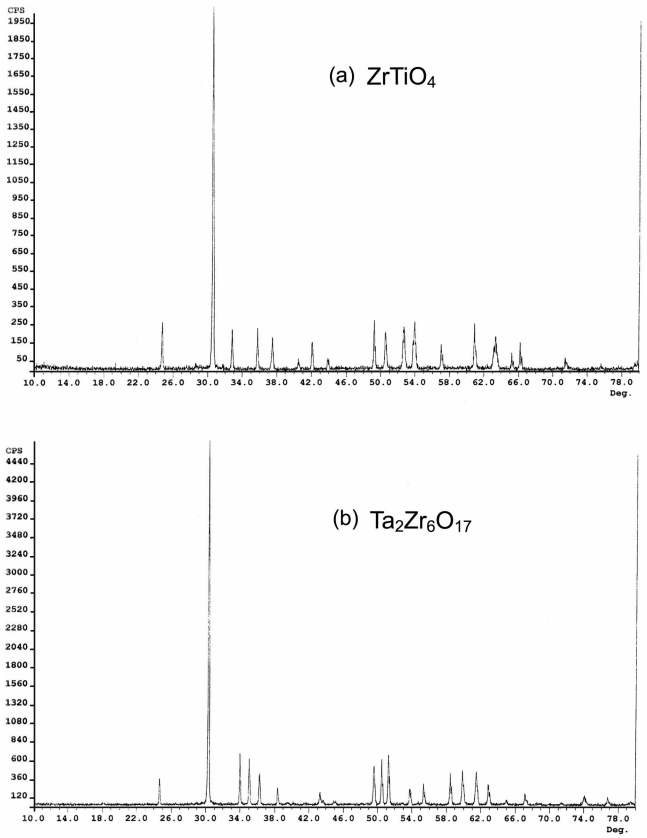

Figure 2. XRD patterns of (a) $ZrTiO_4$ and (b) $Ta_2Zr_6O_{17}$ films.

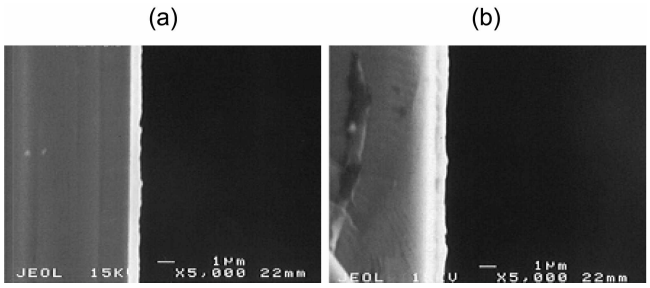

Figure 3. SEM images of (a) $ZrTiO_4$[7] and (b) $Ta_2Zr_6O_{17}$ films at cross section (white region) after annealing at 770 °C.

Figure 2 displays the x-ray patterns of orthorhombic $ZrTiO_4$ and $Ta_2Zr_6O_{17}$ obtained from the films, in which the patterns correspond to the x-ray powder diffraction data (JCPDS) of the bulks.

The SEM images of $ZrTiO_4$[7] and $Ta_2Zr_6O_{17}$ films fabricated after several coating cycles are shown in Figure 3. Each cross-sectional part of Figure 3(a) and (b) displays uniform thickness throughout the film. The formation of few voids and cracks of the film coming from the process of pyrolysis produces less dense specimen than the bulk, so the difference in dielectric property between the film and bulk can be expected. The dielectric constant of the voids is almost the same as that of the air (k = 1.006). Those defects induce the reduction of the dielectric property in total film system. K. Natori *et al.* contended that "the local dielectric

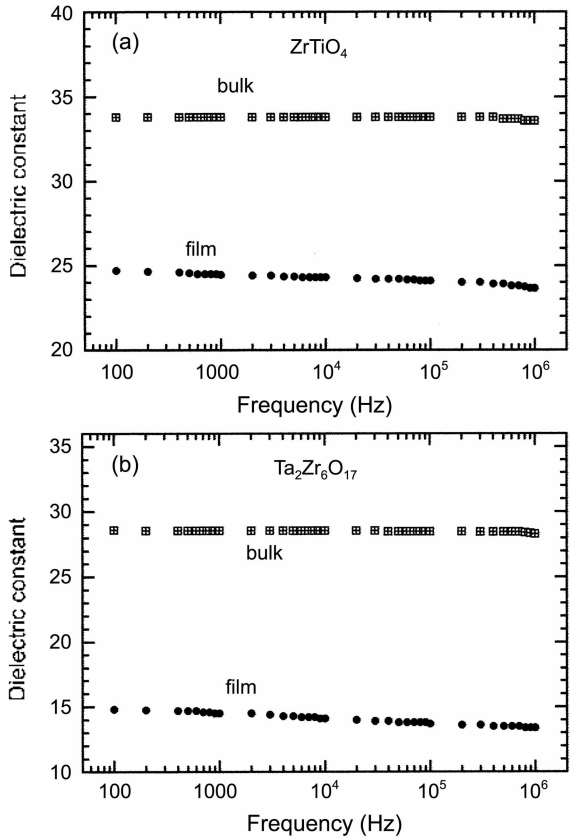

Figure 4. Dielectric constant vs. frequency for bulk and film in (a) $ZrTiO_4$ and (b) $Ta_2Zr_6O_{17}$ at 20 °C.

constant at the edge site has a reduced value due to the absence of an enforcing field effected by the nearest neighbor dipole in the adjacent layer, which fact yields a smaller effective dielectric constant in a thinner sample structure"[15] through the simulation of Lorentz's local field theory. Therefore, the reduction of dielectric constant of the film drawn in Figure 4 mainly comes from the "interfacial effects" caused by the surface and bottom layers/electrodes and the existence of the voids/cracks in film. Compared with the previous report,[7] the dielectric constant of $ZrTiO_4$ in bulk showed the same result, approximately 34. The difference in dielectric constant of $ZrTiO_4$ film from this experiment (k = 24 at 1 MHz)) and the previous report (k = 28 to 31 at 1 MHz for the film thickness 160 to 341 nm)[7] is mainly due to the difference in thickness of the film fabricated and the different contribution of the voids/cracks on the property during formation of the film.

Of the discovered single phases, $ZrTiO_4$ and $Ta_2Zr_6O_{17}$, $ZrTiO_4$ displayed higher dielectric constant than that of $Ta_2Zr_6O_{17}$. However, both $ZrTiO_4$ and $Ta_2Zr_6O_{17}$ show stable characteristics in measured frequency range as can be seen in Figure 4(a) and (b). They do not exhibit any significant difference in dielectric constant at frequency range, 100 Hz-1 MHz, especially in bulk. We can find that the dielectric constant of thin film is a little more dependent on the frequency than the case of bulk. The contribution of surface at layer/electrode to the total dielectric property in film is larger than that in bulk and so is the space charge stored at layer/electrode. As the measuring frequency increases, the capacitance formed at layer/electrode can be partially extracted. Thus, the reduction of dielectric constant at high frequency can be observed in the thin film.

If we use series-connected capacitor model[16] for the film, the capacitance component in series, C_{series}, is composed of the substantial capacitance, C_f, and the interfacial capacitance, C_i, such as

$$1 / C_{series} = 1/C_f + 1/C_i \quad (2)$$

, which is very simplified in case of film. Actually, there are other factors influencing dielectric properties such as oxygen diffusion, chemical reaction, changes in defect, or trace of contamination on the interface/surface.[16,17] In case of multilayer film, the component C_i that is connected in series with C_f can be classified into series-connected layer/electrode capacitance, C_{dl}, and layer/layer capacitance, C_{ll}. So, the equation (2) is expressed again

$$1 / C_{series} = 1/C_f + 1/C_{dl} + 1/C_{ll}. \quad (3)$$

On each single layer, the boundary between grain and grain causes another parallel capacitance, C_{gg}, to the C_f, C_{dl}, and C_{ll}. The corresponding equivalent circuit can be represented as shown in Figure 5. Then the observed (total) capacitance, C, is made up of C_{series} and C_{gg} in parallel and described as

$$C = C_{series} + C_{gg} \quad (4)$$

where $C_{series} = 1/(1/C_f + 1/C_{dl} + 1/C_{ll})$.

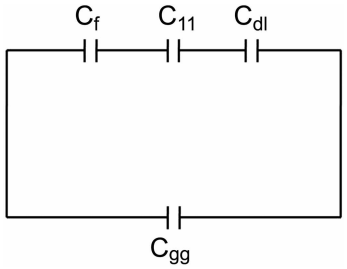

Figure 5. Equivalent circuit of capacitor model in $ZrTiO_4$ and $Ta_2Zr_6O_{17}$ films.

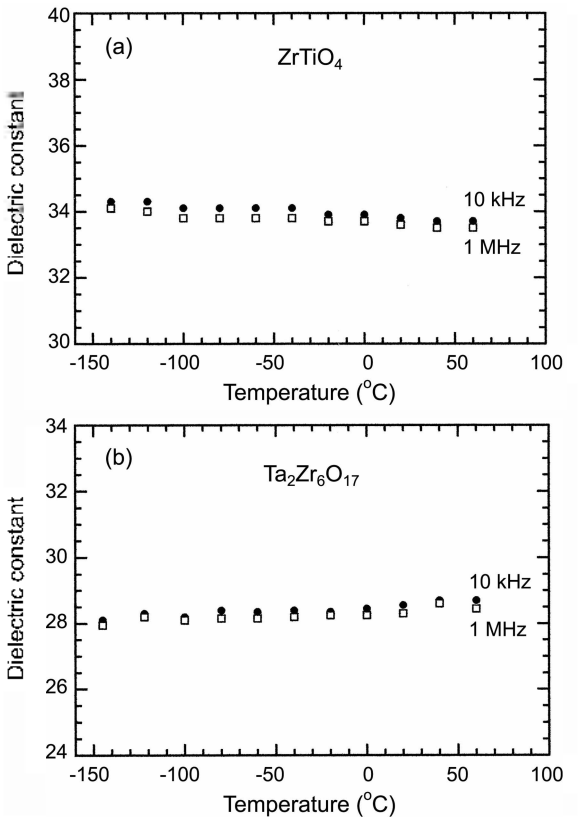

Figure 6. Dielectric constant vs. temperature at 10 kHz and 1 MHz for the bulk (a) $ZrTiO_4$ and (b) $Ta_2Zr_6O_{17}$.

According to the equation (4), the capacitance in parallel, C_{gg}, makes the observed capacitance of the film increase. On the other hand, series-connected capacitance, C_{series} is always smaller than each capacitance, C_f, C_{dl}, or C_{ll} by the equation (3). Thus a large contribution of the series-connected components of C_{dl} and C_{ll} decisively reduces the capacitance in series, C_{series}, and eventually makes the observed capacitance of the film decrease, which is in good agreement to K. Natori's study.[15]

The dielectric constants of bulk $ZrTiO_4$ and $Ta_2Zr_6O_{17}$ in temperature range −140 to 60 °C are illustrated in Figure 6. The constants, approximately 34 and 28.5 at 1 MHz, are almost constant in the measurement range, indicating that $ZrTiO_4$ and $Ta_2Zr_6O_{17}$ are very stable dielectrics and can be utilized in wide temperature and frequency ranges. $ZrTiO_4$ synthesized by the usual solid solution method has already been known for a dielectric resonator in telecommunication system,[18-20] an electronic fiber,[21] a refractory oxide,[22] and a high charge storage capacitor.[23]

Conclusion

As a short processing route for the synthesis of new ceramic films at a moderately low temperature and for the identification of their electrical properties, composition-combinatorial approach through surface sol-gel process was applied to ternary oxides system, ZrO_2-TiO_2-Ta_2O_5, and two single phases of dielectric oxide films, $ZrTiO_4$ and $Ta_2Zr_6O_{17}$, could be synthesized. Their dielectric constants, 24 and 14 at 20 °C, showed stable characteristics in wide frequency range, and were lower than those of the bulks, 34 and 28.5, due to the interfacial effects appeared in film. Bulks of $ZrTiO_4$ and $Ta_2Zr_6O_{17}$ also showed very stable dielectric properties in the temperature range, −140 to 60 °C, and the frequency range, 100 Hz to 1 MHz. The simplicity of the synthetic method on substrate, where the chemical reaction occurs by thermal controlling, shows a number of possibilities for preparing other multi-component thin films. The experimental results indicate that the dielectric property of the film can be adjusted to some degree by controlling the synthetic process conditions and the film thickness.

References

1. Nisonoff, A.; Hopper, J. E.; Spring, S. B. *The Antibody Molecule*; Academic Press: New York, 1975.
2. Xiang, X.-D.; Sun, X.; Briceno, G.; Lou, Y.; Wang, K.-A.; Chang, H.; Wakkace-Freedman, W. G.; Chen, S.-W.; Schultz, P. G. *Science* **1995**, *268*, 1738.
3. (a) Dover, R. B.; Schneemeyer, L. F.; Fleming, R. M. *Nature* **1998**, *392*, 162. (b) Kim, H.-K.; Sathaye, S. D.; Hwang, Y. K.; Jhung, S. H.; Hwang, J.-S.; Kwon, S. H.; Park, S.-E.; Chang, J.-S. *Bull. Korean Chem. Soc.* **2005**, *26*(11), 1881.
4. Ichinose, I.; Senzu, H.; Kunitake, T. *Chem. Mater.* **1997**, *9*, 1296.
5. Ichinose, I.; Kawakami, T.; Kunitake, T. *Adv. Mater.* **1998**, *10*, 535.
6. Fang, M.; Kim, C. H.; Martin, B. R.; Mallouk, T. E. *J. Nanopar. Res.* **1999**, *1*, 43.
7. Kim, C. H.; Lee, M. *Bull. Korean Chem. Soc.* **2002**, *23*(5), 741.
8. Zou, H.; Lin, Y. S. *Applied Catalysis A: General* **2004**, *265*, 35.
9. Cosentino, I. C.; Muccillo, E. N. S.; Muccillo, R. *J. Sol-Gel Science and Technol.* **2006**, *37*, 31.
10. Shinriki, H.; Nakata, M. *IEEE Trans. Electron Devices* **1991**, *ED-38*, 455.
11. Fujikawa, H.; Taga, T. J. *Appl. Phys.* **1994**, *75*, 2538.
12. Cava, R. F.; Peck Jr. W. F.; Krajewski, J. J. *Nature* **1995**, *377*, 215.
13. Russell, R. A.; Phule, P. P. *Mater. Science and Eng. B* **1993**, *21*, 88.
14. Ro, Y.-A.; Kim, S.-J.; Lee, Y.-K.; Kim, C. H. *Bull. Korean Chem. Soc.* **2001**, *22*, 1231.
15. Natori, K.; Otani, D.; Sano, N. *Appl. Phys. Let.* **1998**, *73*, 632.
16. Li, H.-C.; Si, W.; West, A. D.; Xi, X. X. *Appl. Phys. Let.* **1998**, *73*, 464.
17. Basceri, C.; Streiffer, S. K.; Kingon, A. I. *J. Appl. Phys.* **1997**, *82*, 2497.
18. Wolfram, G.; Globel, E. *Mater. Res. Bull.* **1981**, *16*, 1455.
19. Wakino, K.; Minai, K.; Tamura, H. *J. Am. Ceram. Soc.* **1984**, *67*, 278.
20. Heiao, Y.-C.; Wu, L.; Wei, C.-C. *Mater. Res. Bull.* **1988**, *23*, 1687.
21. Bhattacharya, A. K.; Hartridge, A.; Mallick, K. K.; Tayler, D. *J. Mat. Sci.* **1996**, *31*, 5583.
22. Elissalde, C.; Cross, E.; Randall, C. A. *J. Am. Ceram. Soc.* **1996**, *79*, 2041.
23. Bianco, A.; Gusmano, G.; Freer, R.; Smith, P. *J. Eur. Ceram. Soc.* **1999**, *19*, 959.