Elaboration and Ionic Conduction of Apatite-Type Rare Earth Oxides

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One of the most important tasks in SOFC research is the reduction of operating temperature down to 700°C. This requires extremely thin and dense Y_2O_3 – stabilized ZrO_2 (YSZ) electrolyte or alternative more conductive electrolytes. So far, high oxide ion mobility has been reported in a small number of structural families, such as fluorite (doped ceria) and perovskites (lanthanum gallates), but these materials also exhibit too high electronic conductivity in reducing atmospheres and strong reactivity toward standard electrodes materials. Rare earth based apatites have recently attracted considerable attention because of their high ionic conductivity and the known chemical stability of the apatite structure.

The present study is centered on the synthesis and the characterization of apatite type materials $La_{10}\,Si_6\,O_{27}$, for an application as intermediate temperature electrolytes. Substitutions on the La and Si sites were studied, with the following compositions : $La_{10-x}\,AE_x\,Si_6\,O_{27-x/2}$, with AE = Ca and Sr, $La_{10-x}\,Y_x\,Si_6\,O_{27}$ and $La_{10-x}\,Ge_6\,O_{27-3x/2}$.

Ceramics were elaborated by the mixed oxide route. Phase purity was characterized by X-Ray Diffraction. Lattice parameters were determined to control cationic substitutions in the apatite structure.

It appears that undoped and also Sr and Ca doped silicates don't exhibit secondary phases. Densities greater than 95% of the theoretical densities were achieved for all Si-based materials. Concerning Ge-based ceramics, we can notice that we obtained samples without secondary phases, the presence of which depends on the calcination temperature. High densities were also achieved, above 97% of the theoretical densities. Using dilatometry experiments, it was also possible to correlate the nature of the doping elements and the sintering temperature with the density of the materials.

We measured conductivity using Impedance Spectroscopy between 600°C and 950°C under air, over the frequency range 10^6 to 10^{-1} Hz. The collected data show that Ge-based materials exhibit the highest conducting properties in the 700-800 °C temperature range, with values close to 1.4 10^{-2} $S.cm^{-1}$ at 700 °C. Similar materials were previously studied, such as $La_{10}Ge_6O_{27}$. Nakayama *et al.* (1) reported weaker conductivities while Arikawa *et al.* (2) announced values close to 1.08 10^{-2} $S.cm^{-1}$ at 700 °C. At the same temperature, Sr-doped ceramics also show interesting behaviours, since conductivities close to 1.2 10^{-2} $S.cm^{-1}$ have been reached. Moreover, these electrolytes exhibit low activation energies.

Acknowledgments

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References

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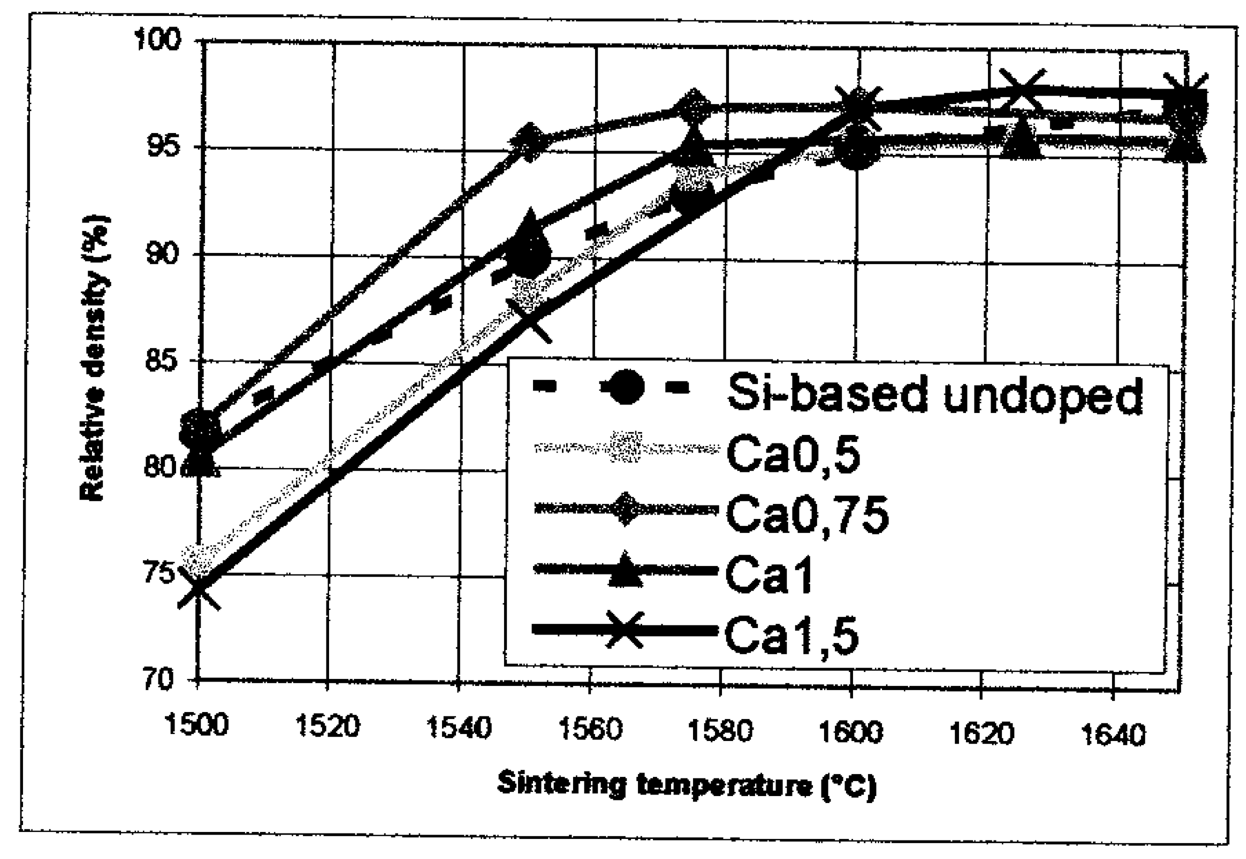

Figure 1 : Influence of Ca doping on the variations of the relative density of Si-based materials as a function of sintering temperature.

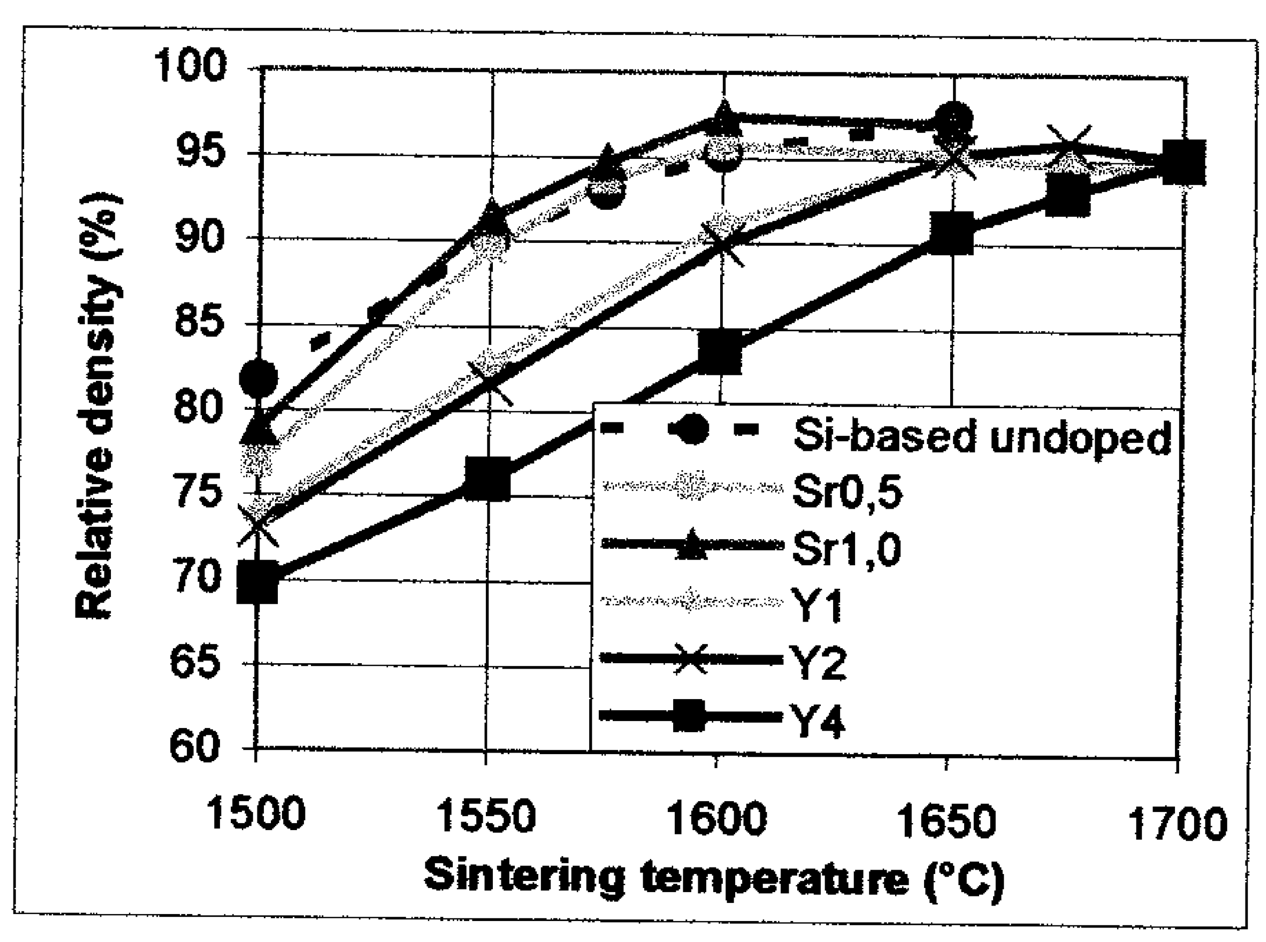

Figure 2 : Influence of Sr and Y doping on the variations of the relative density of Si-based materials as a function of sintering temperature.

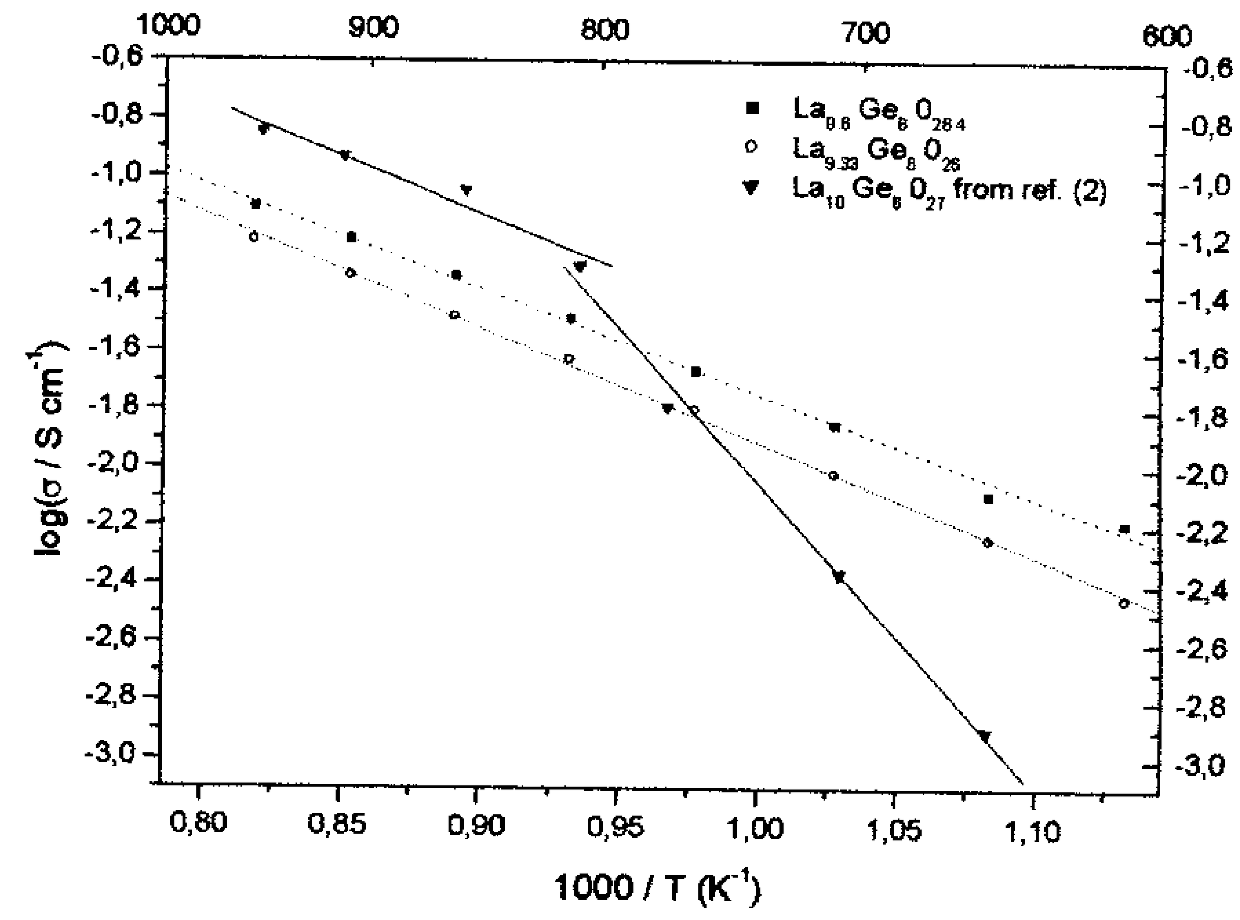

Figure 3 : Arrhenius plots of the electrical conductivity of Ge-based apatites.