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Low-temperature sintering of $BaZrO_3$ and $BaCeO_3$ barrier materials

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$BaCe_{0.99}Y_{0.01}O_{3-\delta}$ ceramics with a density over 95% was obtained by free sintering at 1000 °C using a combination of a fine precursor powder with a melt-forming sintering aid.

Recent studies demonstrated the excellent chemical resistance of $BaCeO_3$ ceramics to molten Y(R)-Ba cuprates, which is comparable with that of $BaZrO_3$.[1] Along with chemical stability, high density is crucial for barrier materials in order to prevent capillary penetration of the melt. A problem that complicates the use of $BaZrO_3$- and $BaCeO_3$-based barrier materials deals with high sintering temperatures necessary for the production of high-density ceramics.

The properties of $BaZrO_3$ and $BaCeO_3$ ceramics were studied because of the high proton conductivity of their yttrium and rare earth doped derivatives. A high density of $BaZrO_3$-based materials was usually achieved at T ~ 1700 °C.[2,3] Lower Tamman temperature allows one to perform the sintering of M-doped $BaCeO_3$ ceramics at 1500–1550 °C.[4,5] It was found that both Y-doped $BaZrO_3$ and $BaCeO_3$ are stable at sintering temperatures.[2,4] The finely dispersed precursor powders obtained using chemical synthesis methods promoted a further decrease in the sintering temperature of Nd-doped $BaCeO_3$ to 1300 °C.[6] In this case, the sinterability of oxide powders demonstrated a strong dependence on powder processing conditions. At the same time, widely used sintering activation techniques based on the introduction of various sintering aids were not systematically applied to these materials. The aim of this work was to perform low-temperature sintering processes in $BaZrO_3$ and $BaCeO_3$ ceramics by means of a combination of finely dispersed starting powders with melt-forming sintering aids.

The powders of $BaZr_{1-x}Y_xO_{3-\delta}$ and $BaCe_{1-x}Y_xO_{3-\delta}$ (x = 0, 0.01) were obtained by oxalate coprecipitation in water–alcohol mixtures at 80 °C followed by thermal decomposition of dried residues. CuO (0.5–1 wt%) and a PVA binder (1 wt%

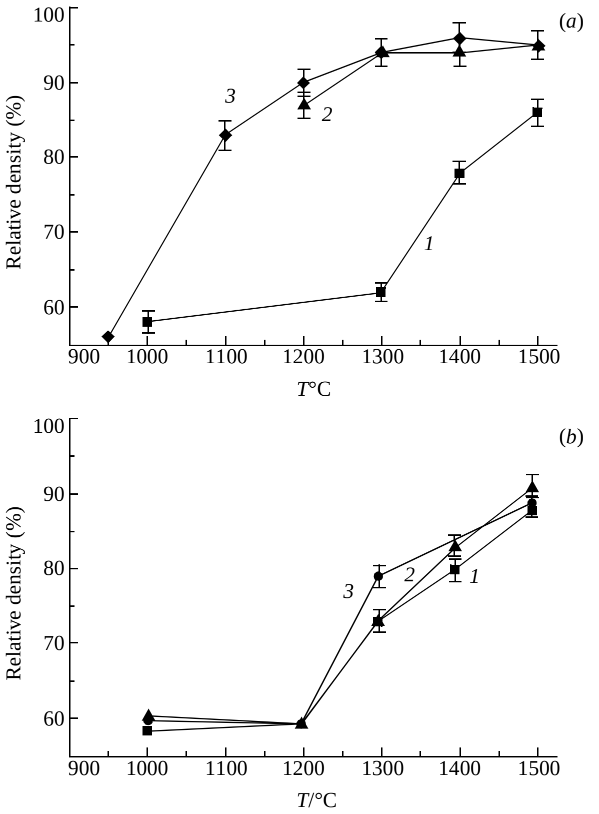

Figure 1 Density of $BaZr_{1-x}Y_xO_{3-\delta}$ ceramics after isothermal sintering at various temperatures: (*a*) undoped $BaZrO_3$ ($x = 0$); (*b*) Y-doped $BaZrO_3$ ($x = 0.01$). The amounts of CuO are 0% (curve *1*; reference sample); 0.5% (curve *2*) and 1% (curve *3*).

PVA/oxide) were added during deagglomeration of powders in a planetary ball mill under isopropanol. Dried powders were pressed as pellets and sintered in air at 950 °C ≤ T ≤ 1500 °C for 6 h. The density of ceramic samples was measured by both geometric and Archimedes methods. Specimens for SEM studies were prepared by polishing ceramic samples followed by etching with dilute HNO_3 (30 s).

Preliminary sintering experiments demonstrated that high sinterability of $BaZrO_3$ and $BaCeO_3$ can be observed only in single phase powders. XRD analysis of thermal decomposition products of oxalate precursors demonstrated that, in both cases, thermolysis was accompanied by the formation of $BaCO_3$ and individual Zr or Ce oxides. Formation of complex oxides from these intermediates is usually completed at 1000–1100 °C, so that thermal decomposition of $BaMeO_3$ precursors was followed by isothermal annealing of powders at 1100 °C.

An analysis of the densification processes of as-obtained powders revealed that a reference sample of undoped $BaCeO_3$ powder displays moderate sinterability; the density values > 90% were achieved at $T > 1300$ °C. A similarly processed $BaZrO_3$ powder demonstrated significantly poorer sintering activity. In spite of small grain size, the density of the obtained ceramics did not exceed 85% even after sintering at $T = 1500$ °C [curves *1*, Figures 1(*a*) and 2(*a*)].

The dominating mass transport mechanism in the sintering of finely dispersed powders is grain boundary diffusion.[7] Its intensity could be enhanced by increasing the number of defects using heterovalent replacement of Zr and Ce with Y. Meanwhile, a comparison of the density values at the same sintering temperatures for doped and undoped $BaZrO_3$ and $BaCeO_3$ powders shows that Y doping has a limited effect on the sinterability of powders [curves *1*, Figures 1(*a*),(*b*), 2(*a*),(*b*)]. This feature can be related to the relatively high strength of the interparticle necks having the major impact on the sintering behaviour.

The best known method of reducing sintering temperatures is based on the introduction of melt-forming sintering aids that are responsible for a liquid-phase sintering mechanism. CuO is known to form low-melting eutectics with a large number of substances; cuprate melts demonstrate excellent wetting of $BaZrO_3$ and $BaCeO_3$ surfaces,[1] which promotes uniform distribution of the liquid along $BaMeO_3$ grain boundaries at the first stages of sintering. It can be seen [Figure 1(*a*)] that the introduction of 0.5% CuO into a $BaZrO_3$ precursor results in a significant enhancement of sintering parameters and in density values over 90% at 1300 °C. However, doping with CuO unexpectedly has a little or no effect on the sinterability of Y-doped $BaZrO_3$ [Figure 1(*b*)]. The reason of this phenomenon can be attributed to the reduced stability of $BaZr_{0.9}Y_{0.1}O_{3-\delta}$ in contact with cuprate melts.

A combination of finely dispersed starting powders with CuO doping is especially effective for $BaCeO_3$ ceramics (Figure 2). In this case, the sintering behaviours of both Y-doped and undoped $BaCeO_3$ powders are similar. In the former case, a combination of liquid-phase sintering with grain boundary diffusion acceleration by Y doping results in a small synergistic effect: the density values of Y-doped samples at reduced sintering temperatures are higher by 3–4%. Another important feature of the CuO-assisted sintering of $BaCeO_3$ powders consists in high density values (93–96%) at unusually low temperatures (1000 °C), which was never observed previously in this kind of ceramics.

The fundamental background of this phenomenon needs more detailed investigation, though it obviously deals with the features of liquid-phase sintering in a finely dispersed ceramic system. Indeed, the sintering behaviour of $BaCeO_3$ powders shows several characteristics of liquid phase sintering processes. An acceleration effect appears yet at a small doping level (0.5%), while a further increase of the dopant amount has a very limited influence on densification [curves *2*, *3*, Figure 2(*a*),(*b*)]. Further experiments on isothermal sintering at various temperatures demonstrated that most part of densification occurs in a short time (within 1 h) after approaching a sintering temperature. The densification of CuO-doped samples is accompanied by significant grain growth due to an accelerating effect of a liquid on

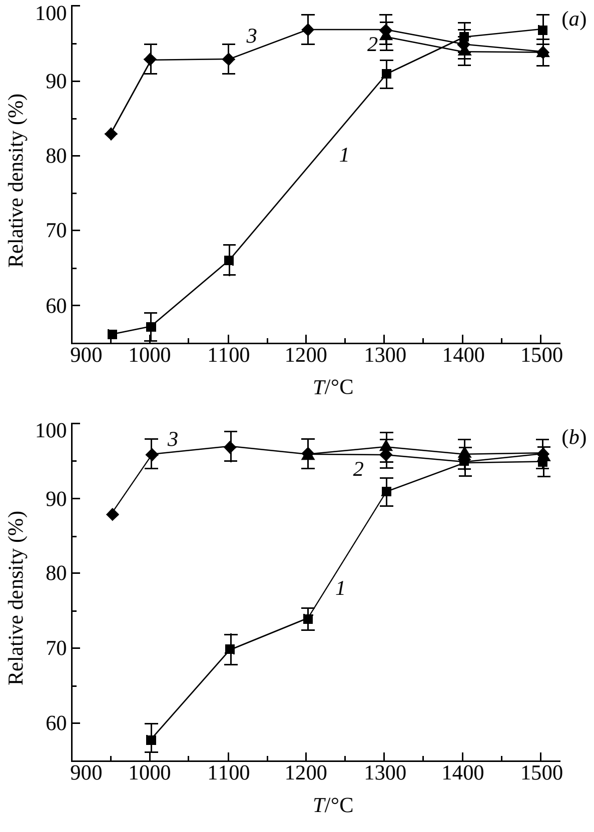

Figure 2 Density of $BaCe_{1-x}Y_xO_{3-\delta}$ ceramics *vs.* sintering temperature: (*a*) undoped $BaCeO_3$ ($x = 0$); (*b*) Y-doped $BaCeO_3$ ($x = 0.01$). The amounts of CuO are 0% (curve *1*; reference sample); 0.5% (curve *2*) and 1% (curve *3*).

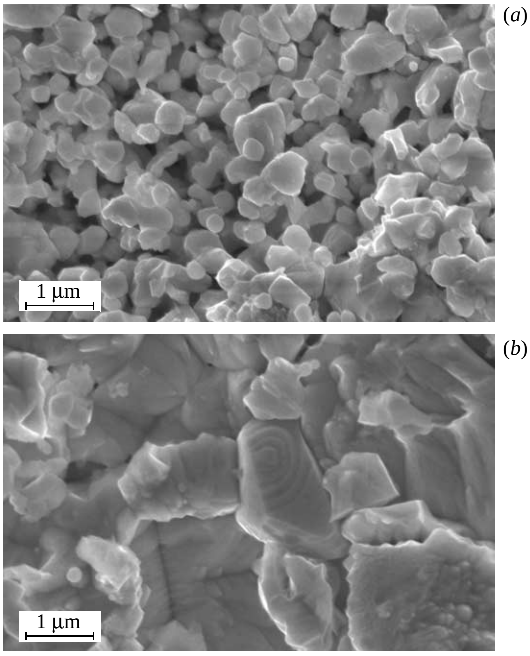

Figure 3 SEM micrographs of $BaCe_{0.99}Y_{0.01}O_{3-\delta}$ ceramics sintered at 1200 °C for 6 h: (*a*) undoped; (*b*) doped with 1% CuO.

the intergrain mass transport (Figure 3). A further development of this process results in significant dedensification of samples due to exaggerated grain growth during continuous thermal processing [curves *2*, *3*, Figure 2(*a*)]. At the same time, several features of sintering behaviour are not typical of liquid-phase sintering processes; they are inherent to the low-temperature sintering of fine powders. It concerns the high sensitivity of $BaCeO_3$ densification parameters to small variations in powder processing conditions; thus, a powder preparation procedure should be carefully optimised.

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