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Interactions of complex barium oxides with molten HTSC cuprates

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The experiments confirmed the absence of interactions or chemical corrosion in $BaMO_3$–HTSC melts for M = Zr, Ce or Hf.

It is well known that the quality and properties of high-temperature superconductor materials obtained by melt technologies are closely related to the purity of raw materials. The second factor affecting the product purity is the stability of container materials used in processing. If such a material can react with the melt (typically, a Cu-rich barium cuprate with small yttrium or rare-earth additions), its components will contaminate the HTSC material and promote the degradation of physical properties of the superconducting sample.

The resistance of traditional barrier materials (Pt, MgO, Al_2O_3 and ZrO_2) to molten cuprates is ensured mostly by kinetic factors.[1] The behaviour of MgO and Al_2O_3 is characterised by low rates of their reactions with a liquid phase and the dissolution of reaction products,[1–3] while for Pt and ZrO_2 the reaction products are almost insoluble in the melt and form flakes and/or product layers coating the surface of the primary barrier material.[4–6] Both Mg and Al ions are trapped by $YBa_2Cu_3O_x$ (Y-123) single crystals and ceramics. The interaction of Pt and ZrO_2 barrier materials with melts results in an uncontrolled change in stoichiometry and, hence, in the poor reproducibility of processing conditions. Due to these circumstances, further efforts are needed in order to extend the spectrum of available barrier materials. Here we report an experimental study of the fundamental background of $BaMO_3$-based barrier materials stability in the cuprate melts.

$BaMO_3$ precursor powders were obtained by the oxalate coprecipitation method. Aqueous solutions of the corresponding nitrates taken in a stoichiometric ratio were added dropwise to a solution of ammonium oxalate in water–ethanol mixture (4:1) at 80 °C. After stirring, the residue was filtered off and air dried. Thermal treatment of dried precursors was performed in air at 800–1100 °C for 6 h.

In order to study the interaction of $BaMO_3$ (M = Zr, Ce, Hf, Ti or Th) with molten cuprates, the powders of RE(Y)-123 were mixed with binary oxides and pressed into pellets. The pellets were annealed at 950 and 1050 °C for 24–48 h.[7] The XRD analysis of crashed samples was performed using a STADI P diffractometer and a Guinier–de Wolf FR-552 focusing chamber (CuKα). Germanium was used as an internal standard.

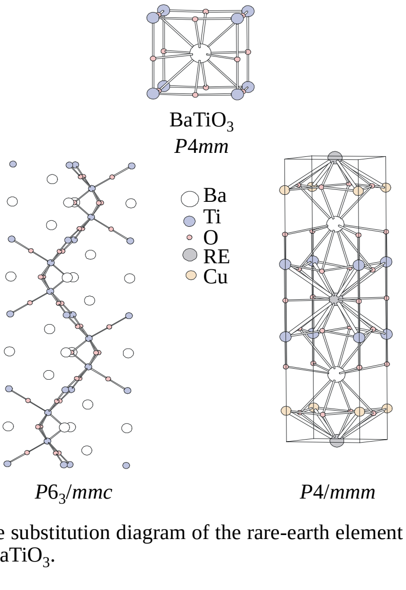

Figure 1 The substitution diagram of the rare-earth element into different positions of $BaTiO_3$.

Table 1 Goldschmidt factors for binary oxides.

AXO_3	t	$\Delta G^{f}_{ox}(BaMO_3)$ at 1273 K	$\Delta G(1)$/ kJ mol^{-1}
$BaThO_3$	0.914	–35	–3
$BaCeO_3$	0.943	–49	–46
$BaZrO_3$	1.011	–129	–286
$BaHfO_3$	1.016	–176	–427
$BaTiO_3$	1.07	–184	–452

For studying the interaction of $BaMO_3$ (M = Ce, Zr or Hf) ceramics with a cuprate melt, $BaCuO_2$ and $YBa_2Cu_3O_x$ were mixed with CuO in a molar ratio of 4:2:5, often used for HTSC single-crystal growth, then pressed into pellets and placed on the surface of sintered $BaMO_3$ ceramics. During further thermal processing, the coupled ceramic sandwich was annealed at 1020 °C in air for 12 h and slowly cooled. The cross sections of original ceramics, as well as annealed samples, were analysed by EDX using a SEM microprobe (JEOL JSM-840A, $U = 20$ kV), a TEM nanoprobe (Philips CM-30, $U = 200$ kV) and a scanning ion microscope[8] (University of Chicago SIM facility).

The *in situ* measurements of the melt–ceramics contact angle were performed by recording images with a digital camera (50 frames per second). To determine the droplet profile and to find the contact angle, the movie was processed by the DSA1 (Drop Shape Analysis) software (Kross GmbH).

Preliminary analysis of $BaMO_3$ stability using the Goldschmidt tolerance factor t and the free energy of $BaMO_3$ formation from individual oxides[9] (Table 1) demonstrates that barium titanate is the most stable binary oxide among others. A more detailed evaluation of $BaMO_3$ resistance to cuprate melts is complicated by the lack of reliable data on the thermodynamic parameters at high temperatures and equilibrium phase relationships in $BaMO_3$–RE_2O_3 (CuO) systems.

Meanwhile, an experimental study demonstrated a significant interaction of $BaTiO_3$ with Y-RE oxides and $Y(RE)Ba_2Cu_3O_x$ at $T > 1000$ °C, especially pronounced for cuprate-containing phases. The character of reaction products demonstrates a correlation with the effective ionic radius of the rare-earth cation.[10] For large cations like La^{3+} or Pr^{3+}, the interaction results in the substitution of Ba^{2+} for RE^{3+} at the centre of a perovskite cell. To compensate the surplus positive charge, some Ti^{4+} is replaced by Cu^{2+} [Figure 1(*b*)].[11,13] For smaller RE cations (Ho^{3+}, Y^{3+}) the substitution occurs at the Ti^{4+} position. To compensate a negative charge, oxygen vacancies are formed [Figure 1(*a*)].[12] The products of this reaction are similar to the H-phase of $BaTiO_3$. For average ionic radii (Gd^{3+}, Tb^{3+} and Eu^{3+}), both of the substitution schemes can take place simultaneously. The possible reaction products for seveal rare-earth oxides are given in Table 2. The presence of copper oxide in

Table 2 Products of the reactions between $BaTiO_3$ and rare-earth oxides.

RE	The products of the reaction $BaTiO_3 + BaCuO_2 + RE_2O_3(REO)$
Y	$YBa_3Ti_2O_{8.5}$ (41-121), CuO
Er	$Ba_{12}Er_{4.67}Ti_8O_{35}$ (43-419), CuO
Ho	$Ba_{12}Ho_{4.67}Ti_8O_{35}$ (43-420), CuO
Dy	$Ba_{12}Dy_{4.67}Ti_8O_{35}$ (43-421), CuO
Tb	$Ba_2Cu_2Tb_2Ti_2O_{11}$ (47-428), $Ba_{12}Tb_{4.67}Ti_8O_{35}$ (unknown)
Gd	$Ba_{12}Gd_{4.67}Ti_8O_{35}$ (43-422), $Ba_2Cu_2Gd_2Ti_2O_{11}$ (48-996)
Eu	$Ba_{12}Eu_{4.67}Ti_8O_{35}$ (43-423), $Ba_2Cu_2Eu_2Ti_2O_{11}$ (47-427)
Nd	$Nd_2Ba_2Ti_2Cu_2O_{11}$ (47-499), $BaCuO_2$
Pr	$Pr_2Ba_2Ti_2Cu_2O_{11}$ (unknown), $BaCuO_2$
La	$BaLaCuTiO_{5.5}$ (45-603), $(Ba,La)_2CuO_4$, $CuLaO_2$
Cu	$BaTiO_3$, CuO, $BaCuO_2$

the reaction zone always results in a significant increase in the reaction rate, which can be attributed to liquid phase formation at high *T* and mass-transport acceleration. Generally, the stability of $BaTiO_3$ is insufficient for barrier ceramics applications. Even a lower stability was demonstrated by $BaThO_3$ powder, which reacts not only with Y(RE)-123 phases, forming new binary barium cuprate and thoria, but also with a CuO melt. In this case, the poor resistance to interaction with cuprates correlates with the low thermodynamic stability of the binary oxide.

Powders of $BaZrO_3$, $BaCeO_3$ and $BaHfO_3$ do not react with binary barium oxides even in the presence of CuO. Their stability was evaluated using a high-density ceramics obtained by the sintering of finely dispersed $BaMO_3$ powders.

The investigation of the ceramic–melt reaction boundary by SEM, TEM, EDX and SIM (Figure 2) confirmed the absence of copper oxides inside the bulk barrier material, while some droplets were found at grain boundaries or inside the pores.

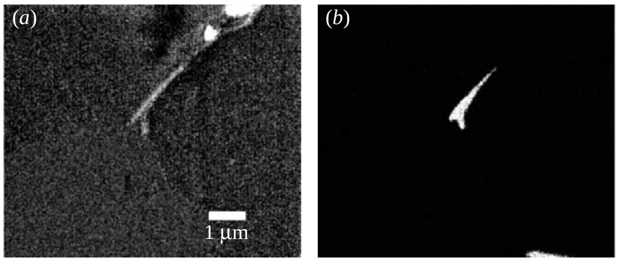

Figure 2 SIM images of $BaCeO_3$ after the interaction with a HTSC melt: (*a*) Ba^{2+} and (*b*) Cu^{2+}.

The measurements of contact angles for $BaMO_3$–cuprate melt boundaries showed 10° for $BaCeO_3$ and 15° for $BaHfO_3$. These values show at the good resistivity of a ceramic surface to the penetration of a melt.

The instability of binary barium–thorium oxide in a cuprate environment can be explained by thermodynamic factors. It was found that $BaTiO_3$ reaction with Y(RE)–Ba–Cu–O melts leads to the fast formation of $Ba_kTi_nRE_mO_{k+2n+3m/2}$ (n = 0–4) phases.

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