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Copper-doped $BaZrO_3$ crucibles for YBCO single crystal growth

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Abstract

The corrosion resistance of $BaZrO_3$ to molten barium cuprates is controlled by secondary phases, and requires high chemical and phase purity, as well as high density for sustained flux containment. The high sintering temperatures required for solid-state derived powders is a significant obstacle inhibiting more widespread use of high density $BaZrO_3$. We have investigated the use of Cu^{2+} doping to enable practical sintering temperatures whilst still producing corrosion resistant ceramics. Low levels of copper addition (0.2 wt.% CuO equiv.) produced densities of >97% theoretical using sintering temperatures as low as 1400 °C, as long as the dopant was added after all powder calcination steps, i.e. immediately before forming/sintering. Corrosion resistance at 0.2 wt.% CuO equiv. was equal to un-doped materials fabricated using the same powder processing method.

Keywords: Sintering; Corrosion; Superconductivity; Substrates; Perovskites

1. Introduction

YBCO single crystals are slowly grown from molten barium cuprate fluxes which are corrosive to all known crucible materials except high quality $BaZrO_3$. Common crucible materials including all metals, Al_2O_3, MgO and Y_2O_3 are highly reactive with the $BaCuO_2$–CuO flux required for YBCO single crystal growth, causing contamination of the flux and frequently YBCO crystals.[1,2] Yttria stabilised ZrO_2 is still commonly used because its reaction product ($BaZrO_3$) is not soluble in the melt and hence high purity crystals are obtainable, but reaction with the melt causes numerous practical limitations in crystal growth.[1,2] Ideally the crucible material should be inert to the molten flux.

Barium zirconate ($BaZrO_3$) is the most inert crucible material for the generation of high purity single crystal doped barium cuprate superconductors, e.g. YBCO and other rare earth barium cuprates. The corrosion resistance of $BaZrO_3$ is strongly affected by secondary phases, which degrade its performance. The high phase purity required for sustained flux containment is difficult to achieve. Pure single phase $BaZrO_3$ can only be achieved with a 1:1 mole ratio at thermodynamic equilibrium. Secondary phases occur with an excess of BaO or ZrO_2, or incomplete reaction of reagents during the formation of $BaZrO_3$. In the pure BaO–ZrO_2 system, Zr-rich second phases (especially ZrO_2) are particularly detrimental to corrosion resistance because reaction with flux to form $BaZrO_3$ is accompanied by dramatic expansion in solid volume (e.g. 100 vol.% for ZrO_2).[3] Whilst barium-rich phases do not produce damaging expansion and are much less detrimental, they are at least partially soluble in the flux and must be minimised. Solid-state powder processing (i.e. from $BaCO_3$ and ZrO_2) requires repeated milling and calcining of precursor powders to ensure fine particle size and phase purity. Chemical contaminates present in starting reagents or accumulated during processing that are insoluble in $BaZrO_3$ will cause secondary phases, which are likely to react with the flux. Secondary phase abundance can be optimised by overall Ba:Zr + Hf stoichiometry, homogeneity from process optimisation, and chemical purity.[1–3]

Despite the potential benefits of chemical synthesis methods,[4] solid-state reaction remains the most efficient and successful method for the production of $BaZrO_3$ crucibles, but excessive sintering temperatures inhibit its widespread use.[3] $BaZrO_3$ is a highly refractory material, with a melting point in excess of 2600 °C. Sintering to densities of greater than 97% requires fine particle size, control of pre-sintered microstructure and high sintering temperatures of at least 1700 °C.[3] The aim of this research was to reduce the sintering temperature of $BaZrO_3$ well below 1700 °C whilst maintaining

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adequate corrosion resistance. Very little research into the use of additives to $BaZrO_3$ ceramics used for barium cuprate processing has been reported in the literature. Previous studies have highlighted problems caused by use of sintering aids for fabrication of crucibles for other ceramics (e.g. Y–ZrO_2).[5] Because CuO is the major component of the flux, no flux or crystal contamination is possible from Cu crucible doping.

Marshall et al.[6] claimed that Cu^{2+} can be substituted into the $BaZrO_3$ lattice either equally between Ba and Zr sites, or in Zr sites. Using starting compositions of $Ba(Zr_{1-x}Cu_x)O_3$ with $0<x<1$, sintered ceramics contained phases including $BaZrO_3$, $BaCuO_2$ and CuO. $BaZr_{0.1}Cu_{0.9}O_y$ was claimed to be single phase. Marshall et al. stated that the efficacy of $BaZrO_3$ as a barrier layer is limited due to its ability to absorb Cu into its lattice and therefore react with the YBCO melt. They asserted that $BaZr_{0.4}Cu_{0.6}O_{3-z}$ or $Ba_{0.7}Cu_{0.3}Zr_{0.7}Cu_{0.3}O_3$ would be superior barrier layers in the fabrication of YBCO films and crystals[6] although no proof of this claim was reported or has been demonstrated to date. This research pre-dated that of Erb who clearly demonstrated the suitability of high quality $BaZrO_3$ for sustained melt containment.[1]

Doping is a simple and potentially effective method for improving sintering properties. Y^{3+} and Cu^{2+} are good candidates because they are part of YBCO crystals, with copper preferred as it is a major component of all barium cuprates. Our aim was to substitute dopants into the $BaZrO_3$ crystal lattice, rather than leaving residual phases which are likely to be reactive with the flux. Limited solid solubility may be adequate if low levels of ionic substitution are sufficient to improve processing properties of $BaZrO_3$.

The timing of dopant addition during solid-state processing can be an important processing variable. Pre-calcination doping can allow for more dispersion throughout the system but may affect powder formation during repeated calcination. Post calcination doping prevents reaction before sintering, but may require more care to ensure uniform dispersion through the material. This research investigated the use of copper compounds on $BaZrO_3$ fabrication by solid-state synthesis, and effects on the corrosion resistance to molten barium cuprates.

2. Method

Based on the procedure utilised by Kirby et al.[3] solid-state processing was conducted using $BaCO_3$ powder (Fluka Chemika, ≥99%), ZrO_2 powder (Doral Specialty Chemicals, Z0.5 grade, ≥99.9%, BET N_2 surface area 20–30 m^2/g), CuO powder (Fluka Chemika, ≥99%) and $Cu[C_2H_3O_2]_2 \cdot H_2O$ powder (Malinckrodt, AR reagent).

All samples were batched with a Ba:[Zr + Hf + Cu] mole ratio of 1.005 (±0.002) based on gravimetric analysis of $BaCO_3$ and loss on ignition analysis of ZrO_2. As stoichiometry is critical to the corrosion resistance of the sintered ceramic and affects processing properties of powders, considerable care is required in its measurement. $BaCO_3$ powder was mixed with ZrO_2 by wet milling in ethanol for 5 min in a ZrO_2 ring mill. Powders were calcined three times in air at 1300 °C for 3 h, with ring milling between calcination treatments to assist solid-state reaction kinetics.

To aid compaction for uniaxial or cold isostatic pressing, 2.5 wt.% hexadecanol was added as a lubricant by ring milling the powder for 5 min in an ethanol solution of hexadecanol before drying at 80 °C. Test pellets were formed by uniaxial pressing at 150 MPa and crucibles were formed using cold isostatic pressing at 140 MPa for 60 s.

CuO doping was conducted by adding 0, 0.2, 0.5, 1 and 5 wt.% CuO to the starting $BaCO_3$ and ZrO_2 powders before the first wet milling. Finished powders were sintered at 1680 °C. After three calcinations of pure $BaZrO_3$, cupric acetate doping was conducted by milling finished powders in ethanol solutions of $Cu[C_2H_3O_2]_2 \cdot H_2O$. Cupric acetate was used because it is readily soluble in ethanol, and along with the solid lubricant (hexadecanol), dispersion of additives in liquid form was expected to be significantly more homogeneous compared to powdered additives. The amount of cupric acetate added was 0.20 and 0.50 wt.% CuO equiv., i.e. acetate was assumed to decompose to CuO during sintering. Sintering was conducted at 1400–1600 °C for 6 h in air.

Sintered densities were measured using Archimedes method in water. Percentage theoretical densities were calculated assuming a crystal density of 6.223 g/cm^3 (ICDD PDF 6-399). Pellets were crushed for powder XRD analysis using an internal standard method to eliminate specimen displacement errors. 1.8 g of each sample was mixed with 1.2 g of corundum (α-Al_2O_3) (Praxair Surface Technologies 1.0 μm C Alumina Polishing Compound) using a mortar and pestle. Specimens were analysed using a Siemens D500 XRD with Cu Kα radiation from 18° to 100° at 1.2°/min using a step size of 0.02°. XRD patterns were analysed by Rietveld refinement using Rietica v.177. A Voigt function with Rietveld asymmetry was used to model peak profile shapes. The internal standard was used to determine instrument zero offset and specimen displacement errors, allowing precise refinement of $BaZrO_3$ lattice parameters. Uncertainties are reported as ±2 estimated standard deviations (E.S.D.) from refinement fitting errors.

A Philips XL30 scanning electron microscope (SEM) was used to study the microstructure and phase purity of the sintered samples. SEM was used to analyse fracture surfaces of sintered samples. A transmission electron microscope (TEM) (JEM3000F) was used for the detection of copper-rich phases by STEM-EDS analysis. Sintered materials were ultrasonically cut into 3.05 mm diameter specimens, hand-polished to 55 μm thickness, dimple ground to 20 μm, ion milled (Gatan PIPS) to electron transparency on a Mo stub, and analysed on a Au slot grid support using a Be double-tilt holder.

Crucibles with a 7 ml volume were tested for melt corrosion resistance to a mixture of Y_2O_3, $BaCO_3$ and CuO in a mole ratio of 1:32:90, respectively, at 1050 °C in air, with the rate of leakage visually observed over 7 days.

3. Results and discussion

Addition of CuO at the beginning of powder processing had a detrimental effect on powder properties and sintered densities.

Table 1
Effect of CuO addition at beginning of powder processing (i.e. CuO added to $BaCO_3$ and ZrO) on sintered density

CuO (wt.%)	Archimedes density ± 0.01 (g/ml)	% Theoretical density ± 0.2%
0	5.99	96.2
0.20	4.36	70.0
0.50	4.59	73.7
1.00	5.12	82.2
5.00	5.59	89.9

Samples sintered at 1680 °C for 6 h.

Table 2
Maintenance of high sintered density at reduced sintering temperatures by cupric acetate addition after powder processing (i.e. immediately prior to forming/sintering) after 6 h sintering at temperatures indicated

CuO equivalent (wt.%)	Sintering temperature (°C)	Density ± 0.01 (g/ml)	% Theoretical density ± 0.2%
0	1680	6.06	97.4
0.20	1680	6.14	98.7
0.50	1680	6.13	98.5
1.00	1680	6.06	97.5
0.50	1600	6.15	98.7
0.50	1500	6.14	98.7
0.50	1400	6.12	98.3
0.20	1600	6.17	99.2
0.20	1500	6.15	98.9
0.20	1400	6.09	97.9

Table 1 shows that low levels of CuO addition caused severe reductions in sintered densities even at 1680 °C, which were partially restored by excessive additions of CuO. Sintering in the pure BaO–ZrO_2 system requires particle sizes well below 1 μm.[1] Addition of CuO prior to powder processing caused substantial particle growth and hard aggregation during calcination (Fig. 1a), resulting in poor sintering properties (Fig. 1c and Table 1) even at 1680 °C. By comparison, the much smaller particles produced using pure $BaZrO_3$ (Fig. 1b) as long as the Ba:Zr + Hf mole ratio is higher than 1,[3,7] which were subsequently doped with cupric acetate, sintered to high density (Fig. 1d) at temperatures as low as 1400 °C.

Although doping at the beginning of powder processing was unsuccessful, the strong effect of Cu^{2+} at 1300 °C suggested an alternative solution to the sintering problem. In the pure BaO–ZrO_2 system, very small particle size is maintained during powder processing by using a slight excess of BaO 3 (also Fig. 1b), so the optimal stage for dopant addition would be after the final powder calcination treatment. By doping finished powders with cupric acetate dissolved in ethanol (to assist homogeneous dopant dispersion), sintering to high density was possible at substantially reduced sintering temperatures (Table 2). All of the post-calcination doped compositions studied produced adequate sintered densities, including the lowest dopant level at the lowest sintering temperature investigated. The amounts of copper required were low, with almost equivalent densities produced

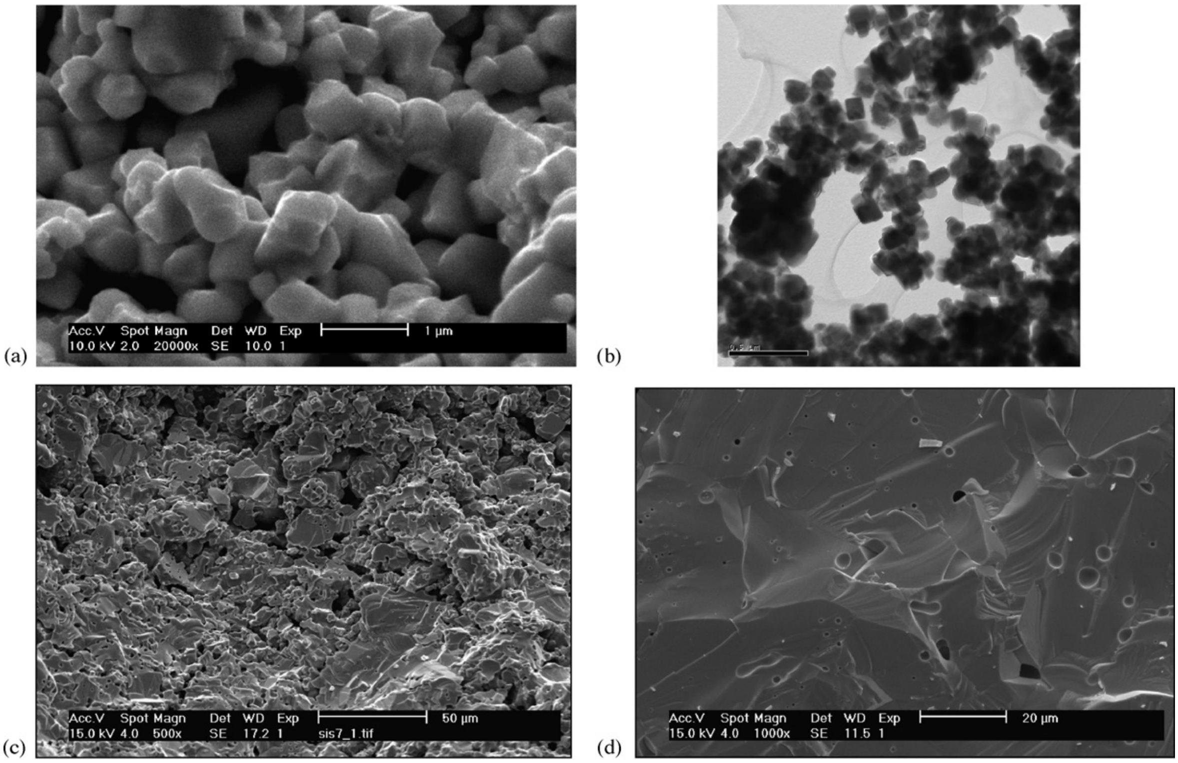

Fig. 1. Effect of doping strategy on particle formation after three calcinations at 1300 °C, and ceramic microstructure after 6 h sintering at 1680 °C. (a) Excessive particle growth and agglomeration due to 0.2 wt.% CuO pre-calcination doping. SEM image, scale bar = 1 μm. (b) Typical Cu-free powder. TEM image used for increased clarity, scale bar = 500 nm. (c) Porous structure of sintered ceramic using pre-calcination 0.2 wt.% CuO doped $BaZrO_3$, scale bar = 50 μm. (d) Dense structure of sintered ceramic using post-calcination 0.2 wt.% $Cu[C_2H_3O_2]_2 \cdot H_2O$ doped $BaZrO_3$, scale bar = 20 μm.

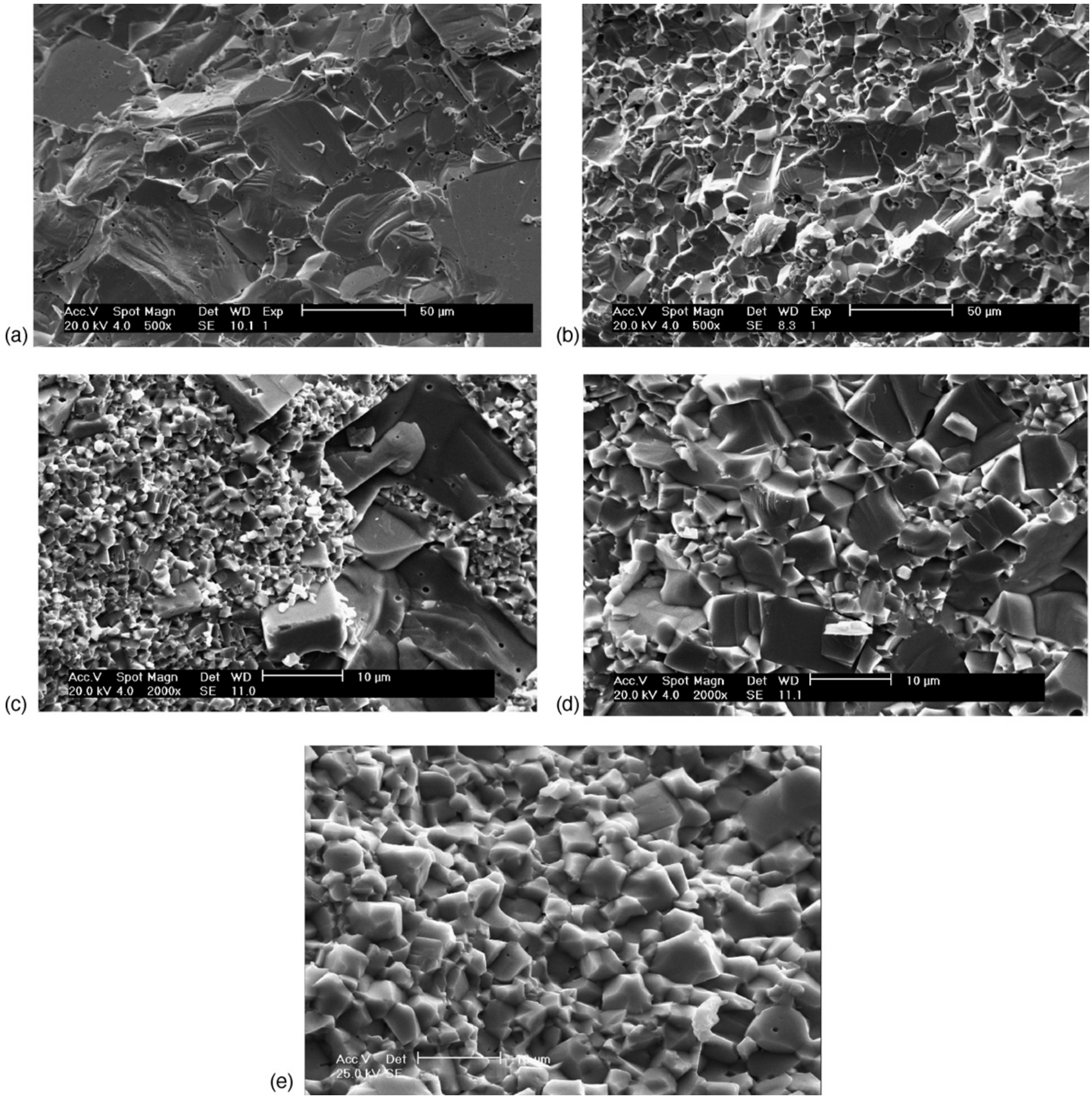

Fig. 2. Fracture surface of dense $BaZrO_3$ produced using post-calcination cupric acetate doping after 6 h sintering at: (a) 0.2 wt.% CuO equiv. 1600 °C, (b) 0.5 wt.% CuO equiv. 1600 °C, (c) 0.2 wt.% CuO equiv. 1500 °C, (d) 0.5 wt.% CuO equiv. 1500 °C, (e) microstructure of un-doped $BaZrO_3$ sintered at 1700 °C for 6 h.[7]

by 0.2 wt.% as higher addition levels, hence it appears likely that even lower levels of cupric acetate addition warrant further investigation. All previous studies on solid-state derived pure $BaZrO_3$ powders have required sintering temperatures of at least 1700 °C to reliably produce melt tight crucibles,[1–3,7] hence this appears to represent a useful processing improvement for more widespread application of dense corrosion resistant $BaZrO_3$ ceramics.

The general microstructures of cupric acetate doped sintered ceramics is illustrated in Fig. 2. Sintering at 1600 °C produced relatively large grain sizes, and intragranular fracture shows strong sintering was achieved at temperatures well below that required for equivalent undoped materials. Grain sizes and fracture surfaces of 0.5 wt.% CuO equiv. sintered at 1500 °C were very similar to those of undoped $BaZrO_3$ sintered at 1700 °C (Fig. 2e), and the large grains that formed (~10–20 µm in Fig. 2c) were smaller than large grains observed in undoped

Table 3

$BaZrO_3$ lattice parameters after sintering for 6 h at indicated temperatures with various levels of copper doping

Sintering temperature (°C)	CuO (wt.%)	Cu acetate (wt.% CuO equiv.)	Lattice parameter, *a* (Å) (±2 E.S.D.)
1680	0		4.1910 (2)
1680	0.20		4.1907 (2)
1680	0.50		4.1906 (2)
1680	1.00		4.1905 (2)
1680	5.00		4.1908 (3)
1680		0.20	4.1906 (2)
1680		0.50	4.1906 (2)
1680		1.00	4.1906 (2)
1500		0.20	4.1910 (2)
1500		0.50	4.1908 (2)

Uncertainties are ±2 E.S.D. in the last significant figure.

Table 4
Effect of Ba:[Zr + Hf] mole ratio and cupric acetate addition on the suitability of $BaZrO_3$ crucibles for sustained containment of YBCO melts at 1050 °C

Ba:[Zr + Hf] mole ratio	CuO equivalent (wt.%)	Sintering temperature (°C)	Time melt remained above two-third original level (days)	Time melt remained above half of original level (days)	Time melt remained above one-fourth original level (days)
0.961	0	1645	0.5[a]	1.0	1.0
0.961	0	1645	0.5[a]	1.0	1.0
0.995	0	1750	0.5[a]	1.0	1.7
0.996	0	1710	2.4	2.7	3.3
0.997	0	1700	0.5[a]	0.9[a]	1.5
1.002	0	1700	2.7	3.0	3.3
1.002	0	1700	2.7	3.0	3.3
1.003	0	1710	3.4	4.4	7.1
1.005	0	1750	2.8	3.7	5.8
1.006	0	1710	2[a]	2[a]	3.4
1.014	0	1700	2[a]	2[a]	3.4
1.015	0	1750	1.7	2.0	2.8
1.005	0.20	1500	2	3	6
1.005	0.50	1500	2	3	6

Samples sintered for 6 h.

[a] Estimation from a later time during corrosion exposure.

materials.[3,7] Copper doping, both from CuO and cupric acetate caused grain growth at elevated concentrations or temperatures, however the ceramics sintered at 1500 °C containing either 0.2 or 0.5 wt.% CuO equiv. were suitable for flux containment (Table 4).

Cu^{2+} compounds had no effect on the lattice parameters of $BaZrO_3$ sintered at up to 1680 °C. Table 3 shows that Cu^{2+} is essentially insoluble in the $BaZrO_3$ crystal lattice after cooling from up to 1680 °C to ambient temperature over approximately 5 h, for a bulk Ba:Zr + Hf mole ratio of 1.005 ± 0.002. The solubility of Cu^{2+} whilst at elevated temperature has not been evaluated here. This result is in contrast to Marshal et al. who on the basis of optical and SEM-EDS analysis claimed a single phase was formed containing up to 10% Cu substitution.[6] No *direct* evidence was provided for the existence of this phase, merely the lack of detection of secondary phases by XRD. No attempt was made to check for ionic substitution using the standard technique of lattice parameter measurement. The current study showed lattice substitution was not detectable by XRD, suggesting addition of CuO (or equivalent) lead to secondary phases in crucible materials. The contribution of Cu-doping to overall phase impurity at low levels needed for sintering improvement appeared minor as most grain boundaries showed no detectable Cu by STEM-EDS analysis. A continuous grain boundary phase did not form at low dopant levels investigated, which is consistent with the corrosion performance observed. Very small amounts of a Cu-rich triple point material were observed by STEM-EDS analysis in a sample containing 0.5 wt.% CuO sintered at 1600 °C, consistent with the conclusion from XRD analysis that CuO is relatively insoluble in $BaZrO_3$.

As shown in Table 2, only small amounts of cupric acetate were required for large reductions in the sintering temperature. The effect of such levels of addition on corrosion resistance (Table 4) were minor compared to other limitations inherent in the solid-state fabrication process used, such as limited solid-state reaction of powders during processing. Results suggest that even lower amounts of cupric acetate doping warrant investigation as adequate densities were produced at the lowest level studied. The improved sintering properties from Cu-doping using the process outlined here, provides a means of significantly improving the industrial fabrication of high density $BaZrO_3$ with minimal impact on corrosion resistance.

4. Conclusions

Addition of Cu^{2+} compounds during $BaZrO_3$ fabrication has been demonstrated as an effective method of significantly reducing the sintering temperatures of $BaZrO_3$, if carried out at the correct stage of powder processing. XRD measurement of $BaZrO_3$ lattice parameters showed Cu^{2+} to be essentially insoluble in the $BaZrO_3$ crystal lattice at ambient temperature, hence secondary phases were formed which were detected by TEM. Despite a small contribution to phase impurity, the dopant levels required to reduce sintering temperatures were low and did not significantly affect the corrosion resistance of $BaZrO_3$ crucibles formed using the standard solid-state powder synthesis method.

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