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A compositional and structural study of the phase $BaZr_{1-x}Cu_xO_{3-z}$

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Ceramics of the nominal composition $BaZr_{1-x}Cu_xO_{3-z}$ were made by reacting powders of $BaCuO_2$ and $BaZrO_3$. Scanning electron microscopy–energy dispersive X-ray analysis and X-ray diffraction analyses were performed on all samples to obtain compositional and structural information. The $BaZrO_3$ structure was found to exist over a wide range of compositions, indicating that copper substitutes on both barium and zirconium sites. Two different substitution regimes are suggested. The results are discussed with regard to the possible usage of $BaZr_{1-x}Cu_xO_{3-z}$ compounds as barrier layers on alumina substrates or crucibles during melt processing or crystal growth of superconducting $YBa_2Cu_3O_{7-x}$(YBCO).

1. Introduction

Zirconia is now in common use both as a substrate for YBCO thick films and as a crucible for crystal growth, as it consistently yields films and crystals with good superconducting properties [1, 2]. Research has shown the presence of non-superconducting reaction products based on the mixed oxides of barium, copper and zirconium, in particular a phase with the crystallographic structure of $BaZrO_3$, but also containing significant amounts of copper [3–8]. Many researchers have concluded that the copper substitutes on the zirconium sites, giving $Ba(Zr_{1-x}Cu_x)O_3$, but energy dispersive X-ray (EDX) analysis shows compositions with less than 50 cation at % Ba which do not conform to this identification [3]. This then suggests either that the copper substitutes on both the barium and zirconium sites, giving $(Ba_{1-y}Cu_y)(Zr_{1-x}Cu_x)O_{3-z}$, or that these phases are some entirely different ternary phase, referred to at this stage as $(Ba, Zr, Cu)O_x$. Both $BaZrO_3$ and $BaCuO_2$ (the only other relevant binary oxide) are cubic materials, but $BaCuO_2$ has a unit cell over four times larger than that of $BaZrO_3$ and has a much more complex structure [9–11]. This, and the mis-match of oxygen atoms, means that there is no possibility of a solid solution between the two compounds. Stoichiometric $BaZrO_3$ has recently been studied as a substrate material for YBCO thick films [12] although a low value of T_c was observed. It is also synthesized because of its interesting dielectric properties [13].

The $(Ba, Zr, Cu)O_x$ phases have been identified by EDX as small areas in multi-phase, polycrystalline samples, where the individual phases cannot be easily isolated for X-ray diffraction (XRD) analysis. Structural identification *in situ*, by TEM [6], indicates that $BaZr_{1-x}Cu_xO_{3-z}$ for $x \leqslant 0.3$ is of the $BaZrO_3$ structure, but no other information currently exists on the nature of the $(Ba, Zr, Cu)O_x$ phases in general.

One of the motivations for this study was to identify a stable barrier layer material for use with alumina substrates and crucibles, thus avoiding the high cost of zirconia and its unsuitable dielectric properties in certain microwave applications [14]. Research in this area has investigated barrier layers of yttria-stabilized zirconia [15], $(Ba_{1-y}Cu_y)ZrO_3$ [16], silver [17] and $BaSO_4$ [18]. In particular, Bailey *et al.* [16] have found that $BaZrO_3$ does not adhere to alumina substrates, but an improvement in the properties of YBCO thick films can be made using barrier layers of nominal composition $Ba_{0.6}Cu_{0.4}ZrO_3$.

The aim of the work described in this paper was to synthesize single-phase ceramics of ternary phases of $Ba(Zr_{1-x}Cu_x)O_{3-z}$, with $0 < x < 1$, and obtain both structural and compositional information to establish more clearly the nature of these ternary phases.

2. Experimental procedure

Powders were reacted from mixtures of $BaZrO_3$ (Johnson Matthey-Alfa 99%) and $BaCuO_2$ (prepared in-house). The $BaCuO_2$ was synthesized by reaction of $BaCO_3$ (BDH-Analar 99%) and CuO (BDH-Analar 98%) at 900 °C, in air, for 48 h with three intermediate grindings. Both the $BaZrO_3$ and the $BaCuO_2$ were checked by XRD analysis and found to conform to the JCPDS standards. Powders of the nominal composition $Ba(Zr_{1-x}Cu_x)O_{3-z}$ were placed in an yttria-stabilized zirconia crucible and reacted in a muffle furnace in air, up to three times at various temperatures. Between each firing the powders were re-ground and analysed by XRD. The temperatures were chosen to be as high as possible without reaction with the crucible. Initially BZC1 was reacted at 1450 °C, being the maximum temperature of the furnace. Successive powders in the series were then reacted at progressively lower temperatures, as some adhesion to the

0022-2461

crucible was observed. This process was continued as far as BZC6, where melting and severe crucible reaction and cracking occurred at 1350 °C (although BZC5 had been fired at 1360 °C without problems). BZC9 was then successfully fired at temperatures between 900 °C and 930 °C, without crucible reaction. As it was observed that $BaCuO_2$ and BZC9 turned from a brown colour in the unreacted state to a dark grey after firing, the colour change was then used as the criterion for choosing an appropriate firing temperature. Powders BZC8-6 were fired at progressively higher temperatures as x decreased. Pellets were pressed from the powders and these were fired once more on an yttria-stabilized zirconia tile. Four pellets (BZC1, 3, 5 and 6) were made at both a lower and higher temperature to compare the two processes. The

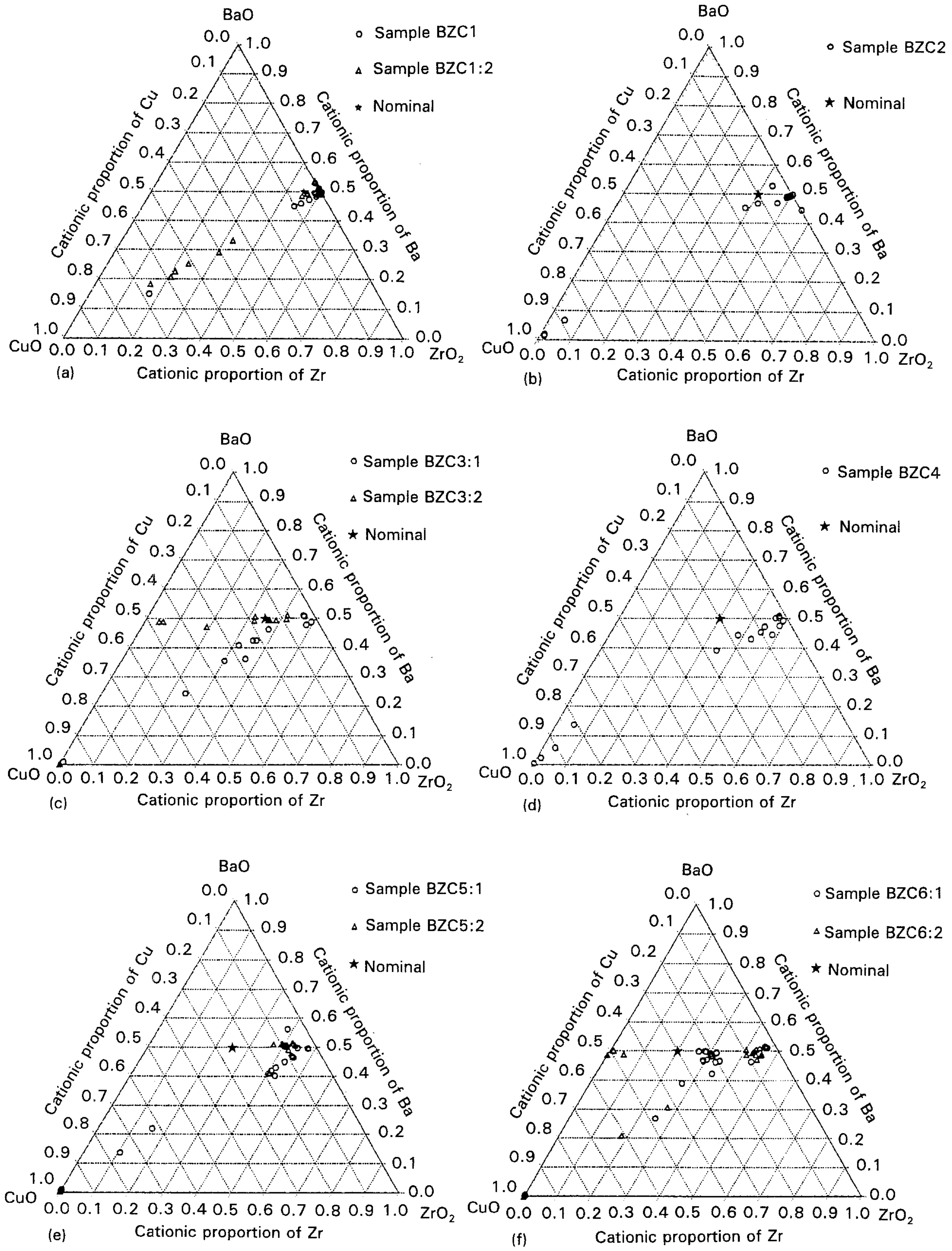

Figure 1 (a–i) Ternary phase diagrams showing EDX analyses obtained from sections of pellets BZC1–9, respectively. (j) The main tie-lines and compositions referred to in the text.

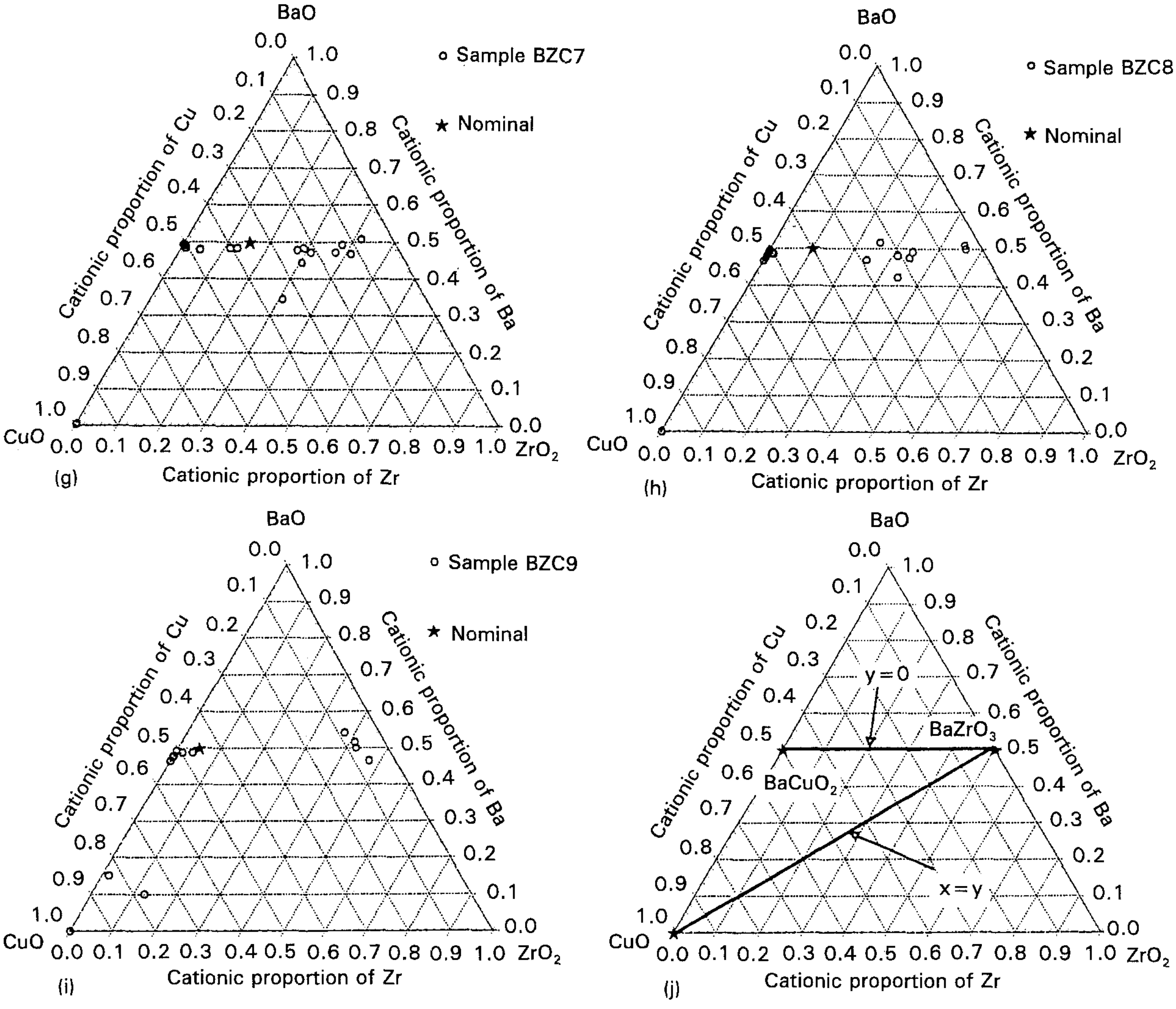

Figure 1 Continued.

TABLE I Processing parameters used for the preparation of pellets of nominal composition $BaZr_{1-x}Cu_xO_{3-z}$.

Nominal composition			
Sample	x	cationic at % Cu	Heat treatment
BZC1:1	0.1	5	2×8 h 1450 °C Pellet: 8 h 1450 °C
BZC1:2	0.1	5	8 h 970 °C, 8 h 990 °C, 8 h 1010 °C, 8 h 1050 °C Pellet 8 h 1100 °C
BZC2	0.2	10	8 h 1450 °C, 8 h 1435 °C Pellet 8 h 1400 °C
BZC3:1	0.3	15	8 h 1400 °C, 8 h 1380 °C Pellet 8 h 1375 °C
BZC3:2	0.3	15	8 h 940 °C, 8 h 960 °C Pellet 8 h 970 °C
BZC4	0.4	20	2×8 h 1375 °C Pellet 8 h 1360 °C
BZC5:1	0.5	25	2×8 h 1360 °C Pellet 8 h 1350 °C
BZC5:2	0.5	25	8 h 930 °C, 8 h 940 °C Pellet 8 h 950 °C
BZC6:1	0.6	30	2×8 h 910 °C Pellet 8 h 910 °C
BZC6:2	0.6	30	2×8 h 910 °C Pellet 8 h 950 °C
BZC7	0.7	35	2×8 h 910 °C Pellet 8 h 910 °C
BZC8	0.8	40	2×8 h 915 °C Pellet 8 h 910 °C
BZC9	0.9	45	8 h 930 °C, 8 h 920 °C Pellet 8 h 900 °C

preparation of all the samples are summarized in Table I.

XRD data were taken on the finished pellets using a Siemens powder diffractometer with 2θ in the range 25–60°. EDX analyses were performed on polished cross-sections of the pellets (prepared as in [3]) using a Jeol 6300 scanning electron microscope with LINK analyser. For each pellet, between 15 and 20 spot analyses were taken at points distributed throughout the samples. In addition to barium, copper and zirconium, yttrium was also analysed for, because yttria is a constituent of the zirconia crucibles and tiles. However, no yttrium was detected in any of the samples.

3. Results

From optical examination of the polished pellets it was clear that only the first in the series (BZC1, $x = 0.1$) was truly single phase. EDX analysis showed CuO in all pellets, except BZC1, with areas of $BaCuO_2$ also appearing in BZC6-9. The remaining analyses showed a range of compositions in all cases, generally more zirconium-rich than the target composition and some with lower barium content. These results are shown in Fig. 1.

XRD analysis confirmed the multi-phase nature of pellets BZC2-9 (Fig. 2). The (1 1 0), (1 1 1), (2 0 0) and (2 1 1) peaks of the $BaZrO_3$ phase were seen clearly up

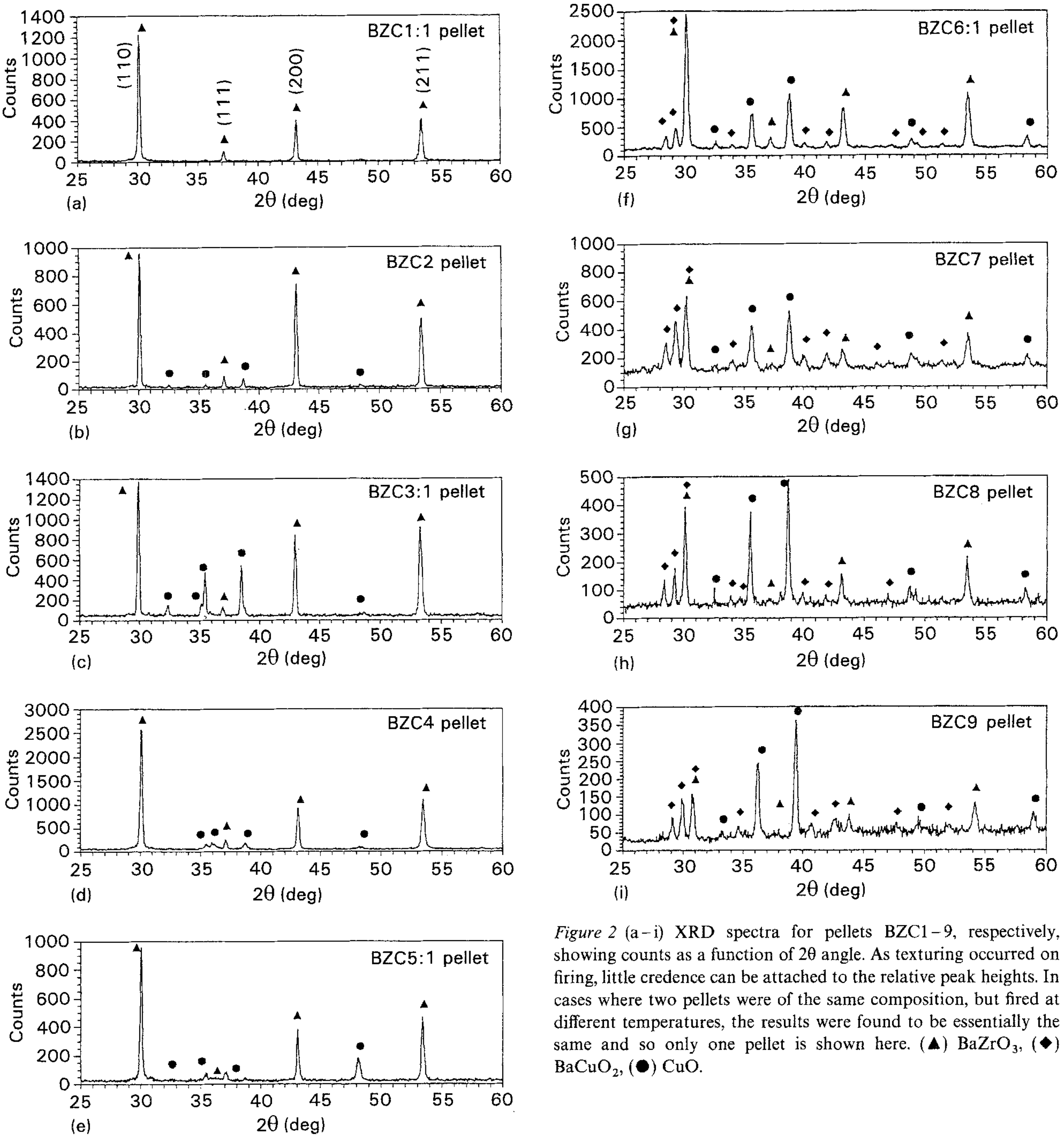

Figure 2 (a–i) XRD spectra for pellets BZC1–9, respectively, showing counts as a function of 2θ angle. As texturing occurred on firing, little credence can be attached to the relative peak heights. In cases where two pellets were of the same composition, but fired at different temperatures, the results were found to be essentially the same and so only one pellet is shown here. (▲) $BaZrO_3$, (◆) $BaCuO_2$, (●) CuO.

to BZC6 and less clearly thereafter. CuO peaks were observed in BZC2-9 with increasing intensity as more copper was added. From BZC6 upwards, the pattern shows increasing complexity due to the presence of extra peaks associated with $BaCuO_2$ (characterized by a triplet of peaks at $2\theta = 28° - 30°$, coinciding with a $BaZrO_3$ peak at 30°). For some samples XRD was carried out on two pellets made using different heat treatments. Because the results were found to be essentially the same, we have only shown one set of data.

4. Discussion

The $BaZrO_3$ structure is identified by XRD up to quite large proportions of copper, although EDX analysis shows a range of compositions of all three cations. This suggests that copper substitution occurs, probably on both the barium and zirconium sites because many compositions of less than 50 cationic at % Ba were seen. However, the tendency for substitution of zirconium is greater than for barium, as the majority of the data points still lie approximately along the $BaCuO_2 - BaZrO_3$ tie-line. At higher copper content, more $BaCuO_2$ and CuO than $BaZrO_3$ are observed, in both the EDX and XRD data.

Considering a general formula of $Ba_{1-y}Cu_y Zr_{1-x}Cu_xO_{3-z}$ and assuming cation valences of Ba^{2+}, Cu^{3+}, Zr^{4+}, we see that the $y = 0$ case (substitution only on zirconium sites) is only possible for $z > 0$. In other words, compositions along the $BaCuO_2 - BaZrO_3$ tie-line can only be achieved if there are oxygen vacancies. In the case where $y \neq 0$, the oxygen content can only be maintained ($z = 0$) if $x = y$. If copper substitutes equally on both the barium and zirconium sites, there need be no oxygen vacancies. This case corresponds to points along the $CuO - BaZrO_3$ tie-line. We thus identify two different regimes of copper substitution, along the

$BaCuO_2-BaZrO_3$ and $CuO-BaZrO_3$ tie-lines, respectively (see Fig. 1), which are in accordance with the EDX data presented here. This argument is also borne out by the observations of Marshall *et al.* [3] and Wellhöfer *et al.* [4], where the dominant mechanism in crystal boules is substitution on both barium and zirconium sites ($x = y$), and in thick films it is substitution on only zirconium sites ($y = 0$).

BZC1-5 samples show no $BaCuO_2$ in the EDX analyses and the XRD data do not show the characteristic $BaCuO_2$ peaks at $2\theta = 28° - 30°$. In the EDX analyses of BZC6-9 and also in those reported elsewhere [3], there is evidence of a gap in the composition distributions at around $x = 30$ cationic at % Cu along the $BaCuO_2-BaZrO_3$ tie-line. Finally, the response of the powders to heat treatment changed dramatically between BZC5 and BZC6, as indicated in Table I, with the processing temperatures having to be dropped by 400 °C to avoid crucible reaction. All these facts suggest that the limit of the $BaZrO_3$-based phase occurs at around $x = 0.6$ or 30 cationic at % Cu. It is worth noting that along the $CuO-BaZrO_3$ tie-line the limit of copper substitution appears to be somewhat higher than this. Further work, however, is necessary to investigate the conditions required for each regime before it is possible to draw any detailed conclusions.

The use of $BaZrO_3$ as a barrier layer is thus limited by its ability to absorb copper into its lattice and hence react with YBCO. These results suggest that a composition of $BaZr_{0.4}Cu_{0.6}O_{3-z}$ or $Ba_{0.7}Cu_{0.3}Zr_{0.7}Cu_{0.3}O_3$ may be much less reactive with YBCO as they are unlikely to absorb more copper and Bailey *et al.* [16] found an optimum composition of (nominally) $Ba_{0.6}Cu_{0.4}ZrO_3$. However, this phase was not prepared beforehand and no EDX data are reported to confirm the exact composition. More work is necessary to find a heat treatment that will yield a single phase of any of these compositions and to study the influence of different precursors. Further research in this area is in progress to evaluate the suitability of the $Ba_{1-y}Cu_yZr_{1-x}Cu_xO_{3-z}$ compounds as barrier layers on alumina.

5. Conclusion

Ceramics with the starting composition $Ba(Zr_{1-x}Cu_x)O_3$ have been prepared for $0 < x < 1$ and found to contain phases based on $BaZrO_3$, $BaCuO_2$ and CuO. No other phases were observed. Only $BaZr_{0.1}Cu_{0.9}O_y$ was found to be single phase, using the process described here. EDX and XRD results suggest that copper can substitute into the $BaZrO_3$ lattice, either on both the barium and zirconium sites equally, or on to the zirconium sites only, in two different regimes. The two regimes seem to allow different limits of copper substitution into the $BaZrO_3$ lattice with the limit of copper incorporation being at a value of approximately 30 cationic at % Cu. The compounds $BaZr_{0.4}Cu_{0.6}O_{3-z}$ or $Ba_{0.7}Cu_{0.3}Zr_{0.7}Cu_{0.3}O_3$ may be suitable for use as a barrier layer in the fabrication of YBCO thick films and crystals if a heat treatment can be found to synthesize single-phase powders.

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