Hot-Forging of Copper Substituted Bismuth Vanadate Ceramics

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Introduction

Bismuth vanadate with aliovalent copper substitution for vanadium $Bi_4(Cu_xV_{1-x})_2O_{11}$ (BICUVOX), has high oxygen conductivity that makes it a candidate for solid electrolytes in medium temperature SOFCs, gas sensors and gas separation membranes. The structural anisotropy of such compounds (Fig. 1) gives rise to 2-dimensional ionic conductivity, which to date has not been exploited. Previous work on hot-forged bulk ceramics with (Cu,Ti) double substitution yielded modest (11%) crystallographic orientation and modest anisotropy in the conductivity (Fig. 2). The current work describes our attempts to increase the orientation in this family of ceramics.

Hot-forging (HF) or constrained sintering involves applying pressure to a ceramic body while subjecting it to high temperatures. Forging has been used to eliminate porosity, maximize density, reduce sintering times and temperatures, and/or control crystallographic texture. In these experiments, force was applied along the vertical axis in an effort to promote growth in the directions perpendicular to the axis. For the first time, HF was combined with the templated grain growth (TGG) technique, wherein specially synthesized crystallites (the "templates") are dispersed in a matrix of small equiaxed crystallites. The objective is to influence the growth of the bulk microcrystalline structure to result in a textured final body. During sintering, matrix grains that are oriented similarly and adjacent to the templates tend to grow in concert, while matrix grains misoriented against the templates form high energy interfaces and are consumed by the larger template grain.

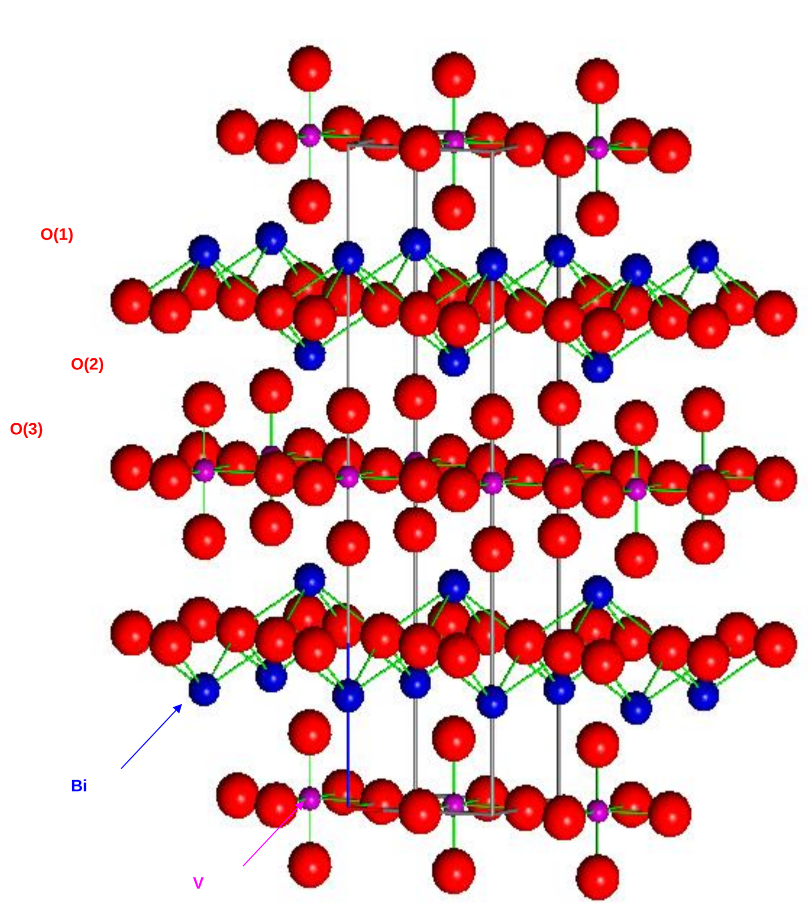

FIG. 1: Schematic of BiVOx crystal structure

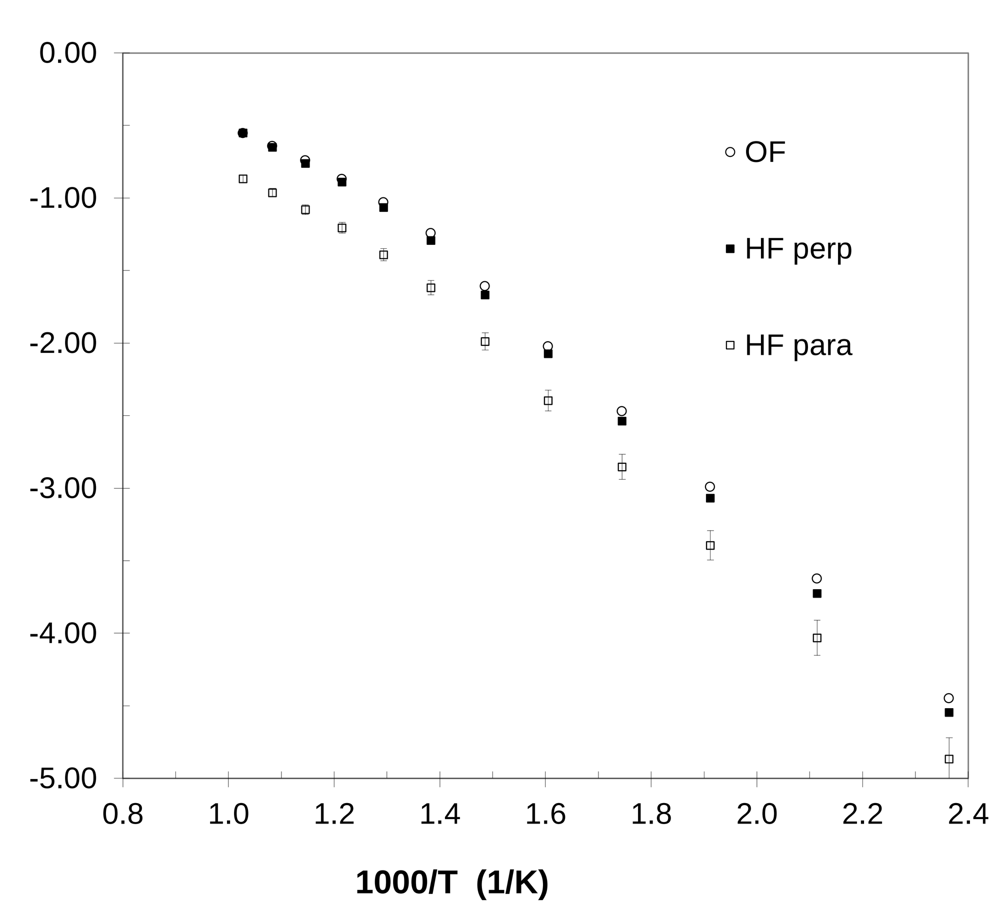

FIG 2: Anisotropic ionic conductivity of HF BiCuTiVOx. (Fuierer *et al.* J. Eur. Cer. Soc. **34** (2014) 943-951.)

Experimental Procedure

Templates of BiCuVOx were produced by molten salt synthesis (Fig. 4). Varying quantities of templates were dispersed, by ball milling, in a matrix of BiCuVOx grains that were synthesized by conventional solid state techniques. Green bodies were dry pressed and pre-sintered to remove the binder and increase mechanical strength. These green bodies were then forged at 750°C for 3 hours with variable loads.

The hot-forge apparatus (Fig. 4) consists of a vertically mounted, clamshell furnace. The ceramic body is pressed between two stacks of refractory rams. Force is applied via load arm.

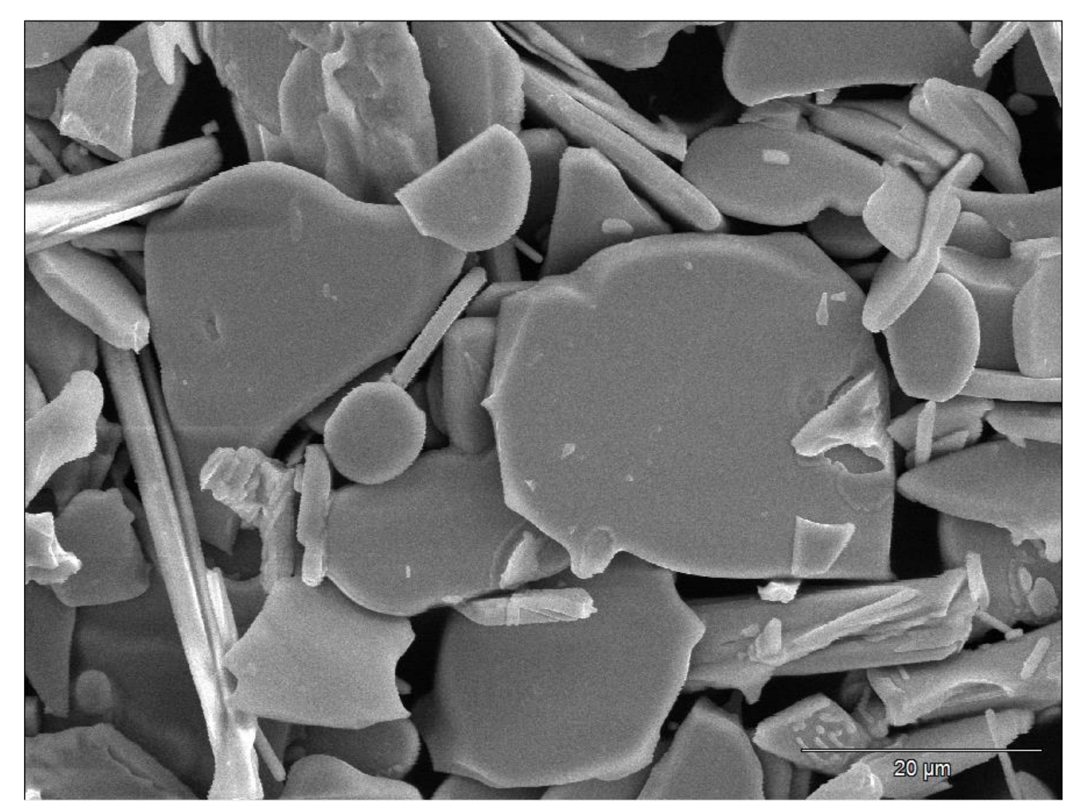

FIG 3: Micrograph of template particles used in forges

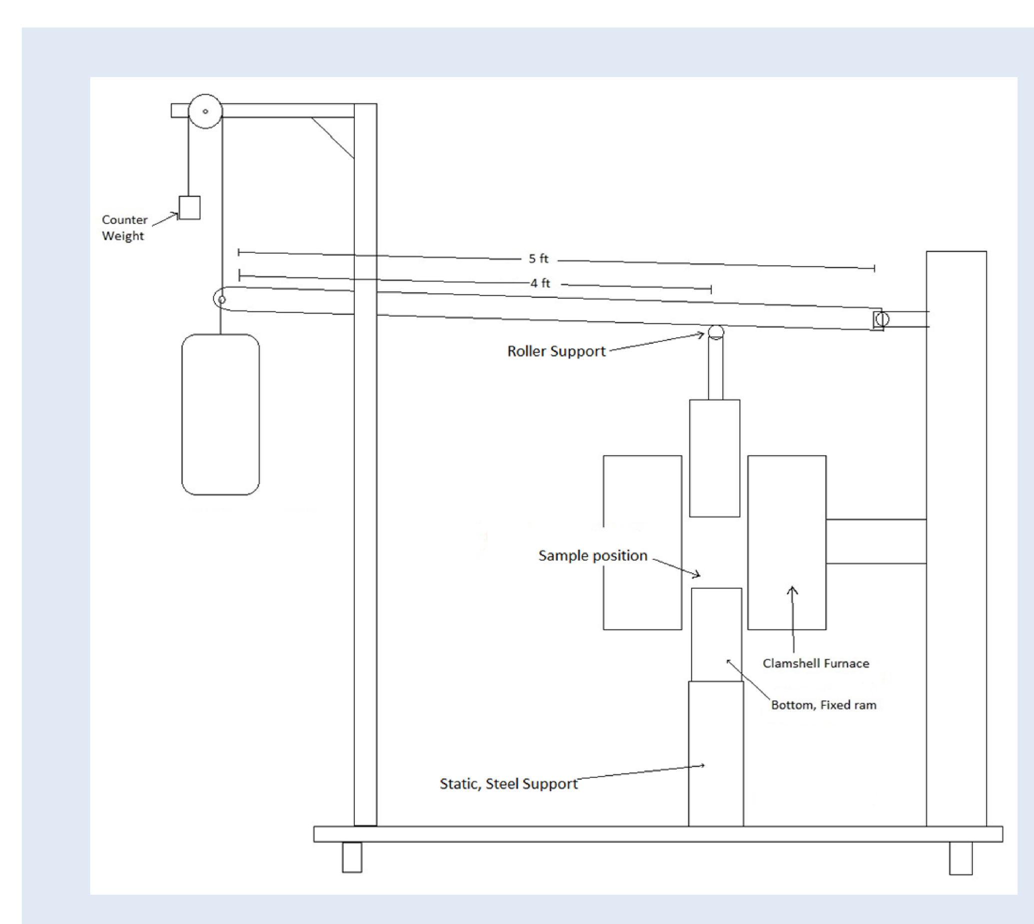

FIG 4: Schematic of hot-forging apparatus

Results

Increased loading systematically increases height contraction and lateral deformation using conventionally prepared powders (Fig. 5). Densities are high, but texture is negligible. Inclusion of template grains appears to increase orientation to some degree. Relative peak heights in XRD patterns (Fig. 6) are used to quantify crystallographic texture.

FIG 5: BiCuVOx forge samples (without templates) with increasing load, (l to r) 736, 1104, 1472, & 1839N

Sample	Load	Content (wt%)	Density	Orientation
4.1	1472 N	10%	96.6%	29%
4.9	1472 N	7%	96.9%	28%
5.1	1716 N	5%	96.1%	16%
5.3	1962 N	5%	95.0%	5%

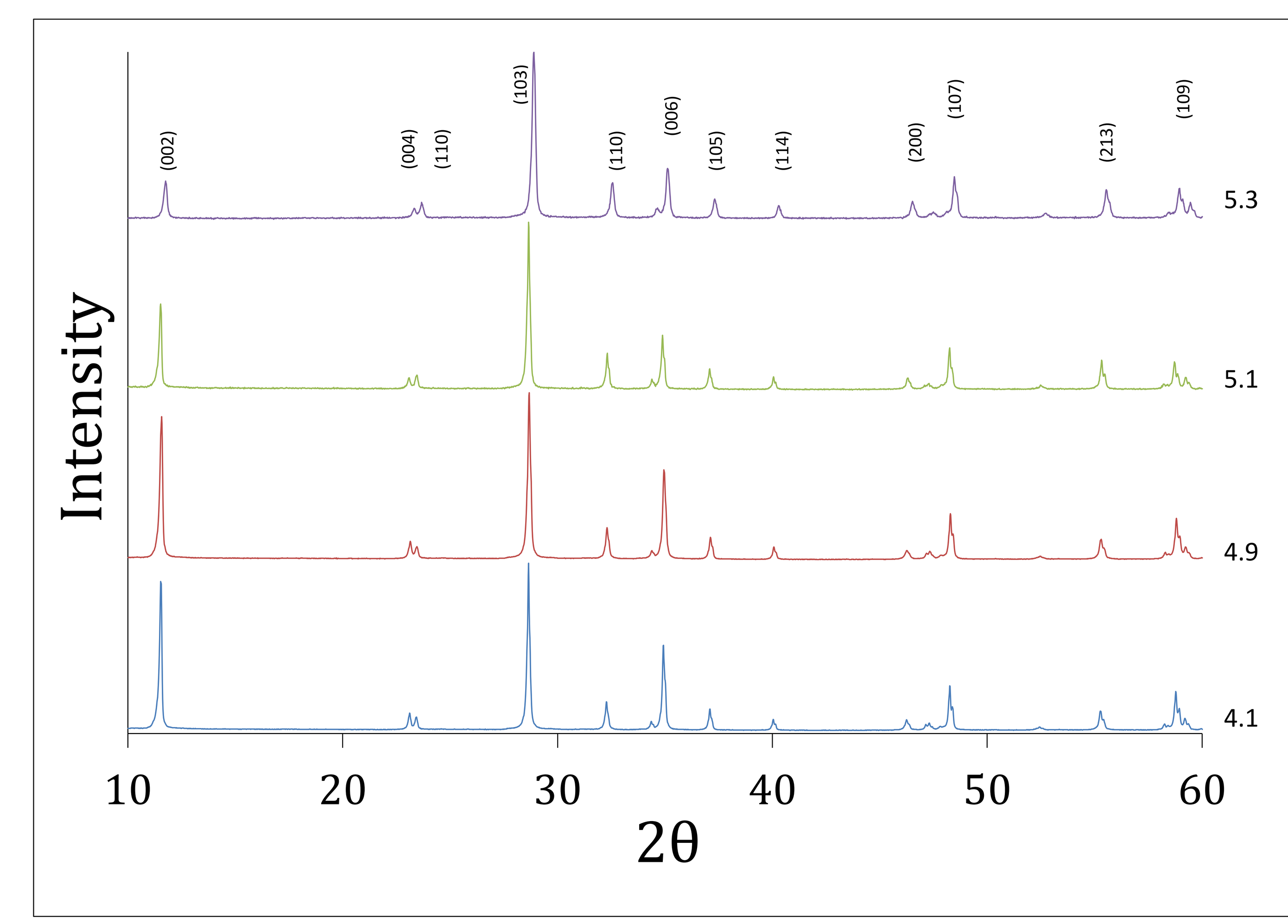

FIG 6: XRD patterns of hot-forged BiCuVOx Samples

Conclusions

HF has produced some of the most dense BICUVOX ceramics to date. Combined HF and TGG approach to texturing has led to modest success thus far, with orientation increasing with increasing content of template.

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