Journal of the European Ceramic Society 21 (2001) 1821–1824
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Studies on preparation, characterisation and ion conductivity of TI-CU double substituted $Bi_4V_2O_{11}$

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Received 4 September 2000; received in revised form 2 November 2000; accepted 15 November 2000

Abstract

This paper reports the studies on the solid state synthesis, densification, microstructure and ion conductivity of double substituted $Bi_4V_2O_{11}$ ($Bi_2V_{0.9}Cu_{0.05}Ti_{0.05}O_{5.4}$). Differential thermal and X-ray analysis indicate that synthesis of the compound can be accomplished at 620–650°C, and the room temperature phase is the tetragonal γ form of $Bi_4V_2O_{11}$. Samples with more than 95% theoretical densities were obtained after sintering at 810°C for several minutes or 750°C for a few hours. The report also includes examination of the microstructure as well as evaluation of the electrical properties with respect to temperature and samples grain size. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: BIMEVOX; Composites; Impedance; Ionic conductivity; Mechanical properties

1. Introduction

Bismuth vanadate ($Bi_4V_2O_{11}$) has three different structural phases of which the high temperature γ phase is an excellent oxygen ion conductor. The attempts for stabilizing the γ phase of bismuth vanadate has led to invention of a new generation of oxygen ion conductor family called BIMEVOX.[1] It has been proved recently,[2,3] that this group of solid electrolytes is capable to improve the performance of oxygen pumps. In BIMEVOX materials, the high temperature γ phase has been stabilized to room temperature by substitution of a part of vanadium by a variety of metal elements (e.g. ME = Cu, Ni, Co, Ti, Zr, . . .).[4–6] Around 300°C the best materials (ME = Cu, Ti) possess ion conductivities nearly two orders of magnitude higher than zirconia based electrolytes.

The purpose of this paper is to investigate the stabilization of the bismuth vanadate's γ phase by substitution of vanadium by Ti and Cu, the sintering behavior and ion conductivity as a function of temperature and samples microstructure.

2. Experimental

Ti-Cu double substituted BIMEVOX powders with nominal composition $Bi_2V_{0.9}Cu_{0.05}Ti_{0.05}O_{5.4}$ were prepared by solid state reaction from stoichiometric amounts of analytical grade oxides (Bi_2O_3, V_2O_5, CuO, and TiO_2; Aldrich, 99.99% purity).

The mixing and grinding was performed by attrition milling using zirconia balls (3 mm in diameter). The optimum condition for milling was proved to be a 40 wt.% suspension of oxide or BITICUVOX.10 powders in ethanol, 150 rpm for 10 h. This condition was chosen to produce particles with mean size less than 0.5 μm (estimated by SEM) and assures also the lowest impurity level caused by zirconia ball abrasion.

After drying, the mixed powders were calcined in a gold crucible for 15 h at 650°C in air. To ensure complete reaction, the materials were milled again and refired at 800°C for 5 h.

DTA/TG measurements on mixtures of the oxides and the compound were made to investigate the solid state reaction process and phase changes respectively. The temperature ramp rate was 5°C/min for heating

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PII: S0955-2219(01)00123-6

and cooling. Powder X-ray diffraction, using the CuK_α source, was applied to characterize the crystal structure and purity of the phases. The synthesized compound were attrition milled for different times (1–25 h). Ceramic samples were formed by uniaxially cold pressing the powder (0.75 g portions) at 350 MPa. A number of different sintering regimes, with respect to temperature and time, were employed to determine the optimum sintering conditions. Sintering temperatures ranged from 710 to 810°C, and sintering time from 5 min to 25 h.

Table 1
Comparison of lattice parameters and theoretical densities of $Bi_2V_{0.9}Cu_{0.1}O_{5.35}$ and $Bi_2V_{0.9}Cu_{0.05}Ti_{0.05}O_{5.4}$

Compound	Lattice parameters (A°)		Theoretical density (g/cm^3)
	a	*c*	
$Bi_2V_{0.9}Cu_{0.1}O_{5.35}$	3.916	15.427	7.805
$Bi_2V_{0.9}Cu_{0.05}Ti_{0.05}O_{5.4}$	3.915	15.41	7.82

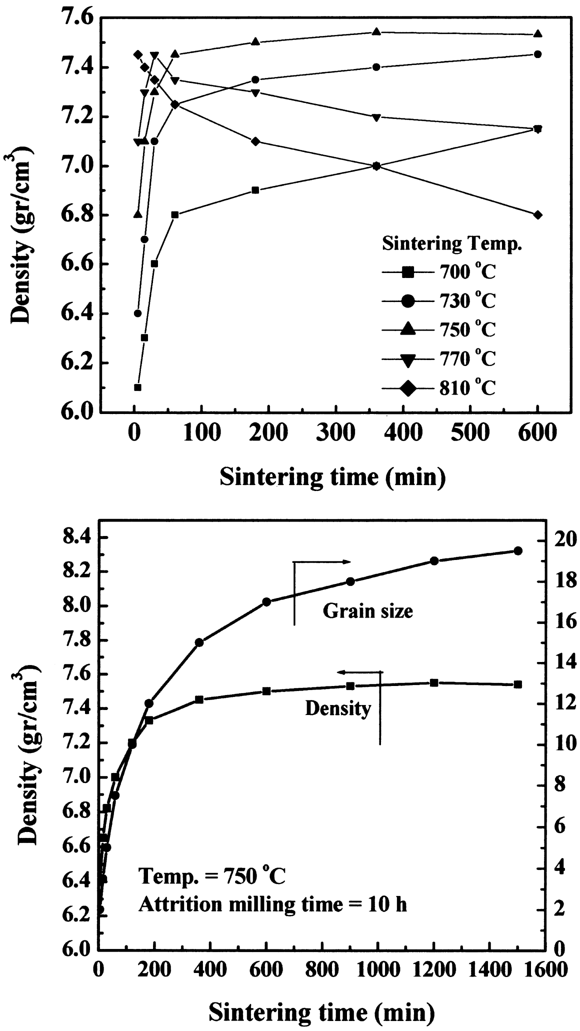

Fig. 1. (a) Density variation of $Bi_2V_{0.9}Cu_{0.05}Ti_{0.05}O_{5.4}$ sintered at different temperature with respect to time. (b) Density and grain size variation of $Bi_2V_{0.9}Cu_{0.05}Ti_{0.05}O_{5.4}$ sample sintered at 750°C with respect to time.

Postsintering densities was measured in isobutyl alcohol, and the microstructures was examined using SEM. The electrical conductivity was measured by the ac two-probe impedance spectroscopy in an automated setup,[7] using a Solartron 1260 impedance spectrometer in the frequency range of 0.01 Hz–10 MHz. Impedance spectra for samples with different grain size were recorded on heating and cooling from 100 to 750°C at 25°C intervals in air. The ion conductivity was obtained from complex impedance data by graphical extrapolation.

3. Results and discussion

3.1. Powder X-ray diffractometry

Powder XRD patterns taken at room temperature indicate that the $Bi_2V_{0.9}Cu_{0.05}Ti_{0.05}O_{5.4}$ compounds are

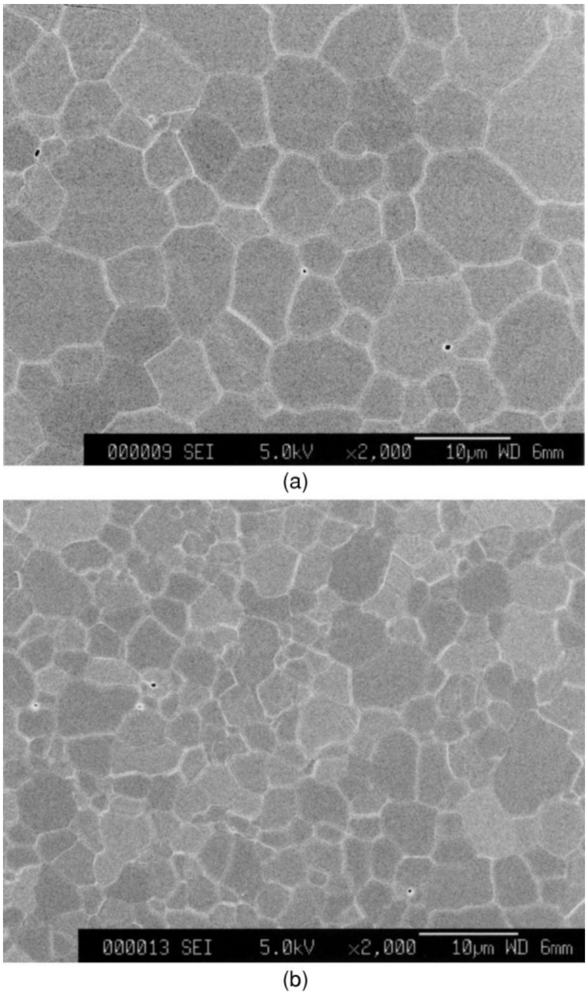

Fig. 2. Microstructure of two $Bi_2V_{0.9}Cu_{0.05}Ti_{0.05}O_{5.4}$ samples sintered at 750°C for 1 (a) and 10 (b) h.

phase pure after double firing at 650 and 800°C. All XRD crystalline peaks correspond to those observed for BICUVOX.10.[5,6,8,9] The lattice parameters and theoretical densities of $Bi_2V_{0.9}Cu_{0.1}O_{5.35}$ and $Bi_2V_{0.9}Cu_{0.05}Ti_{0.05}O_{5.4}$, evaluated at our institute, are summarized in Table 1. It is apparent that there is a small contraction in *c* parameter of the tetragonal crystal, due to the substitution of 50% of Cu by a smaller ion, Ti, which results in a little increase in theoretical density.

3.2. Thermal analysis

The DTA/TG measurements indicate a small endothermic peak in the range 460–480°C on heating and an exothermic peak from 430 to 410°C on cooling which is slightly different from what has been obtained for BICUVOX.10.[6] These features could be attributed to the γ–γ' transformation; the ordering effect of oxygen vacancies which causes an increase in the activation energy of ion conduction at low temperatures ($T < 450°C$).[1,8]

3.3. Sintering behavior and characterization of the microstructure

Attrition milling of the synthesized compound for a number of different time intervals (1–25 h) produced powders with a range of particle sizes from 5 to less than 0.3 μm. The optimum time for producing small particle size powders with good compactibility and low impurity is around 10–15 h.

The densification characteristics of BITICUVOX.10 ceramics and the effects of sintering time and temperature on the microstructure and the density of the samples strongly depend on the initial particle size, shape and grain size distribution. It was possible to produce samples with more than 95% theoretical density using small particle size ($d < 1$ μm) and sintering at 750°C, for a few hours or at 810°C for a few minutes.

These results are in agreement with results obtained by Steil,[10] showing that sintering at high temperature for a prolonged time causes an inhomogeneous grain growth and pore coarsening which induce micro-cracks, reduce density and also the strength of the samples. Fig. 1 (a) shows the density variation of the samples with small initial particle size (0.5 μm), sintered at different temperature vs. time. As it can be seen, the optimum sintering condition for producing dense samples with small grain size (and acceptable mechanical strength), is about 750°C for 1 to 3 h. Fig. 1 (b) shows the variation of the density and grain size of the sample sintered at optimum temperature (750°C) with time. The microstructure of two samples sintered at 750°C for 1 and 10 h, which were conducted in two completely different grain sizes, is shown in Fig. 2.

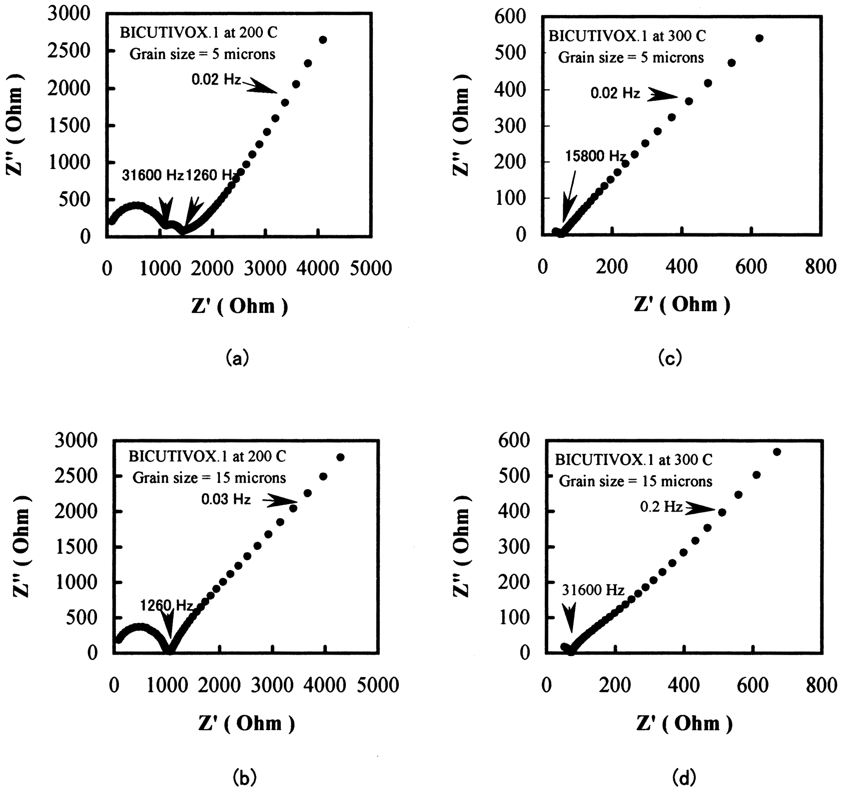

Fig. 3. Nyquist plots for $Bi_2V_{0.9}Cu_{0.05}Ti_{0.05}O_{5.4}$ samples: (a) and (b) at 200°C and (c) and (d) at 300°C for fine and coarse microstructures, respectively.

3.4. Conductivity characterization

Nyquist plots, measured at 200 and 300°C on two different samples with 5 and 15 μm grain size, are presented in Fig. 3. The plot of the small grain size sample at low temperature shows two semicircles attributed to the inter- and intragranular contribution to the impedance. In samples with a large grain size the effect of the grain boundary is small due to the lower density of grain boundaries. At higher temperature (>300°C) the effect of the grain size vanishes and both plots are nearly comparable, although a little effect of grain boundary can be seen in small grain size sample. These results are in accordance with previous results on microstructure dependent impedance of BIMEVOX.1.[11]

The plot of log(σT) vs. $1000/T$ of the samples with two different grain sizes (5 and 15 μm) is given in Fig. 4. Both samples show Arrhenius type straight lines. The slope changes at 460–480°C, which is related to the mentioned order/disorder transformation of oxygen vacancies.

Fig. 4 also shows that the conductivity of the samples at high temperatures ($T > 300$°C) is the same. At low temperature the conductivity of the sample with finer microstructure is slightly smaller than that of the coarse one, which is related to the contribution of the grain boundary to the total resistance.

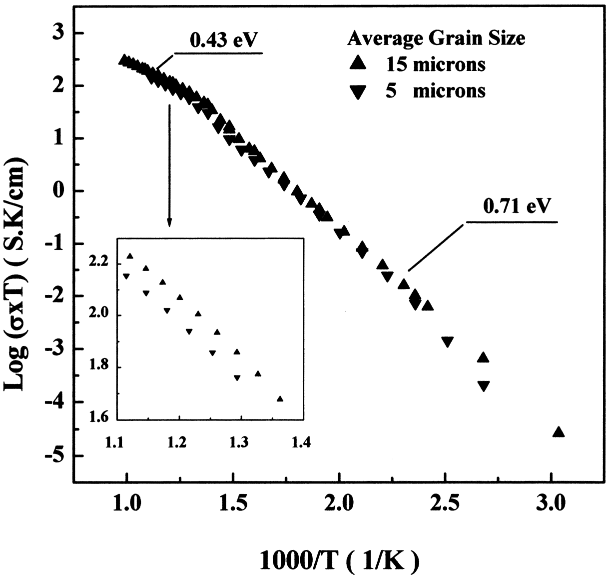

Fig. 4. Arrhenius plots indicating a slight decrease in conductivity for finer microstructure sample.

4. Conclusions

1. The γ phase of $Bi_4V_2O_{11}$ was stabilized at room temperature by 10 atomic percent double substitution of V by Cu and Ti.
2. Sintering of BICUTIVOX.1 powders at 750°C for 1 to 3 h led to the samples possessing more than 95% theoretical density.
3. BICUTIVOX.1 material exhibited high ion conductivity, comparable with BICUVOX.1 compound.
4. Ion conductivity of BICUTIVOX.1 slightly decrease by decreasing the grain size.

Acknowledgements

This work has been supported by University of Tehran, Iran which is gratefully acknowledged.

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