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ANIONIC CONDUCTING OXIDE CERAMICS

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MICROSTRUCTURE - PROPERTY STUDIES OF BICUVOX CERAMICS

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ABSTRACT

The bismuth vanadate composition, $Bi_4V_2O_{11}$, is the parent compound for a new family of oxygen ion conductors. The substitution of various metallic ions for vanadium stabilizes the high temperature γ-phase and leads to a series of compounds which possess the highest oxygen ion conductivities observed for temperatures below 400°C. This paper reports the first studies on the processing, densification and transport properties of copper-doped bismuth vanadate ceramics. Phase-pure materials with densities above 95% of theoretical were obtained using standard ceramic processing approaches. Ionic conductivities in the range of 1×10^{-2} S/cm at 400°C were observed for a variety of sintered samples.

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INTRODUCTION

Oxygen ion conductors have important technological applications in such devices as fuel cells, sensors and oxygen pumps. In electrochemical cells these oxygen ion solid electrolytes are electronic insulators, conductors of O^{2-} and, ideally, perform three functions:[1]

(1) to separate the chemical reactants (either gaseous or liquid)
(2) to block the internal electronic current between cell electrodes
(3) to transport the working ions responsible for the internal current

The most extensively studied oxygen ion conductors are those materials which crystallize with the fluorite structure (CeO_2, ThO_2) or the distorted fluorite structure (ZrO_2, HfO_2), characterized by a stationary fcc cation array and mobile O^{2-} ions occupying the tetrahedral sites of the cation array. High conductivity for O^{2-} develops when M(II) or M(III) ions substitute for M(IV) and introduce anion vacancies.[2] Stabilized zirconias have been widely investigated and are used in the various electrochemical devices. In these systems, however, high conductivity is achieved at temperatures at 800°C and above. The prospect of developing lower operating temperatures for electrochemical devices such as solid oxide fuel cells, oxygen sensors and oxygen pumps has motivated the development of oxygen ion conducting ceramics which exhibit high conductivities at substantially lower temperatures.

It is now evident that several different solid electrolyte systems are able to achieve much higher conductivity than that of stabilized zirconia. Stabilized CeO_2 and the fluorite-type d-phase of Bi_2O_3 are two such materials which exhibit high conductivity for O^{2-} ions. For the latter, there are a number of oxides which stabilize this fcc phase and the resulting materials possess conductivities which are 50 to 100 times greater than stabilized zirconia over the temperature range 500 -700°C.[3] The materials have been well studied, especially the system Er_2O_3-Bi_2O_3. The reduced electrode polarization observed with this material indicates that Er_2O_3-Bi_2O_3 would make a better electrolyte for oxygen pumps than Y_2O_3 stabilized zirconia.[4] More recently, another significant improvement in conductivity was reported for the family of bismuth vanadate compounds based on

$Bi_4V_2O_{11}$.[5] The best materials in this series achieve conductivities which are 50 to 100 times larger than any other oxygen ion conductor in the 300-350°C range.[6] To make a comparison, the conductivity of Cu-doped $Bi_4V_2O_{11}$ at 300°C, $\approx 10^{-3}$ S/cm, is attained by calcia-stabilized zirconia at $\approx$ 800°C. Table I summarizes the low temperature conductivity properties for several oxygen ion conducting solid electrolytes. The potential advantages of the bismuth vanadate system are readily apparent.

Table I. Conductivity Data for Selected Oxygen Ion Conductors.

Compounds	$\sigma_{200^\circ C}$ (S/cm)	$\sigma_{400^\circ C}$ (S/cm)	E_a (eV)	Temp. Range (°C)
CeO_2-Gd (20m%)[1]	2.2×10^{-6}	7.7×10^{-4}	0.89	160-400
Bi_2O_3-Y (27m%)[1]	2.2×10^{-8}	7.4×10^{-5}	1.14	200-700
ZrO_2-Y (6m%)[1]	1×10^{-7}	1.1×10^{-4}	0.98	200-500
$Bi_4V_2O_{11}$[5]	5×10^{-5}	1×10^{-3}	0.45	200-400
$Bi_4V_2O_{11}$-Cu (10m%)[15]	1.6×10^{-4}	4.7×10^{-3}	0.62	125-400
$Bi_4V_2O_{11}$-Cu (10m%)	1.1×10^{-4}	1.9×10^{-2}	0.76	200-450

Research on the bismuth vanadate systems is at its inception. The work to date has largely considered issues associated with structure and transport properties; there has been little research reported on the processing of these materials into high quality ceramics. If the enhanced conductivity properties of these solid electrolytes are to be adapted for a new generation of electrochemical devices with lower operating temperatures, it is vital that ceramic processing approaches be established for these materials. The present paper represents the first of such studies as we report our recent results on the processing, densification and transport properties of bismuth vanadate ceramics. This follows an initial section which provides a brief review of the bismuth vanadate field.

The parent compound for this new family of oxygen ion conductors is $Bi_4V_2O_{11}$. The compound exhibits three structural phases over the temperature range 300-1100 K.[5] DSC measurements indicate transformations at 720 K ($\alpha \rightarrow \beta$) and 840 K ($\beta \rightarrow \gamma$). The α-phase ($a = 5.53$ Å; $b = 5.61$Å; $c = 15.29$Å) exhibits a $3a$ orthorhombic superstructure while the tetragonal β-phase has a $2a$ superstructure. The γ-phase is face-centered tetragonal with lattice parameter $a/\sqrt{2}$ and no superstructure is observed. The c-parameter is the same for all three phases.

The structures of the bismuth vanadate phases are related to the Aurivillius phases, Bi_2MO_6 (M = Mo, W) which consist of perovskite-like layers of M-O corner-sharing octahedra located between $Bi_2O_2^{2+}$ sheets (Figure 1).

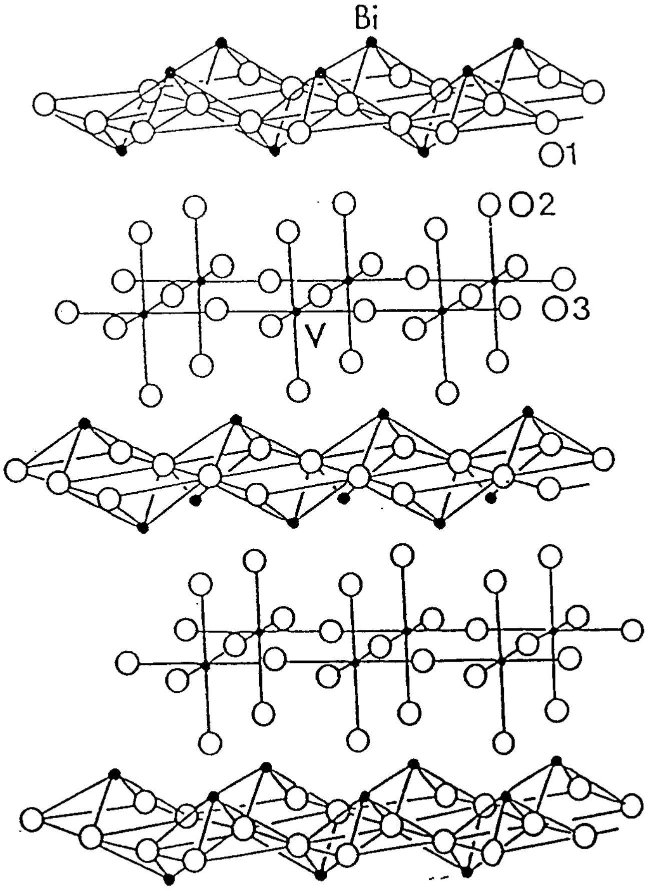

Figure 1. Schematic of the γ-$Bi_4V_2O_{11}$ structure (after Ref.12).

The perovskite layers are oxygen-deficient so that the compound can be formulated as $(Bi_2O_2)^{2+}$ $(VO_{3.5}[\,]_{0.5})^{2-}$ where [ ] represents a vacancy. This suggests that oxygen ions might be mobile within the $VO_{3.5}$ sheets. The initial work on $Bi_4V_2O_{11}$ indicated that this composition possessed high conductivity, especially in the γ-phase, where it reached a conductivity of nearly 1 S/cm at 1000 K.[5] It has been proposed that the perovskite layers contain randomized oxygen ion vacancies which lead to the high oxygen ion conductivity of the γ-phase. At lower temperatures (α and β phases) the oxygen vacancies order and the conductivity decreases accordingly. The conductivity-temperature relationship exhibits discontinuous changes in conductivity and activation energy as $Bi_4V_2O_{11}$ undergoes the different phase transitions.[5] Phase diagram studies of the Bi_2O_3 -V_2O_5 system indicate that $Bi_4V_2O_{11}$ is the end member of a fairly extensive solid solution region.[7] The γ-phase varies from 70.4 mol% Bi_2O_3 to 66.7 mol% Bi_2O_3 while the conductivity gradually decreases with increasing Bi_2O_3 content.

Partial substitution of vanadium by other metallic ions is able to stabilize the high temperature γ-phase to room temperature.[1,6,8,9] As shown in Table II, a wide range of ions are able to accomplish stabilization and this series of materials has been termed BIMEVOX with the general formula, $Bi_4V_{2(1-x)}M_{2x}O_{11-3x}$. Recent studies on single crystals have established more clearly the nature of the phase transitions and the composition range required for stabilization.[10] Using copper-doped $Bi_4V_2O_{11}$ (BICUVOX) as a model system, two composition ranges were identified. For the range $0 \leq x \leq 0.06$, the room temperature phase is orthorhombic and isomorphic to α-$Bi_4V_2O_{11}$. For the range $0.07 \leq x \leq 0.12$, the room temperature phase is tetragonal, of the γ-$Bi_4V_2O_{11}$ form. In this composition range, the presence of a DSC peak at ≈ 500°C suggests that the γ-phase retained at room temperature is not precisely the same one as that which occurs at high temperatures.[10] DSC measurements also show that the phase transitions on heating and cooling have a marked hysteresis. Conductivity measurements have shown a similar type of dependence.[11]

The ability to retain the γ-type phase to room temperature has enabled the BIMEVOX series of materials to emerge as being the best oxygen ion conducting materials below 400°C. This behavior is clearly evident in Figure 2 where the

Table II. Stabilizers of the γ-$Bi_4V_2O_{11}$ Phase.

Ion	Minimum x to Stabilize*	Reference
Nb^{5+}	0.10	1
Ta^{5+}	0.10	1
Ti^{4+}	0.10	1,8
Ge^{4+}	α-phase	8
Zr^{4+}	0.10	1
Al^{3+}	0.10	1
Al^{3+}	α-phase	8
In^{3+}	0.10	1
Ni^{2+}	0.10	1,10
Cu^{2+}	0.07	1,10
Pd^{2+}	0.10	1
Zn^{2+}	0.10	8
Mg^{2+}	0.07	1
Li^{+}	0.10	8
Cu^{2+}/Ni^{2+}	0.05/0.05	9
Cu^{2+}/Zn^{2+}	0.05/0.05	9
Ni^{2+}/Zn^{2+}	0.05/0.05	9
Mo^{6+}/Cu^{2+}	0.05/0.05	9
Cu^{2+}/Pb^{2+}	0.10/0.03	9
Cu^{2+}/Pb^{2+}	0.125/0.03	9

* x is defined in the formula $Bi_4V_{2(1-x)}M_{2x}O_{11-3x}$

conductivity for the BICUVOX system is compared with zirconia, ceria and bismuth oxide-based oxygen ion conductors. Although the other systems are comparable to BICUVOX at 1000 K, it is clearly in this lower temperature range where BICUVOX achieves a distinct improvement in conductivity.

Researchers generally agree that among the various BIMEVOX compositions, the Cu-substituted materials exhibit the highest conductivities. These materials possess conductivities in the range of 1×10^{-3} S/cm at 300°C which is

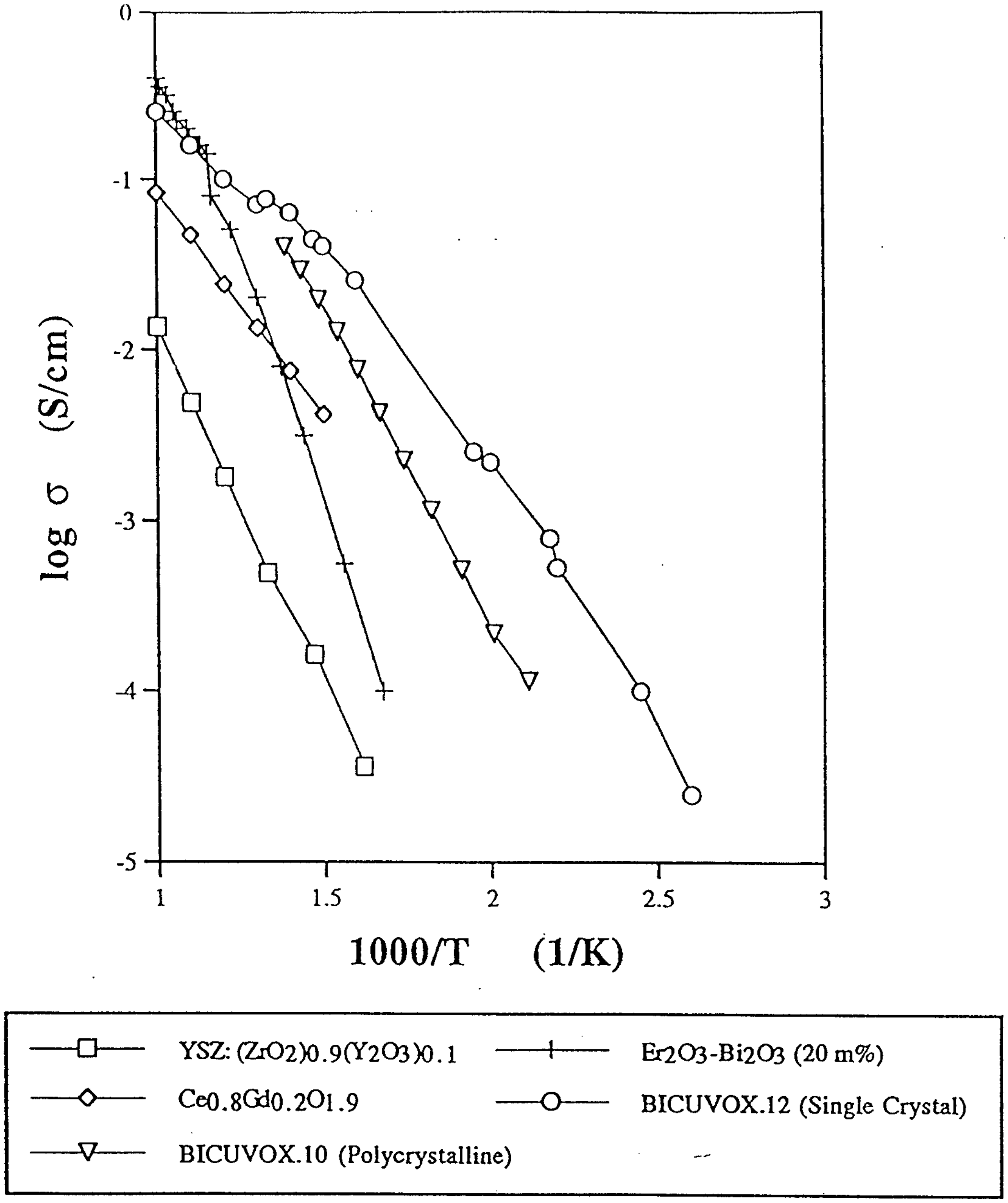

Figure 2. Comparison of Arrhenius plots for selected ionic conductors. The data for polycrystalline BICUVOX is from this study.

approximately 100 times greater than any other oxygen ion solid electrolyte in this temperature range. As mentioned previously, in order to assure complete stabilization, it is necessary to add at least $x = 0.07$. However, the $x = 0.1$

composition ($Bi_4V_{1.8}Cu_{0.2}O_{10.7}$) has been found to possess the optimum conductivity.[1,6] The reasons for this composition dependence have not been addressed. Other BIMEVOX compositions which exhibit comparable conductivity values are those where Ti^{4+} or Ni^{2+} substitute for V^{5+}.[8,10] There is also the report that a double substitution, Pb^{2+} for Bi^{3+} and Nb^{5+} for V^{5+}, produces a high conductivity material.[1]

Detailed studies of the structure-property relationships for BICUVOX compositions have appeared recently.[10] Two very interesting features have now been shown conclusively. First, single crystal studies of BICUVOX compositions indicate that ionic conductivity in these materials is highly anisotropic. The conductivity along the *ab* plane is 10^2 times greater than that along the *c*-axis. Thus, these materials can be considered as two-dimensional oxygen ion conductors as suggested by the structure shown in Figure 1. This is very different behavior than is observed in traditional fluorite-based oxygen ion conductors. Transport is likely to occur in the oxygen-deficient $VO_{3.5}\square_{0.5}$ layer as neutron diffraction studies have established that all the oxygen vacancies in the system are located in this layer.[12] It has been proposed that a ferroelectric-type displacement of V^{5+} along the *c*-axis away from an anion vacancy at an apical site lowers the energy barrier for O^{2-} transport.[1] The substituted Cu^{2+} ions will be coordinated by 4 coplanar oxygen atoms, leaving the apical oxygen sites vacant and facilitating O^{2-} transport between apical oxygen sites in the plane perpendicular to the *c*-axis.

The second feature recently established for these materials is the existence of order-disorder transitions.[10] High resolution X-ray diffraction studies of single crystals have shown that the room temperature phase is not the tetragonal γ-type but a highly complex incommensurate superstructure termed γ'. Below 510°C a partially ordered structure develops in which the periodicity is not commensurate with the main lattice. Thus, as temperatures decrease below 510°C, there is an increase in the activation energy for conduction. Above 510°C there is a progressive disorder which reduces the size of the ordered domains, shortens the coherence length and leads to lower activation energies for conduction.

A vital consideration for electrochemical applications of oxygen ion conductors is the issue of electronic conduction in these materials. The high oxygen conductivity of the doped-Bi_2O_3 systems is quite attractive, however, these materials are easily reduced and device applications are limited to oxygen pumps and sensors operating at higher oxygen concentrations (1-100%).[4] The BIMEVOX systems appear to have similar limitations. Bulk conductivity measurements show very slight changes with oxygen partial pressure, suggesting electronic transport numbers of a few percent.[13] These results are consistent with the potentiometric response and thermoelectric power measurements at reduced partial pressures.[13,14] In both of these cases, the results with stabilized-$Bi_4V_2O_{11}$ compositions deviated significantly from that expected for an ideal oxygen ion conductor. It is likely that electronic conduction arises from the valence change of the vanadium or bismuth components and not by the dopant used to stabilize the γ-phase.

The processing of BIMEVOX materials into high quality polycrystalline ceramics has received relatively little attention. Solid state reaction methods have been used to prepare the BICUVOX phase and the densities reported for sintered materials range from 72 to 92%.[11] In general, it is difficult to evaluate the quality of these materials as few details concerning the processing, sintering behavior or microstructure have been presented. The transport measurements of polycrystalline materials have been the subject of considerably more interest. In view of sample variability, it is not surprising that some samples show a significant hysteresis in conductivity between heating and cooling while others do not.[15] It does appear, however, that there is a change in slope in the Arrhenius curve for polycrystalline ceramics at ≈ 500°C. This is similar to the temperature range where single crystals exhibit order-disorder effects. An equivalent circuit model has been developed to simulate the observed impedance for BICUVOX ceramics .[16]

EXPERIMENTAL METHODS

BICUVOX powders with the nominal composition $Bi_4V_{1.8}Cu_{0.2}O_{10.7}$, were prepared using analytical grade Bi_2O_3, CuO, and V_2O_5. The samples were prepared by mixing appropriate amounts of the oxides, grinding, and then firing at 800°C for 8 hr in air. To ensure complete reaction, the materials were then ground and re-fired at 800°C. The reacted materials were attrition milled in water to achieve an appropriate particle size distribution for sintering. After drying, the powder was sifted through a 400 mesh sieve. These powders were then dry pressed into pellets using a single-action mechanical press under a uniaxial load of 3.4 x 10^5 Pa. The nominal pellet dimensions were 13 mm in diameter by 1.0 mm thick. Samples were then sintered in air at temperatures between 750 and 840°C for times between 1 min and 2 hr.

The powders and sintered pellets were characterized by a variety of techniques including X-ray diffraction (XRD), TGA and DTA. Particle size analysis of the attrition-milled powders was also obtained. Bulk densities of the sintered materials were determined by the Archimedes method using distilled water. Optical microscopy and scanning electron microscopy (SEM) were used to characterize the microstructures of the sintered pellets.

Complex impedance of the ceramic materials was measured using a computer-controlled HP Model 4284A precision LCR meter. A four-point impedance measurement technique was employed using a 0.1 Vrms test signal over the frequency range 20 Hz to 1MHz with 10 points per frequency decade. Sputtered gold films served as blocking contacts to the samples which were cut into parallelepiped specimens (13 x 1.7 x 1.0 mm^3) from the sintered BICUVOX disks. In this initial work, the impedance was measured only over the temperature range 200 to 450°C. Using a computer-controlled furnace, samples were heated to 450°C and measurements were taken in increments of 25°C during cooling. All measurements were carried out in air.

RESULTS AND DISCUSSION

Phase pure materials were produced by solid state reaction of the oxides. The XRD pattern (Figure 3) indicates the presence of no additional peaks other than those expected from the γ-phase of $Bi_4V_2O_{11}$. Thermal properties were consistent with those reported previously for BICUVOX.[11] There is no weight change on heating either the powders or the sintered disks to 600°C. These measurements also indicate that BICUVOX is air stable, does not adsorb moisture and does not change

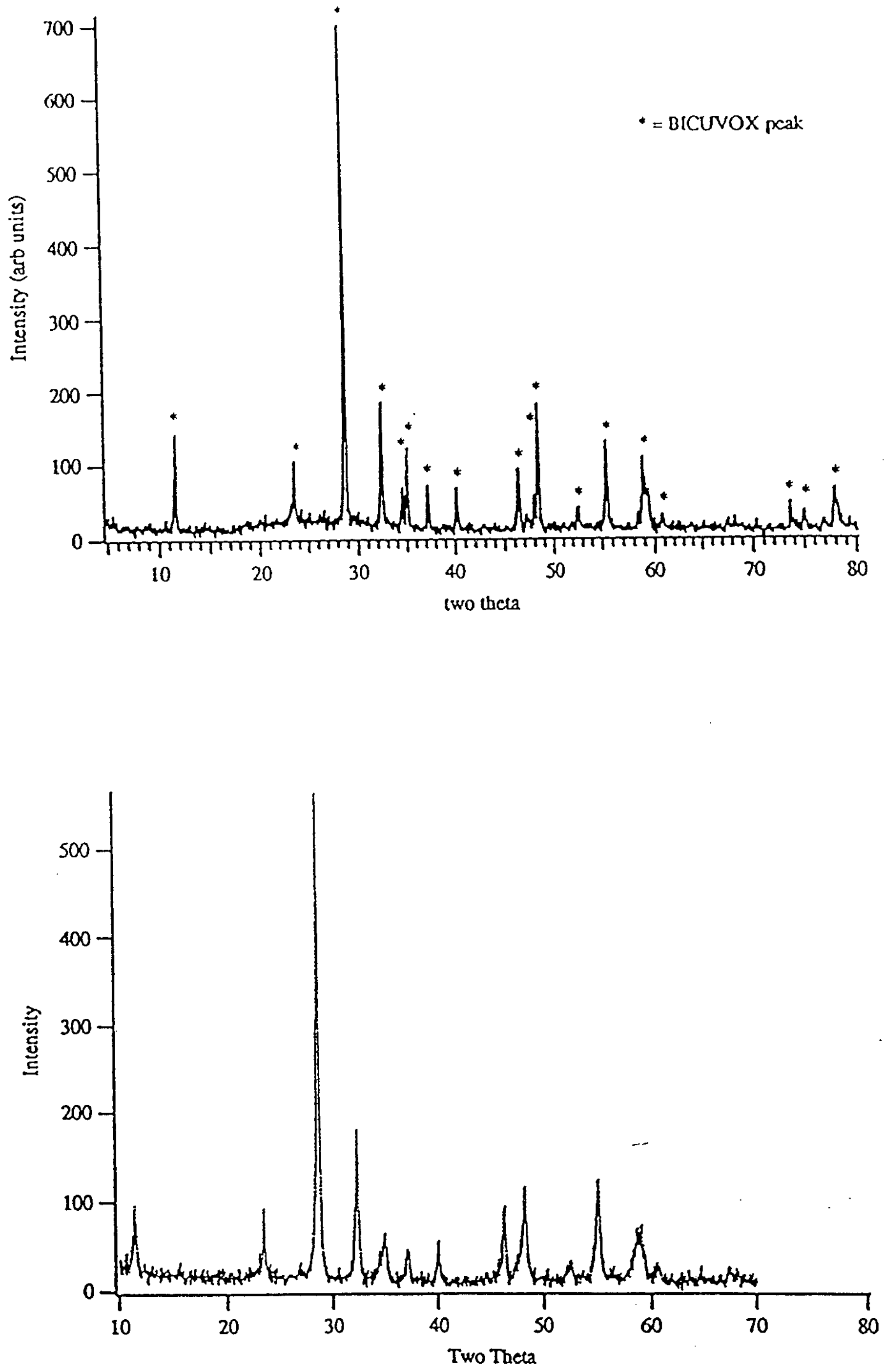

Figure 3. Powder X-ray diffraction patterns for the BICUVOX composition $Bi_4V_{1.8}Cu_{0.2}O_{10.7}$. Top: Sample prepared by solid state reaction of the oxide powders. Bottom: Sample prepared by the Pechini method.

its stoichiometry upon heating. The DTA scans (Figure 4) show evidence of the order-disorder transformation ($\gamma \rightarrow \gamma'$) on both heating and cooling at slightly below 500°C. There is a slight hysteresis effect which has been noted previously.[10]

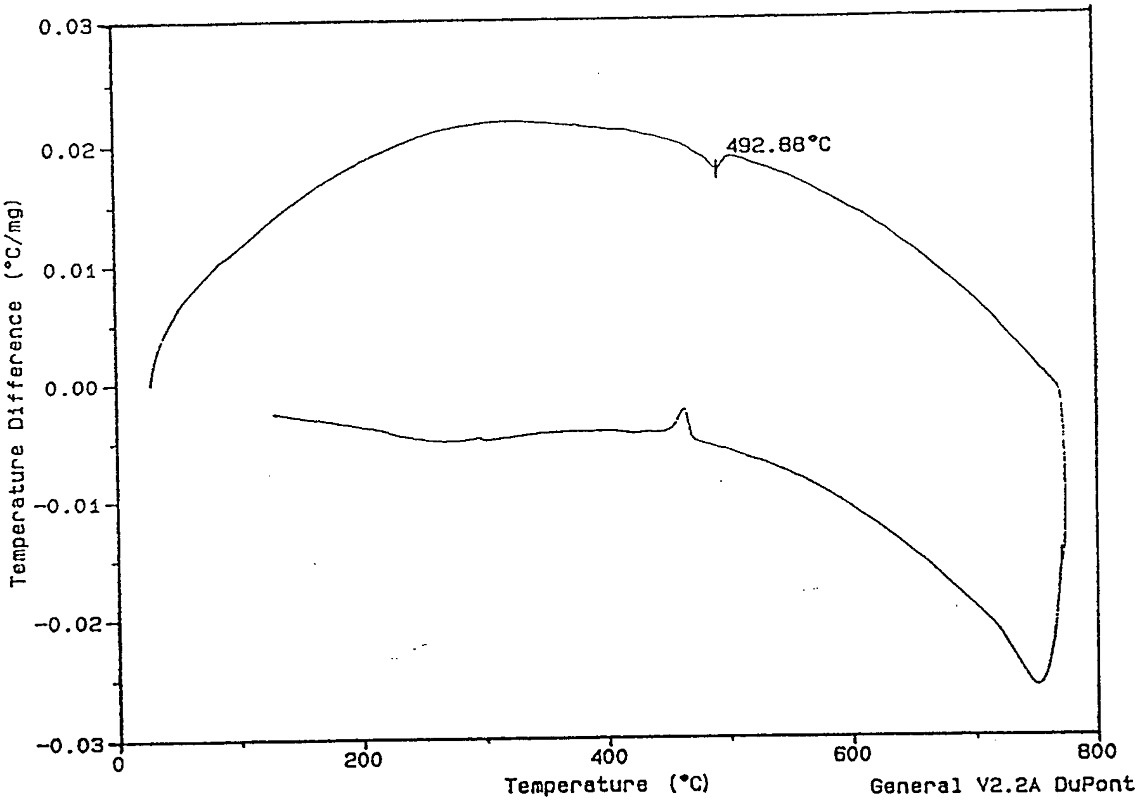

Figure 4. Differential Thermal Analysis (DTA) for the composition $Bi_4V_{1.8}Cu_{0.2}O_{10.7}$. The sample was heated in air at 10°C/min.

In addition to using solid state reactions, we have also synthesized BICUVOX powders by the Pechini method.[17] This approach involves forming a chelate between mixed cations with a hydroxycarboxylic acid. Upon heating to a moderate temperature (150 - 250°C) esterification occurs and a polymeric resin forms. In these first experiments, vanadium triisopropoxide, bismuth nitrate and copper nitrate were added to a solution of citric acid and ethylene glycol. The mole ratio of citric acid to metal ion was 2 and the ratio of citric acid to ethylene glycol was 1:4. The solution was heated to 150°C at which time it polymerized into a brown resin. On heat treatment to 450°C the single phase BICUVOX composition was obtained (Figure 3). This heat treatment temperature is some 300°C less than the solid state reaction approach. The crystallite size of the powders produced by the Pechini method are significantly finer and cause some broadening of the x-ray lines. The lower processing temperatures and finer crystallite size of the Pechini method make this approach worthy of continued investigation.

The sintering studies were carried out only on the powders prepared by the solid state reaction method. Attrition milling produced a bimodal particle size distribution with a primary maximum at 3 µm and a secondary maximum at 0.5 µm. 80% (volume) of the powders were less than 5 µm diameter and 20% were less than 1 µm.

The effects of sintering temperature and time on the density of BICUVOX ceramics are shown in Figure 5. The density values are based on a theoretical density of 7.84 g/cc. It is evident that these materials can readily be sintered to densities in excess of 95%. The temperature range seems flexible and high quality materials are obtained with sintering temperatures between 775°C and 820°C. The samples sintered at 840°C are clearly overfired. The effect of sintering time is not yet clearly established. Microstructure studies indicate that the high density materials have an average grain size in the range of 10µm. Figure 6 is an SEM photo of a sample with ≈ 90% density. The porosity of this sample is quite evident along with the presence of forming cracks. It is believed that the latter arise from powder aggregation effects. The microstructure is equiaxed and there is no evidence of liquid phase formation during sintering as was speculated previously.[15]

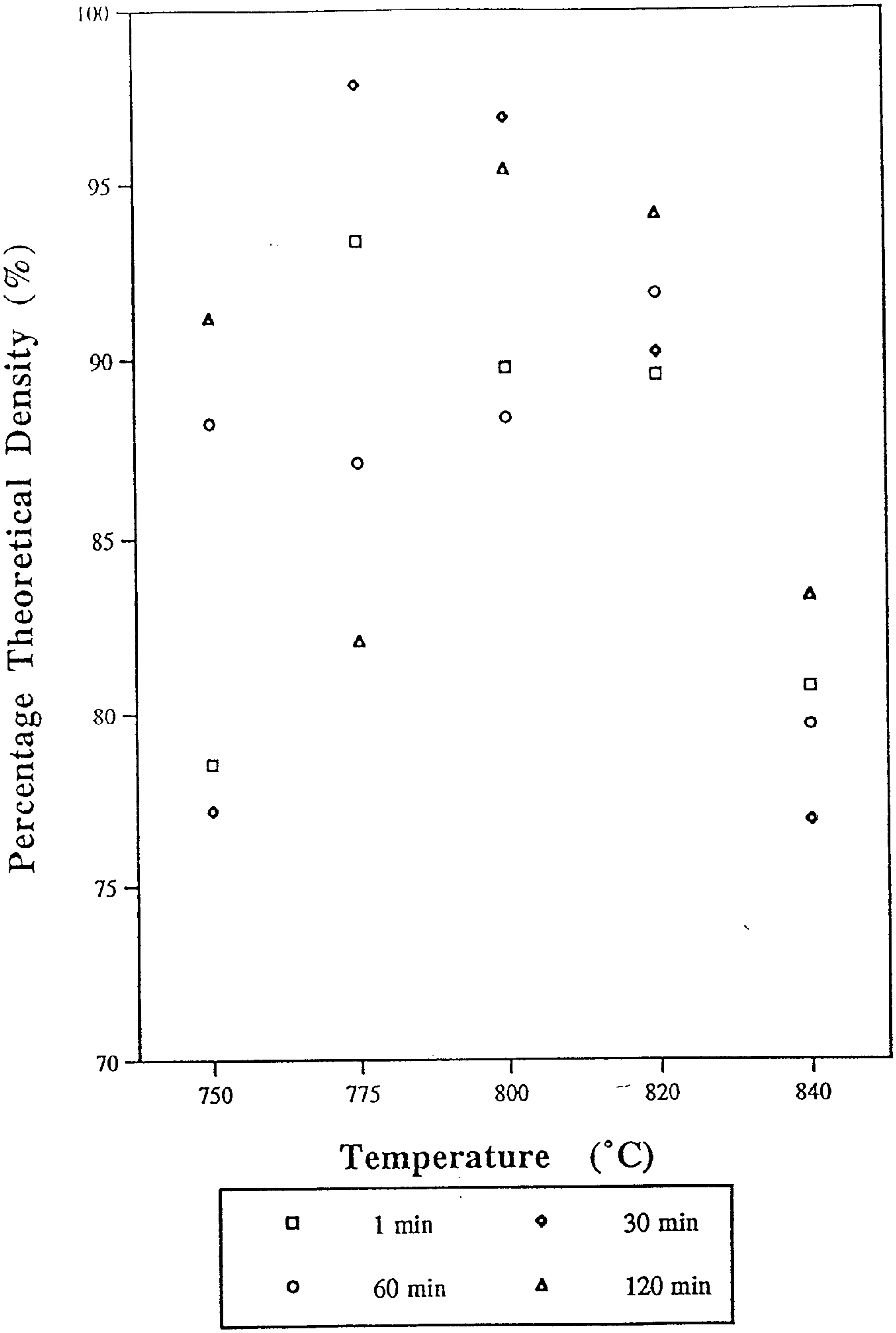

Figure 5. Effect of sintering temperature and time on the density of BICUVOX ceramics.

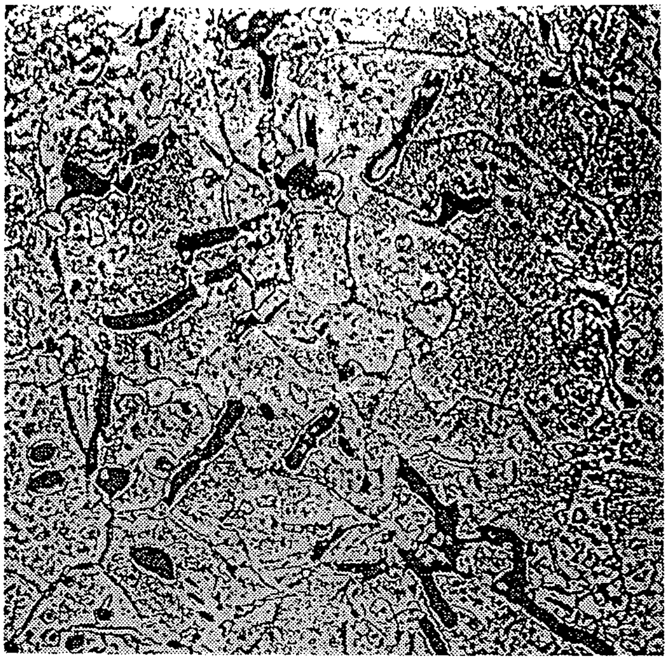

Figure 6. Microstructure of BICUVOX sample sintered at 800°C for 1 min. Magnification: 1700 X.

A representative impedance spectrum for a BICUVOX sample heated to 400°C is shown in Figure 7. A partially resolved semi-circular arc is present between 1 MHz and 5 kHz . At lower frequencies, the semi-circular arc transforms into a smaller, more poorly resolved semi-circular arc. The larger arc is associated with bulk electrolyte properties, while the smaller arc corresponds to electrode polarization phenomena.[18] The intersection of the larger and smaller arcs forms a local minimum, which nearly intersects the real axis and defines the resistive component of the total impedance. This resistive component, which includes both intragrain and grain boundary contributions, was used to derive the conductivity values as a function of temperature for the BICUVOX samples.

The temperature dependence of the BICUVOX conductivity is shown in Figure 8 for a series of ceramic samples sintered at 775°C. The good linearity of

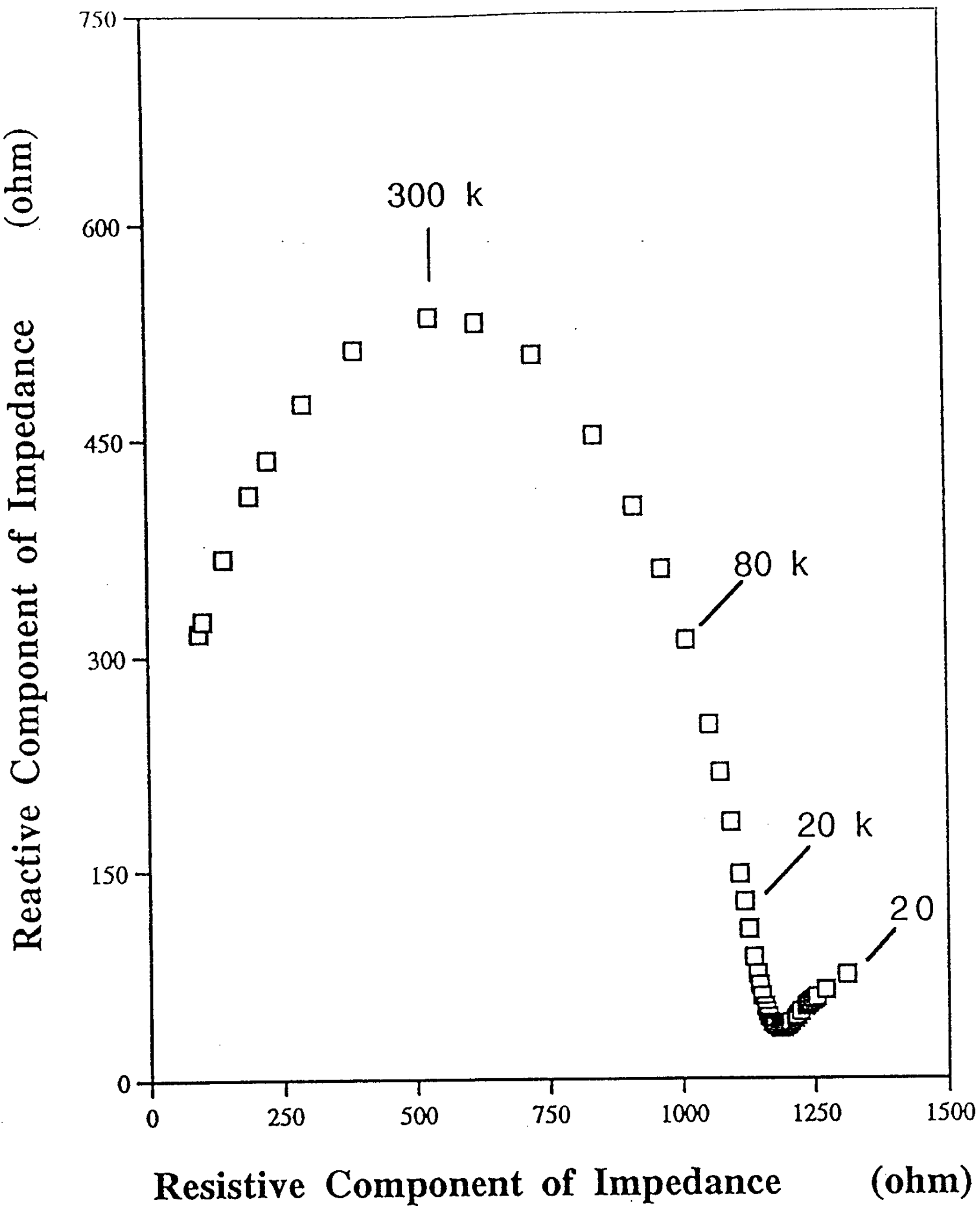

Figure 7. Complex impedance plot for BICUVOX sample at 400°C. Impedance was measured over the frequency range 20 Hz to 1 MHz.

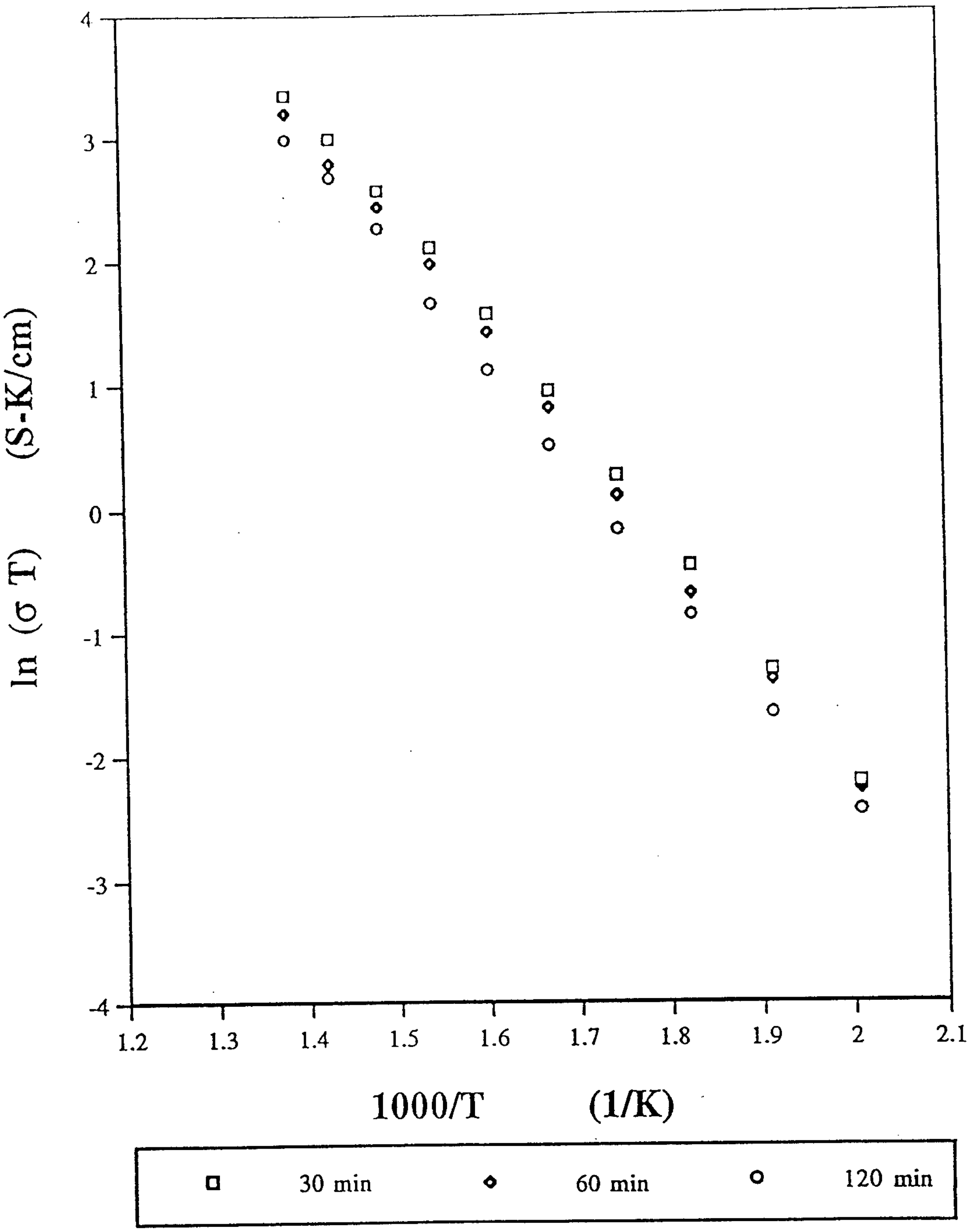

Figure 8. Conductivity-temperature plot for BICUVOX samples sintered at 775°C.

the plot indicates that the conductivity is well described by the Arrhenius relationship over this temperature range:

$$\sigma = \frac{\sigma_o}{T}\exp\left(-E_a/_{kT}\right) \tag{1}$$

where σ_o is the pre-exponential constant and E_a is the activation energy for conduction. It is not surprising that no change in slope is observed since the $\gamma \rightarrow \gamma'$ phase transformation does not occur until nearly 500°C. The behavior shown in Figure 8 is representative of all the BICUVOX ceramics prepared in this investigation; the activation energy for conduction is $\approx$ 0.75 eV and the conductivity at 400°C is in the range of 2 x 10^{-2} S/cm.

Table III lists the electrical properties, E_a and conductivity at 400°C, for a series of samples sintered under different conditions and possessing a variety of densities. With one exception, the activation energies are within ±10% and the conductivities at 400°C are within a factor of two. Thus, the electrical properties seem to be relatively independent of sample density. However, it is evident that additional results are necessary to fully verify this point. The results shown in Table III are quite consistent with those reported for BICUVOX ceramics by other groups.[15]

Table III. Properties of BICUVOX Ceramics.

	Sintering Conditions		Density (g/cc)	$\sigma_{400°C}$ (S/cm)	E_a (eV)
Sample	Temperature (°C)	Time (min)			
B	750	30	6.05	1.4 x 10^{-2}	0.64
D	750	120	7.15	9.5 x 10^{-3}	0.80
F	775	30	7.67	1.9 x 10^{-2}	0.76
H	775	120	6.44	1.4 x 10^{-2}	0.76
J	800	30	7.60	6.8 x 10^{-3}	0.77
L	800	120	7.48	5.2 x 10^{-3}	0.71
O	820	60	7.20	3.6 x 10^{-3}	0.67
P	820	120	7.38	8.6 x 10^{-3}	0.63

CONCLUSIONS

The bismuth vanadate compound, $Bi_4V_2O_{11}$, is the parent phase for a new family of oxygen ion conductors with conductivities 50 to 100 times greater than any other oxygen ion conductor in the 300°C temperature range. Stabilization of the high conductivity γ-phase is readily accomplished by substituting various metal ions for vanadium. These BIMEVOX compounds possess a layered perovskite structure and, contrary to traditional fluorite systems, O^{2-} transport is anisotropic. In addition, these materials exhibit order-disorder transitions at temperatures near 500°C. The high oxygen ion conductivity at low temperatures is attractive for lowering the operating temperature of electrochemical devices, however, the BIMEVOX materials exhibit some degree of electronic conduction at low oxygen partial pressures which may limit their application. The present study has shown that dense ceramics with the conductive BICUVOX composition can be prepared using standard ceramic processing approaches. Sample conductivities of $\approx 1 \times 10^{-2}$ S/cm at 400°C were obtained for a range of density values.

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REFERENCES

1. J.B. Goodenough, A. Manthiram, M. Paranthaman and Y.S. Zhen, Mat. Sci. Eng. **B12**, 357 (1992).
2. T.H. Etsell and S.N. Flengas, Chem. Rev. **70**, 339 (1970).
3. M.J. Verkerk and A.J. Burgraaf, J. Electrochem. Soc. **128**, 75 (1981).
4. I.C. Vinke, K. Seshan, B.A. Boukamp, K.J. de Vries and A.J. Burggraaf, Solid State Ionics **34**, 235 (1989).
5. F. Abraham, M.F. Debreuille-Gresse, G. Mairesse and G. Nowogrocki, Solid State Ionics **28-30**, 529 (1988).

6. F. Abraham, J.C. Boivin, G. Mairesse and G. Nowogrocki, Solid State Ionics **40/41**, 934 (1990).
7. C.K. Lee, D.C. Sinclair and A.R. West, Solid State Ionics **62**, 193 (1993).
8. V. Sharma, A.K. Shukla and J. Gopalakrishnan, Solid State Ionics **58**, 359 (1992).
9. R.N. Vannier, G. Mairesse, F. Abraham and G. Nowogrocki, Solid State Ionics **70/71**, 248 (1994).
10. E. Pernot, M. Anne, M. Bacmann, P. Strobel, J. Fouletier, R.N. Vannier, G. Mairesse, F. Abraham, G. Nowogrocki , Solid State Ionics 70/71, **259** (1994).
11. K. Reiselhuber, G. Dorner and M.W. Breiter, Electrochim. Acta **38**, 969 (1993).
12. M. Anne, M. Bacmann, E. Pernot, F. Abraham, G. Mairesse, and P. Strobel, Physica B **180/181**, 621 (1992).
13. T. Iharada, A. Hammouche, J. Fouletier, M. Kleitz, J.C. Boivin and G. Mairesse, Solid State Ionics **48**, 257 (1991).
14. A.J. Francklin, A.V. Chadwick, J.W. Couves, Solid State Ionics **70/71**, 215 (1994).
15. F. Krok, W. Bogusz, P. Kurek, M. Wasiucionek, W. Jakubowski and J. Dygas, Mat. Sci. Eng. **B21**, 70 (1992).
16. J. Dygas, F. Krok, W. Bogusz, P. Kurek, K. Reiselhuber and M.W. Breiter, Solid State Ionics **70/71**, 239 (1994).
17. M.P. Pechini, U.S. Patent No. 3,330697 (1967).
18. J. E. Bauerle, J. Phys. Chem. Solids **30**, 2657 (1969).