Crystal Growth and Conductivity Investigations on $BiVO_4$ Single Crystals

[1]L. Hoffart, [1]U. Heider, [1]R. A. Huggins, [1]W. Witschel, [2]R. Jooss and [2]A. Lentz
[1]Center for Solar Energy and Hydrogen Research, 89081 Ulm, Germany
[2]Department of Inorganic Chemistry, University of Ulm, 89069 Ulm, Germany

Abstract. Some oxides with the scheelite structure are well known mixed ionic and electronic conductors. This structure family, with the general composition ABO_4, can be described as a layer structure derivative of the fluorite structure. The relations between the structural and the electrical transport properties of these materials have been investigated. The model system used in this work was $BiVO_4$, which shows both electronic and ionic conduction.

Single crystals of bismuth vanadate ($BiVO_4$) were grown using the Czochralski technique. Single crystal boules up to 55 mm in diameter and up to 30 mm long were produced. The crystallographic orientation was determined by the Laue method, and they were cleaved along [001] planes and polished to optically perfect cubes with an edge length of 5 mm.

Two-point ac impedance measurements in the temperature range between 550°C and 700°C were performed. The conductivities were measured as a function of the crystal orientation and showed strong anisotropy as expected from the crystal structure.

1. Introduction

Current approaches to oxygen-conducting solid oxide fuel cells are based upon the use of an yttrium-doped zirconia electrolyte (YSZ), Ni/ZrO_2 cermet negative electrodes and perovskite positive electrodes. Absorption and solid state transport of oxygen play important roles in the cathodic reaction of oxygen in oxygen-based electrochemical systems. Scheelite materials with the general formula ABO_4 are well known for their catalytic behavior during oxidation reactions [1]. It is now well established that the mechanism of these reactions involves oxygen transport in the bulk catalyst [2]. Thus it seemed worthwhile to explore the solid state transport properties of materials in this family, as they might also be useful solid oxide fuel cell components.

Scheelites exist in a wide range of compositions and have a rather open crystal structure that can be simply thought of as a modification of the fluorite structure with an ordered arrangement of the two cations. In the ideal case, the cation sublattice forms an FCC array and the anions are located in tetrahedrally-coordinated interstitial positions. However, because of the difference in the A and B cation sizes, there is a corresponding distortion of the anion lattice. The larger A cations show 8-fold coordination (4 near, and 4 more distant), and the smaller B cations are 4-fold (tetrahedrally) coordinated. This results in a structure that is no longer isotropic, and can best be described as nearly tetragonal, containing close-packed bands or ribbons of corner-sharing BO_4 tetrahedra extending in both the a and b directions.

Bismuth vanadate, $BiVO_4$, was chosen as a model material to study, since Bi-containing scheelites and related materials are known to be particularly active oxidation catalysts [1]. $BiVO_4$ has been reported to be a mixed conductor [3,4], with appreciable electronic conductivity observed at high temperatures. The electronic conductivity has been variously reported as either n-type or p-type [3-5].

The scheelite structure shows a regular series of ribbons of oxygen ions. This layered structure is anisotropic. The crystallographic direction of the layers is clearly in the a - b plane. In the c direction no regular planes can be seen. A schematic picture of this can be seen in Fig. 1.

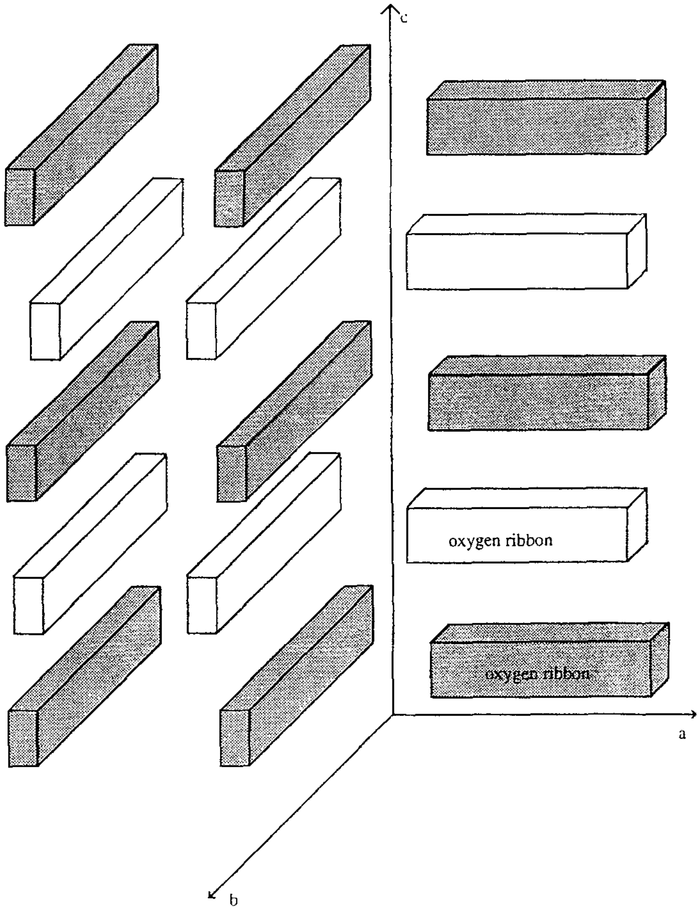

Fig. 1. Directions of the oxygen ion ribbons in the scheelite structure

This two-dimensional feature of this structure should be reflected in anisotropy in some of its physical properties. For example, the ionic conductivity should be significantly different in the a and b directions from that in the c direction.

In this description of the monoclinic scheelite structure the crystallographic c axis is defined to be the longest axis of the unit cell. The reason for the change of the longest b axis to the longest c axis in the monoclinic modification was the transformation of the monoclinic clinobisvanite stucture into the tetragonal structure at higher temperatures. In the tetragonal structure the a and b axis are of the same length and the c axis is the largest one. The conductivity investigations were done in the temperature range where the tetragonal structure is the stable one.

$BiVO_4$ melts congruently at 1219 K and the phase diagram of the Bi_2O_3 - V_2O_5 system has been described by several working groups [6-9]. Bierlein and Sleight [10] reported that slow cooling from the melt gave small crystals with extensive twinning, which can be related to the ferroelastic phase transition upon cooling at 528 K. In 1979 Sleight et. al. grew large crystals of $BiVO_4$ by the Czochralski method under 1 atm of flowing O_2 [11]. The crystal structure was refined from neutron and x-ray powder data by the Rietvield method at different temperatures [11-13]. Space groups of $I4_1/a$ above and $I2/b$ below 528 K were found. The BiO_4 polyhedra are regular above the ferroelastic transition (the undistorted Scheelite structure) but becomes significantly distorted below the transition. A discussion of the structural mechanism of the phase transition is presented in [13], indicating that the lone electron-pair on the Bi^{3+} ion plays a prominent role.

The present paper presents the first experimental study of the transport properties in $BiVO_4$ single crystals.

2. Experimental Procedures

2.1. *Crystal Growth and Crystal Characterization.*

$BiVO_4$ single crystals were grown by the conventional resistance heated Czochralski technique under atmospheric pressure in air. The feed material was high purity Bi_2O_3 (99,9%, Aldrich) and V_2O_5 (99,9%, Aldrich). The materials were first weighed out (Bi_2O_3 : V_2O_5 = 0,48 mol% : 0,52 mol%), mixed thoroughly and then charged into a platinum crucible with a volume of about 500 ml which was situated inside alumina insulation at 1214 K. The crucible was stationary and a Pt wire, which was used as a seed, was rotated at about 8 rpm. The pulling rate was maintained at 1 mm/h. A boule about 55 mm in diameter and 30 mm in length was obtained. This was slowly cooled to room temperature over a period of nearly 12 hours. X-ray examination indicated that the growth axis was <100>. The result was a transparent brownish-yellow crystal.

When using a small crystal oriented in the <001> direction as a seed, twinned crystals grew in all cases.

Growth times longer than one week under air invariably produced black crystals due to oxygen deficiency. The black colour is generally associated with the partial reduction of the vanadium cations in other vanadium compounds [14,15]. Milan [16] has shown that molten

V_2O_5 loses oxygen in air according to eq. (1):

$$V_2O_5 \rightarrow V_2O_{5-x} + \frac{x}{2} O_2 , \qquad 0 < x < 2 \tag{1}$$

For large values of x, a suboxide forms whose amount increases with increasing temperature. We have identified black crystals that form in $BiVO_4$ under these conditions as VO_2 by means of X-ray diffraction. The amount of VO_2 formation appeared to increase as a function of the growth time, as the amount of black coloration was observed to vary in the range of the applied growth rates.

The as-grown crystal boules of this compound generally contained numerous twinning domains due to the ferroelastic transition during cooling, as previously described [10]. However, twin-free crystal cubes 5 mm or less on a side could be cut from the boules for examination. The boules were cleaved with the help of a sharp chisel to give apparently perfect [001] cleavages. The [100] and [010] planes were cut perpendicular to the cleavage surface. The surfaces were polished with diamond paste to a 1/5 µm finish. The orientations of the surfaces were determined by use of the Laue method.

Optical microscopy revealed very good optical transparency without any macroscopic defects.

The crystals have also been characterized by X-ray diffraction (Stoe Stadi P powder diffraction system and 4 circle diffraction system). The resulting parameters were almost in accordance with the literature, as previously mentioned. It was established that the selected crystals were single phase clinobisvanite $BiVO_4$, for a = 5.1935 (3) Å, b = 5.0898 (3) Å, c = 11.6972 (8) Å and g = 90.387° (4) [7,8].

2.2. Conductivity Measurements. Conductivity measurements were performed using impedance spectroscopy. A single crystal (cubic shape) was oriented in the a, b and c directions and platinum electrodes were applied by RF sputtering on the corresponding sides (surface area 0.15 - 0.13 cm^2). After the measurements the surfaces were cleaned and polished again. The conductivity measurements were made in all three crystallographic directions.

To obtain the total conductivity ac impedance spectroscopy (ZAHNER IM5d) was used in a frequency range between 100 mHz and 1 MHz with an ac voltage amplitude of 20 mV. The temperature range investigated was between 400 and 700°C. The measurements were done in air in a 2-point measurement cell with platinum leads. A constant contact on the sample is produced by the use of springs.

3. Results and Discussion

The complex plane plot of the total conductivity in the <100> direction (parallel to the a axis) shows a shift of the first semicircle with increasing temperature to higher frequencies (Fig. 2).

A second semicircle was only visible at the lower temperatures. The general form of the complex plane plot showed no change with temperature. The temperature-dependent decrease of the real component of the impedance indicated an increasing total conductivity at higher temperatures.

These data are shown in the Arrhenius plot in Fig. 3. The conductivity in this crystallographic direction was found to be about 5 x10^{-6} S/cm at 450°C and about 5.4 x10^{-4} S/cm at 700°C. The activation energy of the total conductivity was found to be 1.5 eV from the slope of this linear relation.

The conductivity measurements in the <010> di-

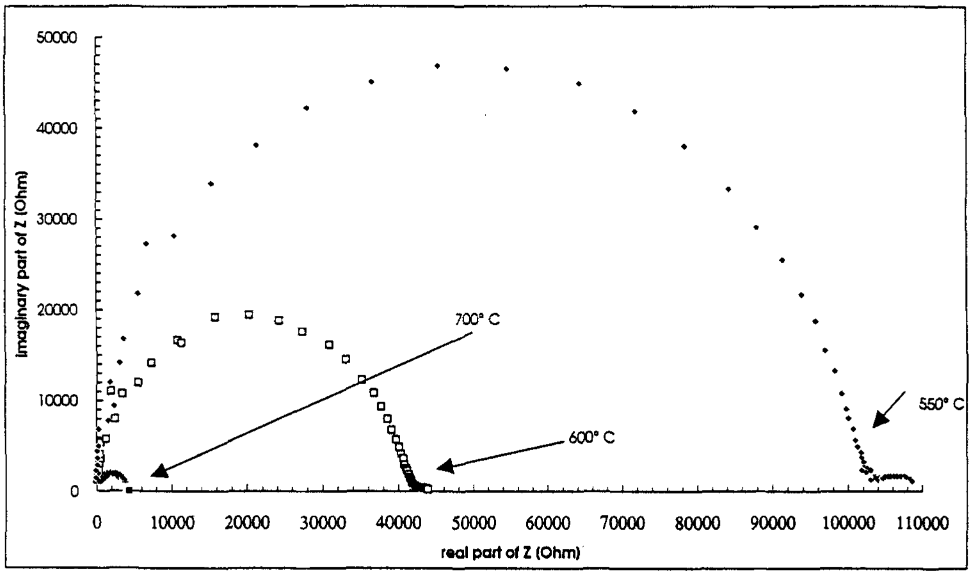

Fig. 2. Complex plane plot of $BiVO_4$ single crystal in the <001> direction as a function of the temperature

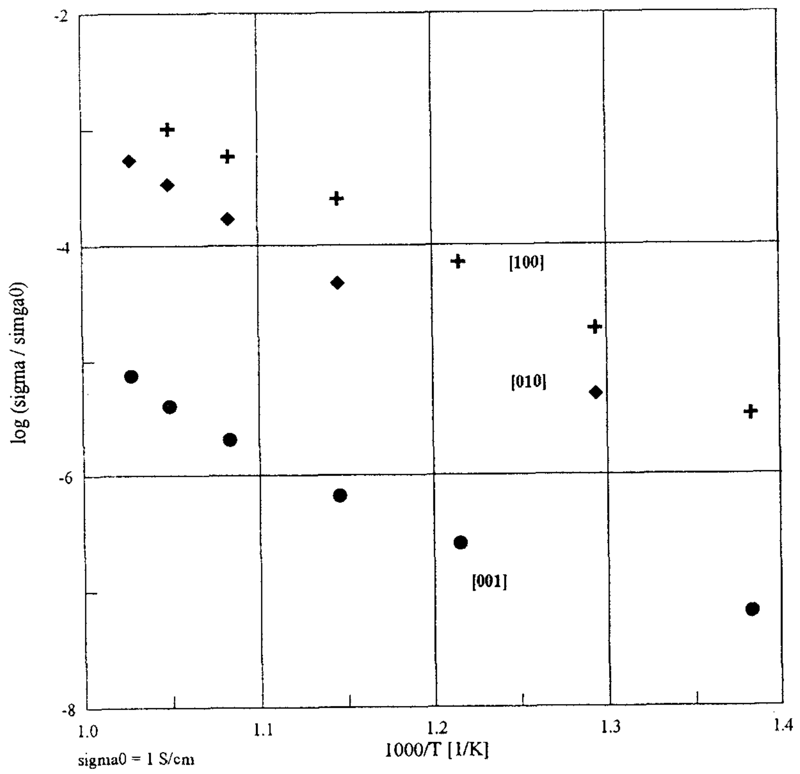

Fig. 3. Arrhenius diagram of the conductivity measurements on $BiVO_4$ single crystal

rection showed similar behavior on the complex plane plot. The measured conductivity at 450°C is about 2.9 $\times 10^{-6}$ S/cm and is about 1 $\times 10^{-3}$ at 700°C. The activation energy for the charge transport process in the b direction was found to be the same as in the <100> direction. These data are also presented in Fig. 3.

The investigation of the conductivity in the <001> direction gave a similar complex plane plot as in the other two cases. However, the total conductivity in this direction was found to be about 1 - 2 orders of magnitude lower than along the other two axes. At 450°C a value of 6.4 $\times 10^{-8}$ S/cm was found and at 700°C the conductivity increased to 7.3 $\times 10^{-6}$ S/cm.

The atomistic mechanism for the transport of the mobile ions along the bands of interconnected tetrahedra remains to be determined.

4. Conclusions

The scheelite structure shows anisotropic charge transport behavior. The ionic conductivity is considerably higher in the crystallographic a - b plane than parallel to the c - axis. The calculated activation energies are different. The activation energy in the a - b plane is about 1.5 eV, whereas it is about 1.2 eV in the c - direction.

These results can be correlated with the anisotropic crystal structure. The continuous bands or ribbons of interconnected tetrahedra in the a-b plane of the scheelite structure provide paths for the motion of oxygen ions. This type of structural feature is not present in the <001> direction.

5. Acknowledgements

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