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ELECTRICAL CHARGE TRANSPORT IN
SINGLE CRYSTAL CALCIUM TUNGSTATE

by

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ABSTRACT

A combination of a.c. and d.c. electrical conductivity measurements was used to characterize the charge transport in single crystals of CaWO_4 which were equilibrated with H_2 - H_2O -Ar gas mixtures. Measurements were made over the temperature range from 900°C to 1300°C and the $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ range from 0.02 to 3.0. The a.c. conductivity at 1000°C varied from 51.4×10^{-6} to 5.89×10^{-6} mho/cm for $P_{\text{H}_2\text{O}}/P_{\text{H}_2} = 0.02$ and 2.0, respectively; the d.c. conductivity changed from 51.0×10^{-6} to 5.42×10^{-6} mho/cm under the same experimental conditions. The partial logarithmic derivative of d.c. conductivity with respect to the water-to-hydrogen gas pressure ratio was $-1/2$ between 1000°C and 1300°C . The transference number of electrons varied from 0.99 to 0.92 at 1000°C for $P_{\text{H}_2\text{O}}/P_{\text{H}_2} = 0.02$ and 2.0 respectively, and independent measurements of the transference number of oxygen gave values of 0.04 to 0.07 over the same range of experimental conditions. All of the results may be described with a paired defect model of oxygen vacancies and oxygen interstitials (majority carriers) and minority electrons.

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I. INTRODUCTION

Stoichiometric ternary oxide compounds may be represented by chemical formulas of the type $A_m B_n O_p$ where m, n, and p are integers. In reality, integral values for these subscripts are nearly impossible to obtain due to the presence of point defects, such as interstitial ions and vacant lattice sites. Compounds in which these subscripts vary from integral values have an excess or deficiency of one or more components and are referred to as non-stoichiometric compounds.

Since lattice defects may significantly affect the electrical properties of matter, a great deal of work has been done to characterize the defect structures of binary metallic oxides. Such studies were extended to ternary oxides by Schmalzried and Wagner¹, who derived defect equilibria in AB_2O_4 compounds. Walters and Grace^{2,3} and George and Grace^{4,5} applied the theory to ABO_3 compounds and performed experimental work with cubic perovskites.

The purpose of this work is to develop information about the defect structure of the ternary oxide, ABO_4 . Experimental work was carried out on single crystal calcium tungstate, which is a tetragonal compound referred to as scheelite.

II. EXPERIMENTAL PROCEDURE

Three types of measurements were made to characterize the electrical conductivity of calcium tungstate. All of these experiments were conducted with single crystal samples which were equilibrated in situ with H_2O-H_2-Ar gas mixtures. Alternating current measurements were made between platinum

electrodes to obtain the total conductivity of the sample; d.c. measurements were made between platinum electrodes to obtain the electronic contribution to the total conductivity; and d.c. measurements were made between platinum and yttria-thoria electrodes to obtain the partial conductivity of oxygen.

In addition, transient, d.c. conductivity measurements were made between platinum electrodes to obtain a chemical diffusion coefficient necessary to describe the process of changing crystal stoichiometry. The measurements were made as the crystal moved from an initial equilibrium state to a final equilibrium state after the introduction of a small step function in the water pressure in the surrounding gas phase.

(1) Sample Preparation

Single crystal slabs of calcium tungstate approximately 7 x 9 x 1.8 mm were polished on silk polishing cloth with one micron alumina and were painted successively with Engelhard 6082 platinum paste and fired at 800°C to form a platinum guard ring and center electrode on one side of the sample. For those measurements made between platinum electrodes the opposite face was completely platinized. For those measurements made between platinum and yttria-thoria electrodes the opposite face was held in mechanical contact with a 10 mm diameter x 6 mm thick yttria-thoria pill which had been polished on 4/0 emery paper. A typical impurity analysis for the CaWO_4 crystals used in this work is given in Table I.

Electrical contacts to the sample were made with 0.010" Pt-30% Rh alloy wires, and temperature was measured with two Pt-6% Rh:Pt-30% Rh thermocouples placed within 1 cm of the sample. Fig. 1 shows a schematic diagram of the sample, wiring, and sample holder which was used for all measurements.

Table I. Spectrographic Analysis of Single Crystal Calcium Tungstate

Impurity	ppm by Weight	Impurity	ppm by Weight
Al	10	Nd	<100
Ba	< 1	Ni	< 10
Fe	<10	Pt	< 10
Mg	< 3	Rh	< 10
Mo	30	Si	< 5
Na	70	Sr	< 50

(2) Electrical Measurements

Guarded a.c. measurements were made with a Wayne-Kerr B221 Mk-III transformer ratio arm bridge. Preliminary measurements showed that there was no frequency dependence over the range from 1000 to 20,000 Hz; therefore, all a.c. measurements were made at 1592 Hz which is the frequency of the bridge's internal power supply. Conductance was read directly from the bridge at balance and was converted to conductivity by multiplying by L/A , where L is the sample thickness and A is the area of the guarded center electrode.

Direct current measurements were made by placing a constant voltage in the range of 100-200 mv across the sample and measuring the current flowing through the sample by monitoring the voltage drop across a 1% precision wire-wound resistor in series with the sample. The sample was ohmic in this region. The precision wire-wound resistor was selected so that its resistance was less than 1% of the sample resistance, and the sample was guarded by connecting the guard ring to the output side of the constant voltage source to maintain the guard ring at the same potential as the working electrode.

Transient d.c. measurements between porous platinum electrodes were made by equilibrating the crystal with a given P_{H_2O}/P_{H_2} ratio, introducing a step function in the P_{H_2O}/P_{H_2} ratio over the crystal, and continuously recording the sample current until equilibrium with the new P_{H_2O}/P_{H_2} was reached.

III. RESULTS

Data on the a.c. and steady state d.c. conductivity as a function of P_{H_2O}/P_{H_2} ratio and temperature are shown in Figs. 2 and 3, respectively. Single crystal samples from four different boules with different orientations were used to obtain this data. Data from both the [110] direction and [001] direction formed a single population, and the least squares slopes and other statistical information calculated from these data appear in Table II A&B for the a.c. and d.c. cases, respectively.

Data taken from Figs. 2 and 3 were used to obtain the dependence of a.c. and d.c. conductivity on reciprocal temperature which appears in Figs. 4 and 5, respectively. The lines in these two figures were drawn according to the least squares parameters listed in Table II C.

The steady state oxygen conductivity at 1000°C as determined by experiments with yttria-thoria electrodes is shown by the solid line in Fig. 6 which was drawn according to the statistics in Table II D. The yttria-thoria blocking electrodes used in these experiments were supplied by Rapp from the population of samples reported by Patterson, Bogren, and Rapp⁶. Data from Patterson et al. were used to correct for electronic leakage and obtain the oxygen conductivity which is shown by the dashed line in Fig. 6.

To obtain the chemical diffusion coefficient Fick's second law was solved for a slab with the boundary conditions corresponding to linear concentration profiles at $t = 0$ and $t = \infty$. The solution to Fick's second law for the average electron concentration yielded

$$\frac{\bar{C}(t) - C(\infty)}{C(0) - C(\infty)} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp[-(2n+1)^2 \pi^2 D t / 4 \ell^2] \quad (1)$$

where 2ℓ is the sample thickness. The transient d.c. conductivity data may be put in the form of $\frac{\bar{\sigma}(t) - \sigma(\infty)}{\sigma(0) - \sigma(\infty)}$, and the technique described by George and Grace⁴ may be employed to obtain values of the chemical diffusion coefficient from Eq. (1).

The transient d.c. data taken in the [001] direction for step functions from low-to-high P_{H_2O}/P_{H_2} ($1 \lesssim P_{H_2O}/P_{H_2} \lesssim 3$) are shown in Figure 7. This line was drawn according to the statistics listed in Table II E. The activation energy for the process of diffusion between two equilibrium states is 6.3 ± 1.3 kcal/mole at an average P_{H_2O}/P_{H_2} of approximately 2.0.

Table II. Statistical Analysis of Conductivity and Diffusion Data

A. A.C. Conductivity Data (Fig.2.)

<u>Temp, °C</u>	<u>Slope*</u>	<u>Intercept</u>	<u>$\ln \sigma^*$</u>
900	-0.372 ± 0.017	-13.798	-13.433 ± 0.026**
1000	-0.470 ± 0.007	-11.715	-11.207 ± 0.009
1100	-0.484 ± 0.007	- 9.699	- 9.102 ± 0.011
1200	-0.454 ± 0.014	- 7.878	- 7.410 ± 0.018
1300	-0.454 ± 0.029	- 6.563	- 6.213 ± 0.032

B. D.C. Conductivity Data (Fig.3.)

<u>Temp, °C</u>	<u>Slope*</u>	<u>Intercept</u>	<u>$\ln \sigma^*$</u>
900	-0.369 ± 0.015	-13.825	-13.470 ± 0.024
1000	-0.487 ± 0.010	-11.788	-11.256 ± 0.014
1100	-0.492 ± 0.009	- 9.712	- 9.139 ± 0.013
1200	-0.471 ± 0.015	- 7.879	- 7.377 ± 0.019
1300	-0.448 ± 0.026	- 6.543	- 6.191 ± 0.030

C. A.C. and D.C. Conductivity Data (Figs. 4 & 5.)

<u>Pressure Ratio</u>		<u>Slope*</u>	<u>Intercept</u>	<u>$\ln \sigma^*$</u>
$\frac{P_{H_2O}}{P_{H_2}} = 1.0$	A.C.	-34.131 ± 0.514	-15.183	-10.416 ± 0.039
	D.C.	-34.100 ± 0.567	-15.163	-10.412 ± 0.043
$\frac{P_{H_2O}}{P_{H_2}} = 0.1$	A.C.	-34.512 ± 0.338	-16.512	- 9.372 ± 0.026
	D.C.	-34.758 ± 0.425	-16.692	- 9.377 ± 0.032

Table II. (cont.d)

D. D.C. Conductivity Data with Yttria-Thoria Electrode (Fig.6.)

<u>Temp, °C</u>	<u>Slope*</u>	<u>Intercept</u>	<u>$\ln \sigma^*$</u>
1000	-0.152 ± 0.048	-13.254	-13.021 ± 0.069
1000 (Corrected Line)	-0.35	-14.45	- - -

E. Diffusion Data (Fig.7.)

<u>Pressure Ratio</u>	<u>Slope*</u>	<u>Intercept</u>	<u>$\ln D^*$</u>
$\frac{P_{H_2O}}{P_{H_2}} \approx 2$	-3.158 ± 0.645	-10.903	-13.202 ± 0.039

* is (one estimated standard deviation)

** σ is given in mho/cm; D is given in cm^2/sec .

IV. DISCUSSION

To understand the defect structure of calcium tungstate it is helpful to use the method of Schmalzried and Wagner¹ to generate the following standard defect equilibria for the compound ABO_4 . These have been written in the notation used by Kröger⁷ with dots and primes denoting positive and negative charges, respectively:

In addition, the crystal-gas equilibria given by

for which

$$K_9 = (P_A/P_B)^2 (P_{H_2O}/P_{H_2})^4 [B_I^{''''''}] / [A_I^{''}]^3 \quad (9')$$

and

for which

$$K_{10} = (P_{H_2O}/P_{H_2}) [V_O^{''}] [e']^2 \quad (10')$$

were also used.

The equilibrium constants for Equations 2 through 10 were put in logarithmic form and differentials were taken to obtain the following:

$$d\ln[V_A'] + d\ln[V_B'''''] + 3d\ln[V_O''] = 0 \quad (11)$$

$$d\ln[V_A'] + d\ln[A_I''] = 0 \quad (12)$$

$$d\ln[V_B'''''] + d\ln[B_I'''''] = 0 \quad (13)$$

$$d\ln[V_O''] + d\ln[O_I'] = 0 \quad (14)$$

$$d\ln[V_B'''''] + d\ln[A_I''] - d\ln[A_B'''] = 0 \quad (15)$$

$$d\ln[V_A'] + d\ln[B_I'''''] - d\ln[B_A'''] = 0 \quad (16)$$

$$d\ln[\oplus] + d\ln[e'] = 0 \quad (17)$$

$$2d\ln(P_A/P_B) - 4d\ln(P_{H_2O}/P_{H_2}) + d\ln[B_I'''''] - 3d\ln[A_I''] = 0 \quad (18)$$

$$d\ln(P_{H_2O}/P_{H_2}) + d\ln[V_O''] + 2d\ln[e'] = 0 \quad (19)$$

Majority defect pairs were selected to obtain the final differential logarithmic equation needed to solve the system of linear equations and to obtain values for the partial logarithmic derivative of majority defect concentration and electron concentration with respect to P_{H_2O}/P_{H_2} ratio at constant total pressure, temperature, and P_A/P_B . This has been done for all possible pairs of fully ionized defects and the results are listed in Table III.

Table III. Partial Logarithmic Derivatives for Fully Ionized Defects in ABO_4 Compounds

Paired Ionic Defects and Minority Electrons		
Majority Paired Defects	$\left[\frac{\partial \ln[i]}{\partial \ln \frac{P_{H_2O}}{P_{H_2}}} \right] \frac{P_A}{P_B}, P, T$	$\left[\frac{\partial \ln[e']}{\partial \ln \frac{P_{H_2O}}{P_{H_2}}} \right] \frac{P_A}{P_B}, P, T$
$A_I^{\bullet\bullet}, A_B^{\bullet\bullet\bullet\bullet}$	-4/3	-1/3
$A_I^{\bullet\bullet}, V_B^{\bullet\bullet\bullet\bullet\bullet}$	-1	-1/2
$B_I^{\bullet\bullet\bullet\bullet\bullet}, A_B^{\bullet\bullet\bullet\bullet}$	-4/5	-1/5
$A_B^{\bullet\bullet\bullet\bullet}, V_O^{\bullet\bullet}$	-2/3	-1/6
$A_I^{\bullet\bullet}, O_I^{\bullet\bullet}$	-1/2	-3/4
$V_B^{\bullet\bullet\bullet\bullet\bullet}, V_O^{\bullet\bullet}$	-1/4	-3/8
$A_I^{\bullet\bullet}, V_A^{\bullet\bullet}$	0	-1
$O_I^{\bullet\bullet}, V_O^{\bullet\bullet}$	0	-1/2
$B_I^{\bullet\bullet\bullet\bullet\bullet}, V_B^{\bullet\bullet\bullet\bullet\bullet}$	0	-1/3
$A_B^{\bullet\bullet\bullet\bullet}, B_A^{\bullet\bullet\bullet\bullet}$	0	0
$B_A^{\bullet\bullet\bullet\bullet}, V_A^{\bullet\bullet}$	+4/3	-1/3
$V_A^{\bullet\bullet}, B_I^{\bullet\bullet\bullet\bullet\bullet}$	+1	-1/2
$B_A^{\bullet\bullet\bullet\bullet}, V_B^{\bullet\bullet\bullet\bullet\bullet}$	+4/5	-1/5
$O_I^{\bullet\bullet}, B_A^{\bullet\bullet\bullet\bullet}$	+2/3	-1/6
$V_A^{\bullet\bullet}, V_O^{\bullet\bullet}$	+1/2	-3/4
$O_I^{\bullet\bullet}, B_I^{\bullet\bullet\bullet\bullet\bullet}$	+1/4	-3/8

Table III. (cont'd)

Paired Ionic-Electronic Defects	
$A_I^{\bullet\bullet}, e'$	-2/3
$V_A^{\cdot\cdot}, \oplus^\bullet$	+2/3
$V_O^{\bullet\bullet}, e'$	-1/3
$O_I^{\cdot\cdot}, \oplus^\bullet$	+1/3
$B_I^{\bullet\bullet\bullet\bullet\bullet}, e'$	-2/7
$V_B^{\cdot\cdot\cdot\cdot\cdot}, \oplus^\bullet$	+2/7
$B_A^{\bullet\bullet\bullet}, e'$	0
$A_B^{\cdot\cdot\cdot\cdot}, \oplus^\bullet$	0

From Table III. it can be seen that the partial logarithmic derivatives are negative for majority and minority electrons and positive for majority and minority electron holes. The excellent fit of straight lines to the electronic d.c. conductivity versus P_{H_2O}/P_{H_2} data and the negative slopes of these lines indicate that the steady d.c. conductivity is due entirely to electrons. Thus, the slopes in Fig. 3 are equal to

$$\frac{\partial \ln[e^-]}{\partial \ln P_{H_2O}/P_{H_2}} \bigg|_{\frac{P_A}{P_B}, P, T} \quad \text{and can be compared with the partial logarithmic}$$

derivatives of electron concentration with respect to water-to-hydrogen pressure ratio listed in Table III. to identify the possible defect structures. Such a comparison shows that the following three models match the -1/2 slope obtained in Fig. 3 at temperatures of 1000°C and above:

1. $A_I^{\bullet\bullet}, V_B^{\cdot\cdot\cdot\cdot\cdot\cdot}$
2. $V_A^{\cdot\cdot}, B_I^{\cdot\cdot\cdot\cdot\cdot\cdot}$
3. $O_I^{\cdot\cdot}, V_O^{\bullet\bullet}$

For all three of these models, electrons are present only as minority carriers. Two of the three defect models call for the presence of a defect with an electrical charge of six, i.e., $V_B^{\cdot\cdot\cdot\cdot\cdot\cdot}$ or $B_I^{\cdot\cdot\cdot\cdot\cdot\cdot}$. Wagner⁸ and Gupta and Weirick⁹ suggest that the concentrations of these defects are not likely to be significant because of their high electrical charge. Gupta and Weirick⁹ chose vacancies on oxygen sites paired with vacancies on calcium sites as a likely model. However, this work shows that vacancies on oxygen sites paired with oxygen interstitials is the only possible model which contains vacancies on oxygen sites.

Since the a.c. conductivity is equal to the total conductivity, additional information can be obtained by examining the a.c. data. For instance, the least squares lines for the a.c. conductivity have slopes almost identical to the slopes of the d.c. lines, and the magnitudes are very close to being equal. The partial conductivity due to electrons measured by d.c. methods may be compared with the total conductivity measured by a.c. methods to obtain the transference number for electrons. Electronic transference numbers at 1000°C obtained in this manner are tabulated in Table IV, for two selected values of P_{H_2O}/P_{H_2} . Electronic transference numbers in the range from 0.92 to 0.99 indicate that, even though electrons are present only as minority carriers, the electrons carry the bulk of the electrical current.

Table IV. Electronic Transference Numbers at 1000°C

$\frac{P_{H_2O}}{P_{H_2}}$	σ_{total} $\mu mho/cm$	σ_e $\mu mho/cm$	t_e
0.02	51.4	51.0	0.99
2.00	5.89	5.42	0.92

Conductivity data from those experiments with yttria-thoria electrodes may be used to estimate the partial conductivity due to oxygen. The partial oxygen conductivity from the dashed line in Fig. 6 may be compared

with the total conductivity from Fig. 2 to obtain the transference number for oxygen. This has been done for $P_{H_2O}/P_{H_2} = 0.02$ and $P_{H_2O}/P_{H_2} = 2.0$, and the results are shown in Table V.

Table V. Oxygen Transference Numbers at 1000°C

$\frac{P_{H_2O}}{P_{H_2}}$	σ_{total} $\mu mho/cm$	σ_0 $\mu mho/cm$	t_0
0.02	51.4	2.1	0.04
2.00	5.89	0.41	0.07

These values of oxygen transference are in fair agreement with the observation that the transference number for electrons ranges from 0.92 to 0.99 at $P_{H_2O}/P_{H_2} = 2.0$ and $P_{H_2O}/P_{H_2} = 0.02$, respectively. The magnitude of the oxygen transference is great enough to suggest that the partial conductivity due to any other species is much less than the partial oxygen conductivity. If the ionic mobilities of all the ionic species are similar, the concentrations of oxygen defects must be greater than the concentrations of the other defects. This would support the $O_I^{''}, V_O^{''}$ paired defect model as the correct choice from the three possibilities.

In the a.c. as well as the d.c. conductivity measurements, identical data were obtained for both the [001] and [110] crystallographic directions. Consequently, data for both directions were used to obtain the least squares

lines in Figs. 2 and 3. Since the c/a ratio of calcium tungstate is 2.17, this type of behavior is quite surprising. However, Edwards and Bullis¹⁰ demonstrated that there are a number of planes which give the crystal a quasi-four-fold symmetry in the [100] direction. This apparently cubic symmetry may provide an explanation of the isotropic behavior of the electrical conductivity.

In order to determine the so-called activation energy for electronic conduction, Eqs. (5) and (10) may be combined; for the case where $[V_0^{''}] = [O_I^{''}]$ the result is

$$K_{20} = [e']^4 \left(\frac{P_{H_2O}}{P_{H_2}} \right)^2 \quad (20)$$

or

$$[e'] = \left(\frac{P_{H_2O}}{P_{H_2}} \right)^{-1/2} \exp \left(- \frac{\Delta H_f^0}{4RT} \right) \exp \left(\frac{\Delta S_f^0}{4R} \right) \quad (21)$$

where ΔH_f^0 and ΔS_f^0 are the standard enthalpy and entropy of formation per mole of conduction electrons. If the main source of electronic scattering during conduction is acoustic vibration, the temperature dependence of the electronic mobility may be ignored. The standard enthalpy of formation per mole of conduction electrons is given by

$$\Delta H_f^0 = -4R \frac{\partial \ln \sigma_e}{\partial 1/T} \quad (22)$$

Thus, from the slopes in Fig. 5 the so-called activation energy is approximately 34 kcal/mole and $\Delta H_f^0 = 270 \pm 5$ kcal/mole. The corresponding activation energy for chemical diffusion from the data in Fig. 7 is 6.3 ± 1.3 kcal/mole. This may be viewed as the enthalpy of motion for diffusion, which is small in comparison to ΔH_f^0 . Thus, the so-called activation energy for conduction is required primarily for the formation of lattice defects and the accompanying lattice disorder.

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Figure Captions

- Fig. 1. Sample holder and support assembly
- Fig. 2. A.C. conductivity as a function of water-to-hydrogen gas pressure ratio
- Fig. 3. D.C. conductivity as a function of water-to-hydrogen gas pressure ratio
- Fig. 4. A.C. conductivity as a function of reciprocal temperature
- Fig. 5. D.C. conductivity as a function of reciprocal temperature
- Fig. 6. D.C. conductivity with a yttria-thoria blocking electrode as a function of water-to-hydrogen gas pressure ratio; ---line represents the oxygen contribution corrected for electronic leakage
- Fig. 7. Chemical diffusion coefficient as a function of reciprocal temperature for [001] direction

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.