Fabrication and Conductivity of a New Compound Ca$_2$Cr$_2$O$_5$

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Abstract

A new brownmillerite-related compound, Ca$_2$Cr$_2$O$_5$, has been prepared. It has been indexed according to an orthorhombic lattice a = 5·750 Å, b = 14·398 Å and c = 5·483 Å. A series of experiments was performed in order to find the appropriate firing temperature. The total conductivity was measured by a four-point method in the range of 690–911°C. Impedance spectroscopy was also employed in the temperature range 343–785°C. Conductivity measurements at different oxygen pressures at 500°C suggest that Ca$_2$Cr$_2$O$_5$ is a predominantly ionic conductor at P$_{O_2}$ = 1–10^{-2} atm.

Es wurde eine neue, dem Brownmillerit verwandte Verbindung mit der Stöchiometrie Ca$_2$Cr$_2$O$_5$ hergestellt. Ihre Struktur wurde als orthorhombisch mit folgenden Gitterparametern identifiziert: a = 5·750 Å, b = 14·398 Å und c = 5·483 Å. Es wurde eine Versuchsreihe zur Klärung der geeigneten Brenntemperatur des neuen Materials durchgeführt. Die Gesamtleitfähigkeit wurde im Temperaturbereich zwischen 690°C und 911°C mittels einer Vier-Punkt-Methode bestimmt. Außerdem wurde im Temperaturbereich von 343°C bis 785°C Impedanz-Spektroskopie eingesetzt. Leitfähigkeitsmessungen bei verschiedenen Sauerstoffpartialdrücken legen dar, daß Ca$_2$Cr$_2$O$_5$ bei 1 atm < P$_{O_2}$ < 10^{-2} atm ein vorwiegend Ionen leitendes Material darstellt.

Un matériau nouveau, Ca$_2$Cr$_2$O$_5$, dont la structure dérive de celle de la brownmillerite, a été synthétisé. La maille est orthorhombique avec des paramètres a = 5·750 Å, b = 14·398 Å et c = 5·483 Å. Une série d'essais a été effectuée afin de déterminer les conditions de synthèse. La conductivité totale a été

mesurée par une technique en quatre points entre 690 et 911°C. La spectroscopie d'impédance a été aussi utilisée entre 343 et 785°C. Les mesures de conductivité sous pression d'oxygène variable à 500°C indiquent que Ca$_2$Cr$_2$O$_5$ est un conducteur ionique dans le domaine de P$_{O_2}$ comprises entre 1 et 10^{-2} atm.

1 Introduction

The compound Ca$_2$Cr$_2$O$_5$ has not been prepared up to now and it has only been considered as the end member of a series of substitutions of the brownmillerite-related compound Ca$_2$Fe$_2$O$_5$, where Cr is used in the place of Fe (Ca$_2$Fe$_{2-x}$Cr$_x$O$_5$).[1–3] In one paper it has been claimed that a single phase was obtained for $x = 0$ to $0·5$,[2] while in another,[3] $x = 1$ was found to be the limit and it was suggested that higher formation temperatures could push that limit even further.

There is another compound, CaCrO$_3$, with the same cation ratio. It has a perovskite structure, but since Cr^{4+} does not usually exist in solid-state compounds under ambient pressure, a high oxygen pressure is necessary for its formation. The compound CaCrO$_3$ has been successfully fabricated by Goodenough *et al.*,[4] at 700°C and a pressure of 65 kbar. The compounds PbCrO$_3$[5] and SrCrO$_3$[6] with similar structure have also been prepared at high pressures.

In this work, Ca$_2$Cr$_2$O$_5$ was prepared and it was found to be isostructural with Ca$_2$Fe$_2$O$_5$.[7] The X-ray diffraction peaks were indexed and the cell parameters were calculated. A number of DC conductivity and impedance spectroscopy experiments as well as measurements at different oxygen pressures suggest that Ca$_2$Cr$_2$O$_5$ is an ionic conductor at P$_{O_2}$ = 1–10^{-2} atm and 500°C.

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2 Experimental

For the fabrication of $Ca_2Cr_2O_5$, $CaCO_3$ (BDH (Merck), Dagenham, UK, Analar, 99·5% min) and Cr_2O_3 (Johnson Matthey, Royston, UK, Specpure) were mixed and ground. The resulting powder was fired at a high temperature (1000–1350°C) and it was ground again. A pellet was formed by uniaxially pressing the powder with 75 MPa and it was fired at the same temperature.

The X-ray diffraction was performed with a Philips PW1710 diffractometer and CuK_α radiation. The diffractometer was operated at 40 kV and 40 mA. Diffraction spectra were usually obtained scanning continuously at a rate of 1° 2Θ/min. The data of Table 1 were collected using a step scan of 0·01° with 5 s at each step. The cell parameters were calculated with a least squares refinement program.

For the four-point DC measurements, the Van der Pauw contact arrangement with Pt pressure contacts was used. A current source was employed along with a Keithley 175 autoranging multimeter.

Impedance spectroscopy was performed using an HP 4192A LF frequency response analyser controlled by an HP microcomputer. The AC signal had an amplitude of 20–110 mV and a frequency which varied from 5 Hz to 13 MHz. The sides of the disk-shaped sample were covered with platinum paste and before the measurements the pellet was fired at 850°C to stabilize the Pt electrodes. Two Pt foils were employed in contact with the Pt-coated sides of the pellet. Measurements were taken after the samples were left at the required temperature for half an hour.

The same arrangement for the sample was used for the measurements at different P_{O_2} values. The gases used were oxygen, air, a 10% O_2–90% N_2 mixture, a 1% O_2–99% N_2 mixture, a 1:10 mixture of the last gas mixture with pure N_2 and finally a CO_2/H_2 mixture. The measurements were performed with a Wayne Kerr Bridge B244, at a frequency of 1592 kHz. The P_{O_2} values were measured using a Pt/YSZ/Pt probe.

3 Results and Discussion

3.1 Firing temperature

Since there is no information about this compound in the literature, a series of experiments was performed in order to find the appropriate firing temperature. The temperatures examined were 1000, 1100, 1200, 1300 and 1350°C. When first fired, a black, partially melted material resulted for all temperatures apart from the sample fired at 1000°C which gave a yellow colour. The black material resulting at temperatures higher than 1000°C became dark green when it was ground.

After this reaction stage, the samples were ground and formed into pellets and subsequently fired at the same temperature that was initially employed in each case. The sample fired at 1000°C became light green, with a density of 2·7 g/cm³, while all the other samples were partially melted and some of them stuck on the alumina crucible. In these cases, long dark crystals were observed on the surface of the pellets and the crucible, and a large dark green stain was created around each of these pellets. From this behaviour, it was evident that a change occurred at temperatures higher than 1000°C and, therefore, the pellet sintered at 1000°C was selected for subsequent work.

3.2 X-Ray diffraction

All the samples were examined by X-ray diffraction. Using the diffraction pattern of the $Ca_2Fe_2O_5$[7] as a guide, the spectrum obtained from the sample fired at 1000°C was indexed on the basis of an orthorhombic unit cell. The cell parameters were calculated to be: $a = 5·7502 \pm 0·0005$ Å, $b = 14·3984 \pm 0·0003$ Å and $c = 5·4833 \pm 0·0005$ Å The observed and calculated d-spacings, as well as the observed relative intensities of the peaks are presented in Table 1. This is an oxygen deficient structure where oxygen vacancies are ordered. The cell volume is 453·98 Å³ and the calculated X-ray density is 3·86 g/cm³. A detailed analysis of the structure will be presented in a subsequent publication.[8]

Thermogravimetric analysis was performed in air, with a heating rate of 15°/min up to 900°C. No weight change could be detected; therefore, the compound did not lose oxygen when heated in air.

Table 1. X-Ray diffraction spectrum of $Ca_2Cr_2O_5$

| 2θ	d_{obs} (Å)	d_{calc} (Å)	Indices	I_{rel}
17·28	5·127	5·124	0 1 1	0·4
18·77	4·724	—	Unknown	2·2
22·24	3·994	—	Unknown	0·5
23·62	3·764	—	Unknown	1·3
24·67	3·606	3·611	0 3 1 / 0 4 0	100·0
31·15	2·869	2·875	2 0 0	4·1
33·50	2·673	2·666	2 2 0 / 1 4 1	11·6
35·13	2·552	2·549	0 2 2 / 0 5 1	4·4
37·97	2·368	2·381	0 3 2	3·0
40·06	2·249	2·249	2 3 1 / 2 4 0	2·2
45·07	2·010	—	Unknown	0·7
49·29	1·847	1·842	2 6 0	9·3
50·47	1·807	1·806	0 6 2 / 0 1 3	10·6
54·28	1·689	1·693	1 2 3	0·9
56·92	1·616	1·617	3 4 1	2·2
58·93	1·566	1·568	1 4 3	0·5
61·90	1·498	1·498	3 6 0	3·0
64·25	1·449	—	Unknown	0·6
64·65	1·441	1·440	3 4 2 / 0 10 0	1·6
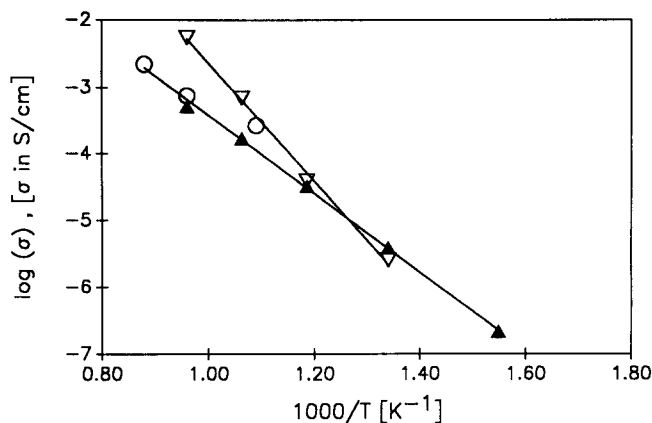
Fig. 1. Temperature dependence of the conductivity of $Ca_2Cr_2O_5$, using DC and impedance techniques. ○, Four-point DC; ▲, impedance, first semicircle; ▽, impedance, second semicircle.

3.3 Four-point conductivity and impedance spectroscopy

The four-point conductivity measurements were performed between 690 and 911°C. A voltage of 10–20 mV and a current of 8–70 μA was used. As can be seen from Fig. 1, the conductivity of $Ca_2Cr_2O_5$ is quite low.

A series of impedance spectroscopy measurements in the range 343 to 785°C was also performed and two semicircles were obtained in the real versus imaginary impedance plot (Fig. 2). This plot is typical for an oxygen conductor, while for a usual electronic conductor the expected plot would consist of points scattered very close to a specific value at the real axis (no capacitive component). Nevertheless, the conduction mechanism is not defined by the shape of the plot. The impedance spectroscopy data show that there are two processes taking place, indicating the possible existence of two phases, e.g. a majority conducting phase and a minority (such as grain boundary) phase with lower conductivity. In such a case there must be a small quantity of the second phase, since there is no obvious/large X-ray diffraction trace. Alternatively, the second semicircle could be attributed to electrode interfacial processes.
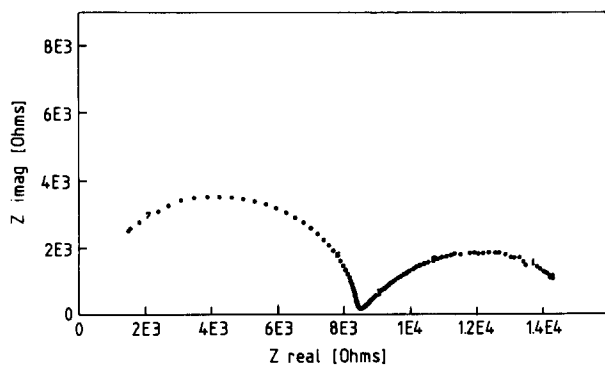
From Fig. 1, it can be seen that the first semicircle is due to a process with an activation energy of $1·16 \pm 0·06$ eV (95% confidence level) and that at the higher temperature range the conductivity values for this semicircle (which are almost equal to the total conductivity at these temperatures) are in general agreement with the four-point conductivity measurements. On the other hand, the process represented by the second semicircle has an activation energy $1·76 \pm 0·13$ eV, which is typical of grain boundaries. From the impedance spectra and the activation energy for the first semicircle, it seems possible that the conductivity of $Ca_2Cr_2O_5$ can be due to oxygen. In order to examine this possibility, measurements at different P_{O_2} were performed.

3.4 Conductivity at different oxygen pressures

The same sample was used for measuring the conductivity at different oxygen pressures at 500°C and the experiment was repeated. The results can be seen in Fig. 3. In both cases the conductivity follows the same behaviour, e.g. constant from $P_{O_2} = 1$ to 10^{-2} atm and increasing for $P_{O_2} = 10^{-17}$ to 10^{-19} atm, which suggests an ionic conduction mechanism for the higher oxygen pressure range and electronic conduction for P_{O_2} less than 10^{-2} atm. It can also be noticed that its value at the higher oxygen pressures becomes slightly more than double when measured for the second time.

In order to examine possible structural changes after exposure to CO_2/H_2 twice that could also account for the non-reproducibility of the conductivity measurements at different P_{O_2} values, X-ray diffraction was performed. Observations of the diffraction spectra shows that there is no significant difference. In order to obtain further data the cell parameters were determined and they were found to
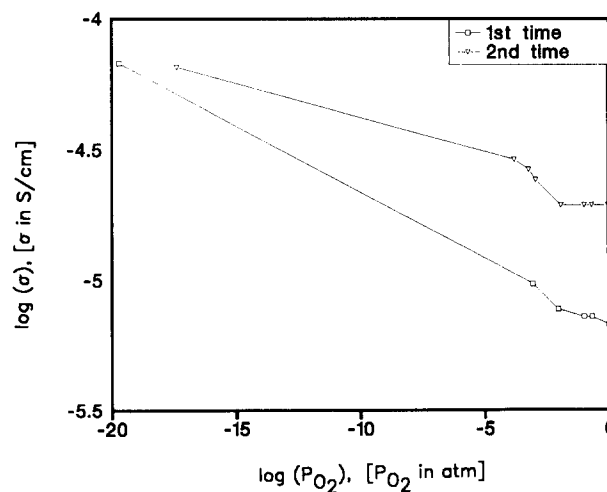

Fig. 2. Impedance spectrum for the cell $Pt/Ca_2Cr_2O_5/Pt$ in air at 570°C.

Fig. 3. The conductivity of $Ca_2Cr_2O_5$ at different oxygen pressures at 500°C.

be the same, within the experimental errors, with those obtained for the material before the measurements. Therefore, any structural change that might have occurred under the CO_2/H_2 atmosphere at $500°C$ must have been reversible.

The increase in conductivity in $Ca_2Cr_2O_5$ at very low oxygen pressures could be explained by the effect of oxygen loss on the defect chemistry of this material:

$$O_o^x \rightarrow \tfrac{1}{2}O_2 + V_o^{\cdot\cdot} + 2e'$$
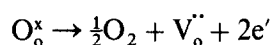
According to this equation, oxygen loss would produce both oxygen vacancies and electrons. Since the electrons have much higher mobilities than the oxygen vacancies, it seems reasonable to suggest that the increase in the observed conductivity at lower partial pressures of oxygen is due to electrons (n-type conductivity).

4 Conclusions

The new material $Ca_2Cr_2O_5$ was synthesized and its structure was determined. Measurements of electrical properties suggest that the material is an ionic conductor at $P_{O_2} = 1-10^{-2}$ with a conductivity of approximately two orders of magnitude lower than that of yttrium-stabilized zirconia. The existence of this material is important, since it is possible that modifications or substitutions could lead to materials with better properties, for use in high-temperature applications. Furthermore, this material is of interest as it may appear as a second phase in solid oxide fuel cell (SOFC) components.[9]

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