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MEASUREMENT OF THERMAL CONSTANTS OF CALCIUM CHROMITE BY LASER FLASH METHOD

K. V. Rajagopalan, Ramprasad, R. Kalyanaraman* and *M. Sundaresan*

ANALYTICAL CHEMISTRY DIVISION B.A.R.C.,
BOMBAY–400 085, INDIA
*METALLURGY DIVISION, BARC

Calcium chromite, $CaCr_2O_4$, was prepared and its purity and stoichiometry were ascertained by chemical analysis and X-ray diffraction methods. The thermal diffusivity, specific heat capacity and thermal conductivity of calcium chromite were measured by Laser Flash method using an Ulvac–Sinku Riko TC–3000 series instrument in the temperature range of 298 to 1100 K. The heat capacity data were utilised to calculate the thermodynamic parameters—enthalpy increments, entropy increments and free energy increments—in the above temperature range.

Interoxidic compounds of alkaline earth metals with the transition metals are of great importance to ferrous industries. Mixed oxides of calcium with iron or chromium give rise to low melting compounds which are used as slags and additives to sintering products. Combinations giving rise to high melting products are used as refractories [1, 2].

Furthermore, nuclear reactors where liquid alkali metals are used as coolants can produce these types of oxides which are identified as corrosion products. Thus, calcium present in liquid sodium or liquid lithium will, in the presence of traces of oxygen, lead to the formation of the double oxide, calcium chromite [3]. Some thermodynamic parameters of calcium chromite calculated from EMF data measured in a galvanic cell containing calcium fluoride solid electrolyte have been reported by us earlier [4]. A study of the thermophysical properties will definitely provide information about the ceramic state of this refractory double oxide.

Among the various methods used for the measurement of thermal constants of solids as a function of temperature, the most sensitive and recent one is the Laser flash method [5, 6] for which only a very small amount of sample is needed. All the three thermal constants, viz. heat capacity, thermal diffusivity and thermal conductivity can be obtained from a single measurement.

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Experimental

Calcium chromite was prepared in the laboratory by mixing stoichiometric amounts of calcium carbonate and chromium oxide, homogenising the mixture thoroughly and sintering at 1450° for about 30 h in air [7].

$$CaCO_3(s) + Cr_2O_3(s) \xrightarrow[30\ h]{1450^\circ} CaCr_2O_4(s) + CO_2(g)$$

The resultant calcium chromite was then characterised by chemical analysis as well as X-ray diffraction methods.

Table 1 Measurements of thermal constants of $CaCr_2O_4$ at different temperatures

Temperature, K	Specific heat capacity, $Jg^{-1}K^{-1}$	Thermal diffusivity, $\times 10^2\ cm^2\ sec^{-1}$	Thermal conductivity, Wmk
297	0.561	1.222	3.126
302	0.557	1.285	3.264
358	0.591	1.216	3.277
393	0.604	1.131	3.115
462	0.631	1.059	3.047
531	0.640	1.000	2.918
582	0.683	0.942	2.928
633	0.675	0.892	2.592
667	0.675	0.928	2.856
773	0.689	0.873	2.746
883	0.722	0.833	2.743
988	0.769	0.787	2.759
1086	0.782	0.764	2.723

Table 2 Thermodynamic parameters of $CaCr_2O_4$

Temperature, K	$H_T^0 - H_{298}^0$, kJ mol^{-1}	$S_T^0 - S_{298}^0$, $JK^{-1}\ g^{-1}$	$-(G_T^0 - G_{298}^0$, kJ mol^{-1}
400	12.21	0.169	1.90
500	25.25	0.309	6.99
600	38.92	0.429	14.80
700	53.05	0.533	24.81
800	67.60	0.626	36.92
900	82.56	0.710	50.80
1000	98.05	0.789	66.62
1100	114.22	0.862	83.67

An Ulvac–Sinku Riko TC 3000 series instrument was used for this study. The source was a ruby-xenon laser. A pulse time of one millisecond was maintained. The output energy of the laser was about 5 joules. The measurement time was six seconds. The temperature range of the measurement was 278 to 1100 K. A Pt–Pt 13% Rh thermocouple fixed to the pellet was used for the temperature measurement. Sapphire was used as the reference sample to standardise the instrument.

About 2 to 3 mm thick pellets of the compound were prepared using a 10 mm diameter die at a pressure of 400 MPa. The pellets were sintered at 1200 K in air for a period of 12 h. The exact dimensions of the pellets were measured using a vernier caliper. The actual density of the pellets was ascertained by finding out the porosity of the pellets. The densities at various temperatures were also calculated using the coefficient of thermal expansion of the sample.

The experimental points were recorded only after we were able to reproduce the values within an error of 3%. After taking the reading at 298 K the sample temperatute was raised to the maximum to get a better thermal equilibrium. The readings were then taken in the descending and ascending orders.

Results and discussion

When a ruby laser pulse is radiated on one side of the thin plate sample with thickness l, the temperature of the other side is changing as shown in Fig. 1.

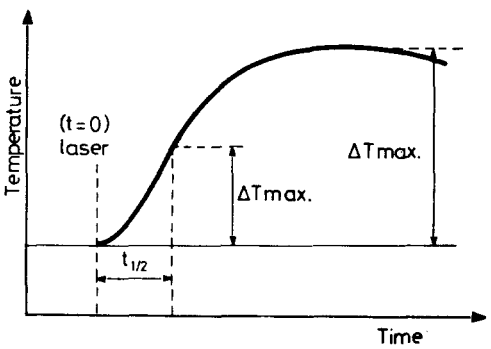

Fig. 1 Temperature rise *vs.* time for the thermal diffusivity measurement

Thermal constants

By solving the thermal conduction equation, the following relation is obtained [8].

$$\alpha = \frac{1.37\, l^2}{\pi^2 t_{\frac{1}{2}}}$$

where α is the thermal diffusivity, l is the sample thickness and $t_{\frac{1}{2}}$ is the time required to raise the temperature of the backside of the sample to half the maximum temperature.

For calculating the specific heat capacity, C_p, of the sample from this measurement, the following relationship involving values for a standard reference sample of sapphire is used

$$C_p d = \frac{l(\text{ref})\, \Delta T_{\max}(\text{ref})\, C_p(\text{ref})\, d(\text{ref})}{l \Delta T_{\max}}$$

Where l is the sample thickness, d is the density of the sample and $\Delta T_{\max}$ is the maximum temperature difference.

The thermal conductivity, K, is calculated using the values of thermal diffusivity α, specific heat capacity C_p and the density d by using the equation

$$K = \alpha C_p d$$

Thermodynamic parameters

The data on the specific heat capacity of $CaCr_2O_4$ at various temperatures were fitted to a polynomial of the form:

$$C_p = A + BT + CT^2 + DT^3 \quad (298\text{–}1100\ \text{K})$$

The first thermodynamic property that can be calculated from the data is the "Enthalpy increments"—the change in heat content when the compound is heated from 298 K to any temperature T up to 1100 K. Thus

$$\begin{aligned} H_T^0 - H_{298}^0 &= \int_{298}^{T} C_p \, dT \\ &= \int_{298}^{T} (A + BT + CT^2 + DT^3)\, dT \\ &= \left[AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} \right]_{298}^{T} \end{aligned}$$

Heat capacity values at different temperatures are used to calculate $\frac{C_p}{T}$ and to plot a graph of $\frac{C_p}{T}$ *vs.* T. The area under the curve at any given temperature T gives the entropy change $S_T^0 - S_{298}^0$.

The enthalpy increments and the entropy change values are used to obtain the free energy change values $-(G_T^0 - G_{298}^0)$ by the relationship

$$S_T^0 - S_{298}^0 = \frac{H_T^0 - S_{298}^0}{T} - \frac{G_T^0 - G_{298}^0}{T}$$

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Zusammenfassung — Kalziumchromit, $CaCr_2O_4$, wurde hergestellt und seine Reinheit und stöchiometrische Zusammensetzung mit Hilfe chemischer Analyse und Röntgendiffraktionsmethoden ermittelt. Anhand eines Ulvac–Sinku Riko TC–3000 Gerätes wurde mit Laser Flash Verfahren die Temperaturleitfähigkeit, die spezifische Wärmekapazität und die Wärmeleitfähigkeit von Kalziumchromit im Temperaturbereich 298–1100 K bestimmt. Die Wärmekapazitätsdaten wurden zur Berechnung der thermodynamischen Größen (Enthalpie-, Entropie-, Freie Energieänderung) in obigem Temperaturbereich benutzt.

Резюме — Получен хромит кальция $CaCr_2O_4$, чистота и стехиометрия которого была установлена химическим и рентгенофазовым анализом. Методом лазерной вспышки, используя прибор Улвак–Синку Рико ТС–3000, были измерены в температурном интервале 298–1100К коэффициенты термической диффузии и термической проводимости, а также удельная теплоемкость. Значения теплоемкостей были использованы для вычисления в указанном выше температурном интервале таких термодинамических параметров, как увеличение энтальпии, энтропии и свободной энергии.