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Heat capacities of calcium chromate and calcium chromite

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Abstract

Heat capacities of calcium chromate ($CaCrO_4$) and calcium chromite (β-$CaCr_2O_4$) were measured at elevated temperatures using the differential scanning calorimetry. The measured heat capacities of $CaCrO_4$ and β-$CaCr_2O_4$ as a function of temperature (measured in J mol^{-1} K^{-1}) are expressed as

$$C_p(\mathrm{CaCrO_4}) = \frac{127.92 + 35.73 \times 10^{-3}T - 2.257 \times 10^6}{T^2} \quad (298-1123\,\mathrm{K})$$

$$C_p(\beta\text{-}\mathrm{CaCr_2O_4}) = \frac{166.69 + 18.33 \times 10^{-3}T - 2.92 \times 10^6}{T^2} \quad (298-1203\,\mathrm{K})$$

Keywords: Heat capacity; Calcium chromate; Calcium chromite

1. Introduction

The intermediate compounds, β-$CaCr_2O_4$ and $CaCrO_4$ form in the system of Ca–Cr–O. β-$CaCr_2O_4$ is stable at high temperatures (above 1295 K) and atmospheric conditions (i.e. air) and is one of the refractory compounds in chromium oxide bearing refractories. As temperature decreases, $CaCrO_4$ becomes more stable at atmospheric conditions. $CaCrO_4$ is soluble in water and contains Cr^{6+} which is known to be toxic and carcinogenic. Investigations have been carried out to understand the Ca–Cr–O system in air and to minimize the formation of Cr^{6+} in chromium oxide bearing refractories [1–3]. $CaCrO_4$ has also been used as a cathode material in thermally activated electrochemical cells [4].

Reliable thermodynamic information is needed to understand the Ca–Cr–O system at elevated temperatures. The heat capacities of β-$CaCr_2O_4$ and $CaCrO_4$ will be very useful to calculate thermodynamic quantities such as enthalpy, entropy, and Gibbs free energy in the Ca–Cr–O system at elevated temperatures. The values of the heat capacity for $CaCrO_4$ in the literature are rather scattered within an interval from 6 to 11% [5–7]. For β-$CaCr_2O_4$, the experimental result by Rajagopalan et al. is different from the calculated values from Kanteeva et al. and Knacke et al. by 18–22% [7–9]. This study determines the heat capacities of β-$CaCr_2O_4$ and $CaCrO_4$ using a differential scanning calorimetry, and an assessment of heat

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capacities in this work and those available in the literature is made.

2. Experimental

2.1. Preparation of materials

The CaO was obtained from calcination of $CaCO_3$ at 1223 K for 6 h. For the preparation of $CaCrO_4$, CaO and Cr_2O_3 were mixed with the mole ratio of 2:1 using a mixer and heated in an MgO crucible at 1123 K under air for 30 days. To prepare β-$CaCr_2O_4$, the 1:1 mole ratio of CaO and Cr_2O_3 were mixed, heated in an MgO crucible at 1673 K under air for 4 h, quenched, ground again, reheated at 1673 K for 4 h under air, and finally quenched using liquid nitrogen to avoid the transformation of β-$CaCr_2O_4$ into $CaCrO_4$ during cooling. After obtaining β-$CaCr_2O_4$ and $CaCrO_4$, the specimens were characterized using XRD. X-ray analysis showed no other phases than β-$CaCr_2O_4$ and $CaCrO_4$ form.

2.2. Measurement

A differential scanning calorimeter (DSC 404, Netzsch Instruments Inc., Paoli, PA) was used to determine the heat capacity of β-$CaCr_2O_4$ and $CaCrO_4$. The scanning mode was used and the heating rate was 10 and 20 K min^{-1}. The stability of β-$CaCr_2O_4$ and $CaCrO_4$ was very sensitive to partial oxygen pressure at elevated temperatures. $CaCrO_4$ was stable up to 1346 K under oxidizing conditions, while β-$CaCr_2O_4$ was stable up to 2443 K under reducing conditions. Air was used as a carrier gas for $CaCrO_4$ to prevent reduction of $CaCrO_4$ to β-$CaCr_2O_4$ during DSC measurements. The argon (99.9999%) was used as a carrier gas for β-$CaCr_2O_4$ to prevent the oxidation of β-$CaCr_2O_4$ to $CaCrO_4$. XRD analysis confirmed that no reaction occurs during DSC measurements. The platinum crucible with an alumina coating inside the crucible was used. The sapphire was used as a standard. The apparatus sensitivity to temperature and thermal response was regularly calibrated to obtain better reproducibility using gold, copper, and α-alumina, and magnesia, the heat capacities of which are well known. The heating rate of the specimen is 10 and 20 K min^{-1}. The specimens of β-$CaCr_2O_4$ and $CaCrO_4$ were screened and the particles ranging from 0.075 to 0.065 mm were used.

3. Results and discussions

3.1. Heat capacities of β-$CaCr_2O_4$ and $CaCrO_4$

The heat capacity measurements for β-$CaCr_2O_4$ and $CaCrO_4$ are shown in Tables 1 and 2. The reproducibility of measurements is within 5%. The heat capacities for β-$CaCr_2O_4$ and $CaCrO_4$ are shown as a function of temperature (measured in J mol^{-1} K^{-1}) in Fig. 1. The best fitting mathematical expressions that describe the relationship between heat capacity and temperature are expressed in Eqs. (1) and (2). Curve fit is constrained at low temperature end.

$$C_p = \frac{127.92 + 35.73 \times 10^{-3} T - 2.257 \times 10^{6}}{T^2} \quad (\text{for } CaCrO_4) \tag{1}$$

$$C_p = \frac{166.69 + 18.33 \times 10^{-3} T - 2.92 \times 10^{6}}{T^2} \quad (\text{for } \beta\text{-}CaCr_2O_4) \tag{2}$$

Table 1
Heat capacity measurements of β-$CaCr_2O_4$

T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})
313	143.09	713	173.93
323	144.68	733	174.70
333	145.59	753	175.61
343	146.30	773	176.06
353	146.63	813	177.17
363	147.61	823	177.73
373	148.62	873	178.49
403	152.43	903	179.61
433	155.95	923	180.00
463	159.04	953	180.90
493	161.62	973	181.38
513	163.02	1003	182.10
533	164.28	1023	182.59
573	166.86	1053	183.32
593	167.72	1073	183.77
633	170.65	1143	185.40
673	172.54	1203	186.73

Table 2
Heat capacity measurements of $CaCrO_4$

T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})
313	116.06	613	144.12
323	118.45	633	145.81
333	119.17	653	147.33
343	121.22	673	148.38
353	121.68	693	149.41
363	122.35	713	150.09
373	123.27	733	150.72
403	126.11	753	151.54
413	127.42	773	152.11
423	128.60	813	152.41
433	129.91	823	152.63
443	131.19	873	153.78
453	132.63	903	155.88
463	133.68	923	157.09
473	134.61	953	158.11
493	136.43	973	158.82
513	137.84	1003	159.21
533	139.01	1023	160.24
553	140.16	1053	163.50
573	141.45	1073	165.15
593	143.13	1123	166.25

3.2. Assessment of heat capacities

The heat capacities of β-$CaCr_2O_4$ and $CaCrO_4$ determined in this study are compared with those in the literature and shown in Figs. 2 and 3. The heat capacity of β-$CaCr_2O_4$ experimentally obtained in this study is in very close agreement with the calculated data from Kanteeva et al. and Knacke et al. [7,8]. The results by Rajagopalan et al. [9] are 16–18% lower than the present study and 18–22% lower than those of Kanteeva et al. and Knacke et al. Laser flash method used by Rajagopalan depends on the specimen density which is the function of temperature. The measurements also require homogeneous surface properties and uniform thickness of specimen. These factors can

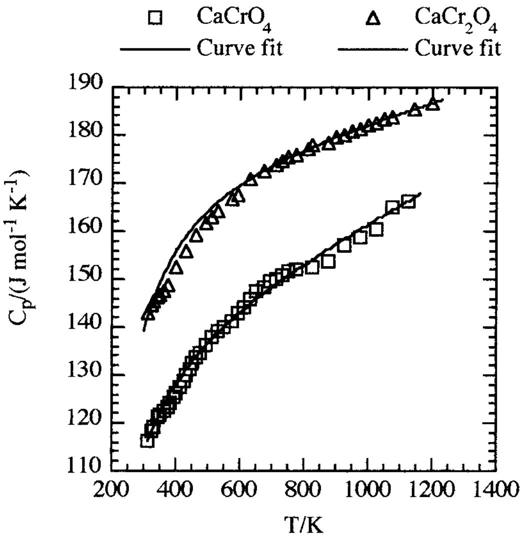

Fig. 1. Heat capacities of $CaCrO_4$ and β-$CaCr_4O_4$ experimentally determined by using differential scanning calorimetry.

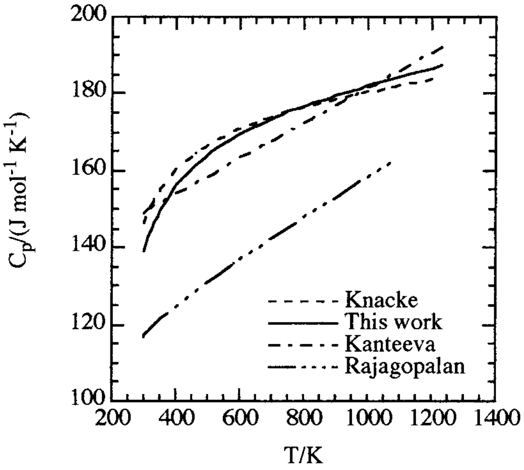

Fig. 2. Comparison among heat capacities of β-$CaCr_2O_4$ obtained in this work and previous values available in the literature.

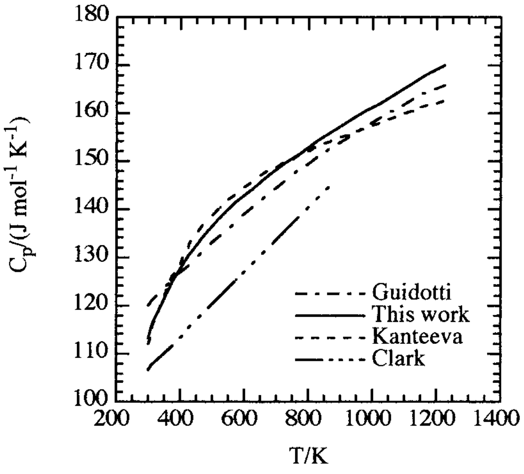

Fig. 3. Comparison among heat capacities of $CaCrO_4$ obtained in this work and previous values available in the literature.

Table 3
Comparison of heat capacities of β-$CaCr_2O_4$[a]

	Method	*a*	*b*	*c*	C_p (298.15 K)	Reference
Kanteeva	Estimated	135.52	46.0	–	149.2	[7]
Knacke	Estimated	169.66	13.26	−2.40	146.6	[8]
Rajagopalan	Laser flash method	107.34	51.39	−0.52	116.81	[9]
Lee	DSC[b]	166.69	18.33	−2.92	139.3	This work

[a] $C_p = (a + b \times 10^{-3}T + c \times 10^6)/T^2$ (J mol^{-1} K^{-1}).

[b] DSC stands for differential scanning calorimetry.

Table 4
Comparison of heat capacities of $CaCrO_4$[a]

	Method	*a*	*b*	*c*	C_p (298.15 K)	Reference
Clark	Calorimetry and DTA	86.74	67.38	–	106.8	[5]
Kanteeva	Estimated	142.84	17.9	−3.21	112.06	[7]
Guidotti	Calorimetry	119.14	39.59	−1.013	120	[6]
Kogan	Low temperature calorimeter	–	–	–	113.18	[10]
Lee	DSC[b]	127.92	35.73	−2.257	113.18	This work

[a] $C_p = (a + b \times 10^{-3}T + c \times 10^6)/T^2$ (J mol^{-1} K^{-1}).

[b] DSC stands for differential scanning calorimetry.

cause the uncertainty of measurements and decrease the accuracy of experimental values.

The heat capacity of $CaCrO_4$ from this study is in good agreement with the data presented by Guidotti et al. and Kanteeva et al. [6,7]. The results by Clark [5] are 5–8% lower than the present study and 5–11% lower than those by Guidotti et al. and Kanteeva et al. Heat capacity by Clark was determined using only three temperatures and, therefore, can not be accepted as sufficiently reliable. The heat capacity of $CaCrO_4$ at 298 K in this study is in excellent agreement with the result from the low temperature heat capacity measurements by Kogan et al. [10]. The constants for mathematical expressions of heat capacities of β-$CaCr_2O_4$ and $CaCrO_4$ are compared with those in the literature and shown in Tables 3 and 4.

4. Conclusions

Heat capacities of $CaCrO_4$ and calcium chromite were measured at elevated temperatures using the differential scanning calorimetry. The values from this study are very close to the calculated values in the literature. The measured heat capacities of $CaCrO_4$ and $CaCr_2O_4$ as a function of temperature (measured in J mol^{-1} K^{-1}) are expressed as

$$C_p(CaCrO_4) = \frac{127.92 + 35.73 \times 10^{-3}T - 2.257 \times 10^6}{T^2}$$

(298−1123 K)

$$C_p(\beta\text{-}CaCr_2O_4) = \frac{166.69 + 18.33 \times 10^{-3}T - 2.92 \times 10^6}{T^2}$$

(298−1203 K)

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