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THERMODYNAMIC PROPERTIES OF STRONTIUM AND BARIUM FELDSPARS

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ABSTRACT

Thermodynamic data on Sr and Ba feldspars, $SrAl_2Si_2O_8$ and $BaAl_2Si_2O_8$ (celsian), are necessary to calculate the thermodynamics of solid solutions in natural feldspars and to understand the geochemical behaviour of these two elements. Previously the enthalpy of formation of Sr feldspar and celsian had been determined by high temperature solution calorimetry in a lead borate melt.

The molar heat capacities of two synthetic Sr and Ba compounds were measured by differential scanning calorimetry between 312 and 712 K. In addition, heat capacities were calculated from a model of the vibrational spectra using optical frequencies measured by IR spectroscopy.

The measured and calculated heat capacity values were used to calculate the standard entropies: $S^{\ominus}_{298.15}(SrAl_2Si_2O_8) = 218.5 \pm 4.0$ J K^{-1} mol^{-1} and $S^{\ominus}_{298.15}(BaAl_2Si_2O_8) = 231.5 \pm 4.0$ J K^{-1} mol^{-1}, and also to propose the recommended equations

$$C_{p,SrAl_2Si_2O_8} = 269.59 + 5.784 \times 10^{-2} T - 5.833 \times 10^{6} T^{-2} \text{ J K}^{-1} \text{ mol}^{-1}$$

and

$$C_{p,BaAl_2Si_2O_8} = 261.05 + 6.640 \times 10^{-2} T - 5.256 \times 10^{6} T^{-2} \text{ J K}^{-1} \text{ mol}^{-1}$$

for $250 < T/\text{K} < 1000$.

INTRODUCTION

Strontium and barium are common isomorphic trace elements in the rock-forming mineral feldspars. A knowledge of the thermodynamic data of Sr and Ba feldspars, $SrAl_2Si_2O_8$ and $BaAl_2Si_2O_8$ (celsian), is necessary to calculate the thermodynamics of solid solutions in natural feldspars and to understand the geochemical behaviour of these elements. The enthalpy of formation of Sr feldspars and celsian has previously been determined by

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high temperature solution calorimetry in a lead borate melt [1]. The aim of the present study, the second part of this investigation, is the experimental determination of the heat capacity of these two compounds, and the computation and extrapolation of these values beyond the experimental range 250–1000 K.

EXPERIMENTAL

Synthesis and characterization of samples

The samples of Sr and Ba feldspars were synthesized by the solid state reaction method. The starting materials were chemically pure strontium and barium carbonates dried for a day at 110 °C, and Al_2O_3 and SiO_2 heated for several hours at 1100 °C. Stoichiometric mixtures of the weighed ingredients were finely ground and pressed in tablets. These tablets were heated in an air furnace at 1300–1400 °C for 5–7 days, then reground, remixed and reheated several times in order to attain a high degree of homogeneity. The absence of starting and irrelevant phases was carefully monitored by X-ray diffraction. The chemical compositions of the synthesized samples determined by wet analysis were close to the theoretical ones [1]. The unit cell parameters of the synthesized samples were measured (see Table 1).

Heat capacity measurements

The differential scanning calorimeter [2] used in this work (Setaram DSC 111) is designed as a Calvet calorimeter: two cylindrical cells, reference and laboratory cells surrounded by thermal fluxmeters, are located in a metallic block, the temperature of which can be linearly programmed. The two fluxmeters are connected in opposition. From observation of the thermal disequilibrium between the two cells during a heat pulse, the heat capacity of the sample contained in the laboratory cell can be obtained as a function of temperature. It should be emphasized that two calibration methods were employed: the direct Joule effect evolved by an electrical resistance located in the laboratory cell was used; and the heat capacity of pure standard

TABLE 1

Unit cell parameters of synthesized samples

Mineral	a (Å)	b (Å)	c (Å)	α (deg)	β (deg)	γ (deg)
$SrAl_2Si_2O_8$	8.3865(22)	12.9663(65)	14.2600(32)	90	115.40(3)	90
$BaAl_2Si_2O_8$	8.6395(28)	13.0405(54)	14.4050(47)	90	115.10(3)	90

alumina crystals (from NIST) were measured and compared with the Joule effect results. Such an apparatus can be operated between 173 and 1023 K.

All heat capacity measurements were performed under purified argon flow using stainless steel calorimetric cells (6 mm diameter, 12 mm length). These gas-tight containers were closed by a nickel O-ring pressed between the cell and the lid. The results are given with an accuracy of about 3% for C_p and ± 0.5 K for T.

RESULTS AND CALCULATIONS

Heat capacity measurements

The molar heat capacities of the two samples ($SrAl_2Si_2O_8$ and $BaAl_2Si_2O_8$) were measured in the temperature range 312–772 K. All these results are gathered in Tables 2 and 3 and reported in Figs. 1 and 2.

Optical measurements

The optical IR spectra of the Sr and Ba feldspar samples were measured in the range 3600–400 cm^{-1} by the routine method using an internal standard with an accuracy of about 5 cm^{-1}. Spectra are shown in Fig. 3.

TABLE 2

Experimental heat capacities of $SrAl_2Si_2O_8$ measured by differential scanning calorimetry: mass of the sample, 25.058 mg; $M = 325.750$ g mol^{-1}

T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}
312.95	237.51	472.75	267.41	632.45	294.71
322.95	234.65	482.75	270.27	642.45	291.85
332.95	231.14	492.65	268.19	652.45	294.06
342.85	236.86	502.65	273.91	662.45	299.91
352.85	240.37	512.65	278.33	672.45	301.21
362.85	246.09	522.65	282.49	682.45	298.35
372.85	246.09	532.65	284.05	692.45	296.14
382.85	247.00	542.65	284.05	702.45	297.70
392.85	252.72	552.65	284.05	712.45	301.21
402.85	258.31	562.65	284.05	722.35	301.21
412.75	257.53	572.55	288.34	732.35	304.85
422.75	263.51	582.55	290.29	742.35	304.85
432.75	269.10	592.55	286.13	752.35	308.36
442.75	266.24	602.55	285.35	762.35	305.50
452.75	266.89	612.55	290.29	772.35	298.35
462.75	269.75	622.55	294.06		

TABLE 3

Experimental heat capacities of $BaAl_2Si_2O_8$ measured by differential scanning calorimetry: mass of the sample, 28.882 mg; $M = 375.360$ g mol^{-1}

T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}
312.95	233.41	472.75	266.42	632.45	292.16
322.95	232.50	482.75	268.89	642.45	288.91
332.95	228.48	492.65	269.97	652.45	292.16
342.85	234.19	502.65	270.97	662.45	297.10
352.85	237.44	512.65	273.44	672.45	299.70
362.85	244.98	522.65	279.16	682.45	294.63
372.85	244.98	532.65	283.32	692.45	293.07
382.85	245.76	542.65	280.85	702.45	297.10
392.85	252.72	552.65	281.63	712.45	298.00
402.85	255.64	562.65	284.23	722.35	298.78
412.75	253.17	572.55	287.48	732.35	298.78
422.75	261.36	582.55	288.39	742.35	303.72
432.75	266.42	592.55	272.92	752.35	303.72
442.75	263.04	602.55	290.86	762.35	302.16
452.75	263.96	612.55	292.42	772.35	302.16
462.75	266.42	622.55	289.95		

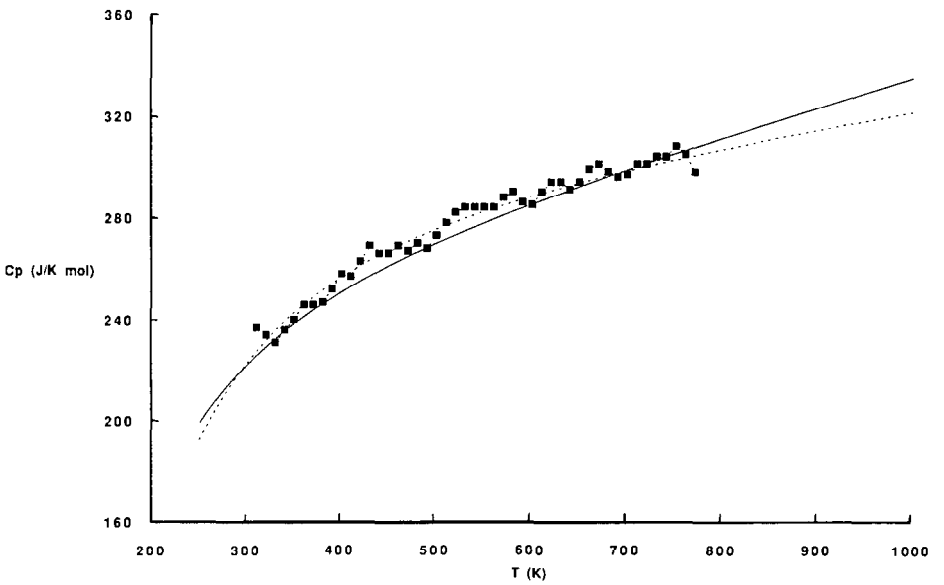

Fig. 1. Plot of the heat capacity of $SrAl_2Si_2O_8$ against temperature: (———) computed from model of vibrational spectrum; (■) experimental values; and (– – –) computed from eqn. (3).

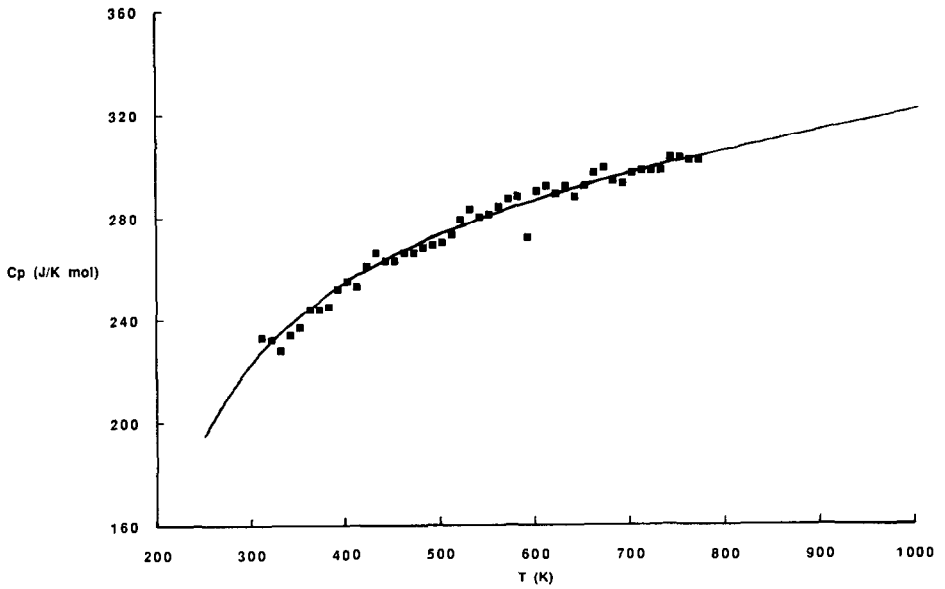

Fig. 2. Plot of the heat capacity of $BaAl_2Si_2O_8$ against temperature: (———) computed from model of vibrational spectrum; (■) experimental values; and (– – –) computed from eqn. (4).

Calculations

Over the past decade, calculation of $C_{p(T)}$, $S^{\ominus}_{(T)}$ and $H^{\ominus}_{(T)}$ values of minerals on the basis of models of vibrational spectra of their crystalline lattices have been widely used [3,4]. The calculated and measured values of

TABLE 4

Parameters for the vibrational spectra model of Ca, Sr and Ba feldspars

Parameters [a]		$CaAl_2Si_2O_8$	$SrAl_2Si_2O_8$	$BaAl_2Si_2O_8$
V	(J bar^{-1})	10.021	10.584	11.066
θ_D	(K)	546	4949 ± 115	4569 ± 115
θ_L	(K)	458	414	382
θ_{E1}	(K)	1531 (12)	1467 (12)	1442 (12)
θ_{E2}	(K)	1333 (4)	1304 (4)	1318 (4)
θ_{E3}	(K)	1024 (12)	1015 (12)	994 (12)
θ_{E4}	(K)	889 (4)	872 (4)	862 (4)
K_s	(kbar)	920	910	900
dK_s/dT	(kb K^{-1})	−0.12	−0.12	−0.12
γ_{th}		1.195	1.139	1.136

[a] V, mol. volume; θ_D, Debye temperature; θ_L, reduced Debye temperature; θ_E, Einstein temperature (number of modes corresponding to θ_D is cited in parentheses), γ_{th}, thermodynamic value of Grüneisen parameter at 298.15 K.

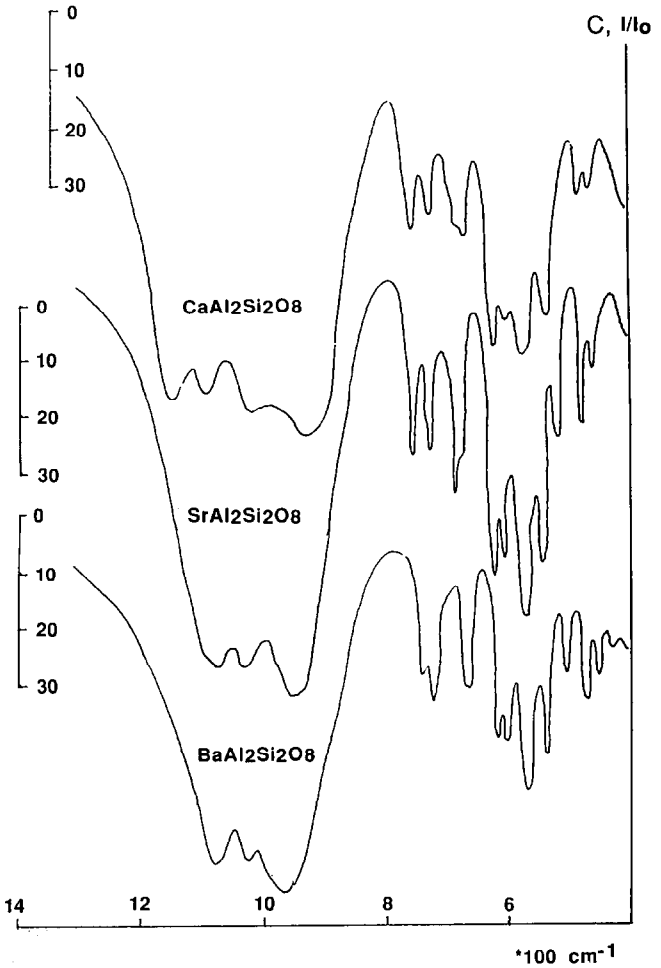

Fig. 3. IR spectra of Ca, Sr and Ba feldspars in the range 1200–400 cm^{-1}.

heat capacities, entropies and enthalpies of the same mineral coincide within 3% in the range 298–1000 K.

For alkaline earth feldspars, both vibrational spectrum methods, acoustic and optical, have only been completely studied for anorthite ($CaAl_2Si_2O_8$). Calculations based on the simple model of vibrational spectra [4] show that for anorthite the differences between measured [5] and calculated C_p, $S_T^\ominus$ and $H_T^\ominus - H_{298.15}^\ominus$ do not exceed $\pm 2\%$ in the range 298–1000 K.

This makes it possible to use the vibrational spectrum of anorthite as a comparison for spectra of the isomorphic minerals $SrAl_2Si_2O_8$ and $BaAl_2Si_2O_8$. The parameters of the model used for anorthite are summarized in Table 4.

The acoustic spectra of $SrAl_2Si_2O_8$ and $BaAl_2Si_2O_8$ have not been studied. Therefore the elastic spectra of these compounds were calculated by

approximating the corresponding Debye temperatures (θ_D) which depend on the average molecular mass of atoms in the crystalline lattice; the basis used for this approximation was the Debye temperature of anorthite [6].

For these three feldspars, the data used are reported in Table 4.

Heat capacity $C_{p(T)}$, entropy $S^{\ominus}_{(T)}$ and enthalpy $H^{\ominus}_{(T)}$ were calculated for Sr and Ba in the feldspars in accordance with the model of vibrational spectra using the parameters mentioned in Table 4, in the range 250–1000 K in increments of 50 K. Values of $C_{p(T)}$ were interpolated using the Meyer–Kelley equation. The error related to this polynomial interpolation lies within $\pm 0.8\%$ which is lower than the accuracy of the calculations.

The following calculated values of standard entropy and equations of heat capacity are in the range 250–1000 K

(1) $SrAl_2Si_2O_8$

$$S^{\ominus}_{298.15} = 218.5 \pm 4.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$C_p = 230.38 + 10.820 \times 10^{-2}T - 3.721 \times 10^{6}T^{-2} \text{ J K}^{-1} \text{ mol}^{-1} \quad (1)$$

(2) $BaAl_2Si_2O_8$

$$S^{\ominus}_{298.15} = 231.5 \pm 4.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$C_p = 247.23 + 8.688 \times 10^{-2}T - 4.532 \times 10^{6}T^{-2} \text{ J K}^{-1} \text{ mol}^{-1} \quad (2)$$

As shown in Figs. 1 and 2, the measured and calculated C_p values between 312 and 772 K are in good agreement (within 2%). This allows the experimental values to be extrapolated and the recommended equations of heat

TABLE 5

Thermodynamic properties [a] of $SrAl_2Si_2O_8$ (monoclinic), $M = 325.750$ g mol^{-1}

T (K)	C_p (J K^{-1} mol^{-1})	$S^{\ominus}_T$ (J K^{-1} mol^{-1})	$(H_T - H_{298})/T$ (J K^{-1} mol^{-1})	Φ (J K^{-1} mol^{-1})	$\Delta_{form}H_T$ (kJ mol^{-1})	$\Delta_{form}G_T$ (kJ mol^{-1})
298.15	221.21	218.50	0.00	218.50	−4248.00	−4023.75
400	256.27	289.03	61.33	227.70	−4247.97	−3947.10
500	275.18	348.41	102.35	246.06	−4246.58	−3872.02
600	288.09	399.78	132.29	267.50	−4244.56	−3797.29
700	298.17	444.98	155.29	289.69	−4242.27	−3722.92
800	306.75	485.36	173.70	311.67	−4239.90	−3648.90
900	314.45	521.94	188.92	333.03	−4237.78	−3575.14
1000	321.60	555.45	201.83	353.62	−4256.49	−3500.13

[a] The standard errors are respectively: C_p, ±5.50; $S^{\ominus}_T$, ±4.00; Φ, ±4.00; $\Delta_{form}H_T$, ±4.70; $\Delta_{form}G_T$, ±4.85. Molar volume = 10.580 J bar^{-1}. Equation of heat capacity (J K^{-1} mol^{-1}): $C_p = 269.59 + 5.784 \times 10^{-2}T - 5.833 \times 10^{6}T^{-2}$ ($298.15 < T < 1000$ K).

TABLE 6

Thermodynamic properties [a] of $BaAl_2Si_2O_8$ (monoclinic) (celsian), $M = 375.360$ g mol^{-1}

T (K)	C_p (J K^{-1} mol^{-1})	$S_T^\ominus$ (J K^{-1} mol^{-1})	$(H_T - H_{298})/T$ (J K^{-1} mol^{-1})	Φ (J K^{-1} mol^{-1})	$\Delta_{form}H_T$ (kJ mol^{-1})	$\Delta_{form}G_T$ (kJ mol^{-1})
298.15	221.71	231.400	0.00	231.40	4244.30	4021.87
400	254.76	301.74	61.15	240.59	4244.83	3945.77
500	273.22	360.72	101.85	258.87	4244.44	3871.04
600	286.29	411.74	131.55	280.19	4243.51	3796.44
700	296.80	456.68	154.43	302.26	4242.24	3722.02
800	305.96	496.92	172.81	324.12	4240.77	3573.78
900	314.22	533.45	188.07	345.38	4239.18	3573.78
1000	322.20	566.98	201.09	365.88	4258.58	3498.42

[a] The standard errors are respectively: C_p, ±5.50; $S_T^\ominus$, ±4.00; Φ, ±4.00; $\Delta_{form}H_T$, ±4.70; $\Delta_{form}G_T$, ±4.85. Molar volume = 11.070 J bar^{-1}. Equation of heat capacity (J K^{-1} mol^{-1}): $C_p = 261.05 + 6.640 \times 10^{-2}T - 5.2568 \times 10^6 T^{-2}$ ($298.15 < T < 1000$ K).

capacity to be proposed for the 250–1000 K range

(1) $SrAl_2Si_2O_8$

$$C_p = 269.59 + 5.784 \times 10^{-2}T - 5.833 \times 10^6 T^{-2} \text{ J K}^{-1} \text{ mol}^{-1} \quad (3)$$

(2) $BaAl_2Si_2O_8$

$$C_p = 261.05 + 6.640 \times 10^{-2}T - 5.2568 \times 10^6 T^{-2} \text{ J K}^{-1} \text{ mol}^{-1} \quad (4)$$

The consistency of the calculated and measured heat capacities demonstrates the reliability of the parameters chosen for the model of the vibrational spectrum. Thus the obtained entropies can be used to calculate the thermodynamic properties of Sr and Ba feldspars. From the $\Delta_{form}H^\ominus_{298.15}$ value [1], the equations of heat capacity and the $S^\ominus_{298.15}$ values suggested in the present paper, the thermodynamic properties of these feldspars were calculated for the temperature range 298.15–1000 K and are listed in Tables 5 and 6.

CONCLUSION

Using the heat capacity values measured between 312 and 712 K and a model of the vibrational spectrum, the thermodynamic properties of Sr and Ba feldspars have been calculated in the temperature range 298.15–1000 K.

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