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High-Temperature Heat Capacity of Li, Sc-Germanate $LiScGeO_4$ and Li, Sc-silicate $LiScSiO_4$

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$LiScGeO_4$ and $LiScSiO_4$ compounds were obtained by solid-phase synthesis from Li_2CO_3, Sc_2O_3, GeO_2 (SiO_2). Their crystal structure has been refined using X-ray diffraction. The high-temperature heat capacity (320−1050 K) of the obtained lithium-scandium germanate and silicate was measured by differential scanning calorimetry. The thermodynamic properties were calculated based on the experimental data about heat capacity.

Keywords: differential scanning calorimetry, solid-phase synthesis, thermodynamic properties.

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1. Introduction

Sustained interest to Ge- and Si-based complex oxide compounds $LiScGeO_4$ and $LiScSiO_4$ has been observed during a long period. This is associated with the possibilities of application as fluorescent [1,2] and laser materials [3,4]. Therefore, the focus was made on the investigation of their structure and optical properties [5–9]. No information on the thermophysical properties of these compounds have been found in the literature. At the same time, the information on heat capacity and other thermodynamic properties facilitates thermodynamic simulation for clarification of phase equilibria and optimization of solid-phase synthesis conditions. At this point, there is no high-temperature heat capacity data for $LiScGeO_4$ and $LiScSiO_4$.

The objective of the study is to determine experimentally high-temperature heat capacity of $LiScGeO_4$ and $LiScSiO_4$ within 320−1050 K and to calculate the key thermodynamic functions using these findings.

2. Experiment

$LiScGeO_4$ and $LiScSiO_4$ were obtained by solid-phase synthesis from precursors: Li_2CO_3 (chemically pure, C.P.), Sc_2O_3 (C.P.), GeO_2 — 99.99%, SiO_2 — 99.99%. To prepare $LiScGeO_4$, the stoichiometric mixture was triturated in an agate mortar and then compressed without binder. Annealing was performed in ML100 muffle furnace in crucibles with lid at 1373 K during 20 h. Then the tablet was triturated, compacted again and annealed at $T = 1423$ K during 20 h. It should be noted that such synthesis of $LiScSiO_4$ did not provided the target product. Therefore, for $LiScSiO_4$, the precursors were triturated in PM 100 (Retsch) planetary mill using a beaker and zirconium oxide balls. Homogenization was performed in alcohol (speed 260 rpm, time — 24 h). The prepared mixture was ignited in a drying oven to remove the alcohol. The dried powder was compressed as a tablet and annealed in air at 1373 K and 1423 K during 20 h. The phase composition of the prepared samples was monitored using Bruker D8 ADVANCE diffractometer (VANTEC linear detector, CuK_α-radiation). The Rietveld refinement is implemented using TOPAS 4.2 software [10]. While the synthesized $LiScGeO_4$ did not contain any impurities, the prepared $LiScSiO_4$ had the total content of unreacted reagents and silicates of other compounds equal to 0.8%.

Tables 1 and 2 list the obtained values of $LiScGeO_4$ and $LiScSiO_4$ lattice cell parameters, and data provided by other authors. It can be seen that they well agree with each other.

The heat capacity of $LiScGeO_4$ and $LiScSiO_4$ was measured by differential scanning calorimetry using STA 449 C Jupiter thermal analyzer (NETZSCH, Germany). The experiment procedure is as described earlier in [13,14]. The measurement error did not exceed 2%.

3. Findings and discussion

The Figure shows the temperature effect on the molar heat capacity of $LiScSiO_4$ and $LiScGeO_4$, respectively. It is shown that heat capacities consistently increase with the temperature increase from 320 K to 1050 K, and $C_p = f(T)$ has no extremums of various kinds. This suggests that oxide compounds within this temperature range have no polymorphous transformations.

The achieved experimental findings in termed of heat capacity are well described by the classical Mayer−Kelly equation [15]:

$$C_p = a + bT - cT^{-2}, \qquad (1)$$

Table 1. $LiScGeO_4$ lattice cell parameters

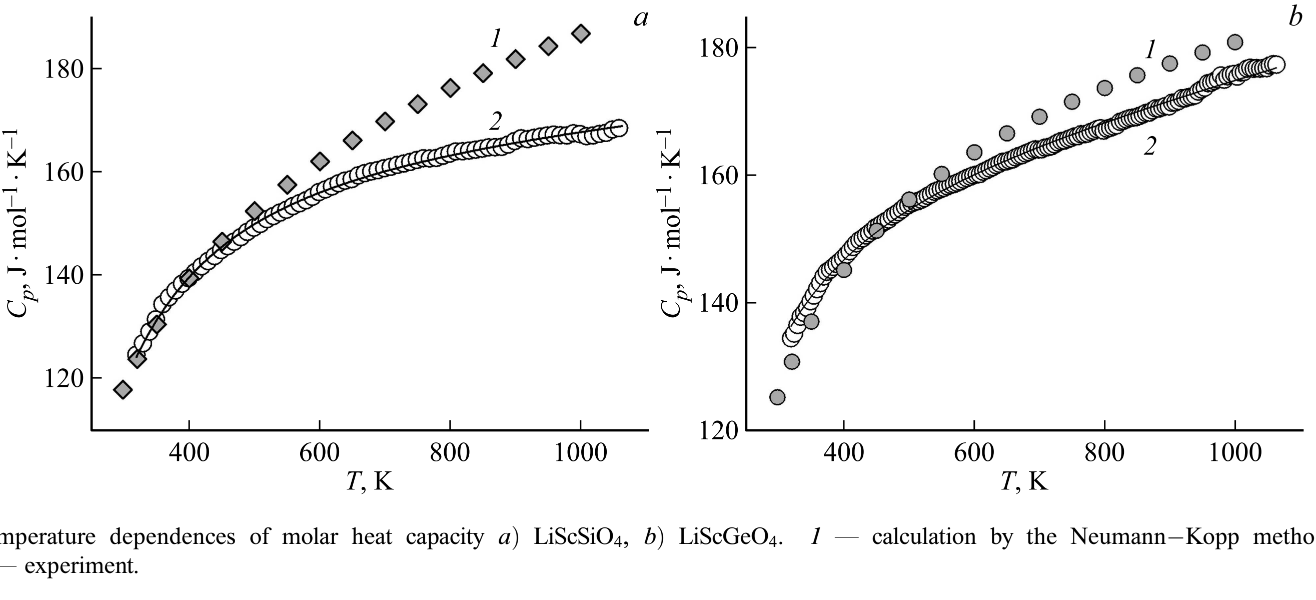
Parameter	$LiScGeO_4$			
a, Å	10.67816(5)	10.673(2)	10.6780	10.6738
b, Å	5.99434(4)	5.9926(11)	5.9942	5.9913
c, Å	4.97007(4)	4.9667(5)	4.9700	4.9689
V, Å^3	318.127(5)	317.67(2)	318.11	317.7608
space group	*Pnma*	*Pnma*	*Pnma*	*Pnma*
reference	This study	[9]	[11]	[12]

Table 2. $LiScSiO_4$ lattice cell parameters

Parameter	$LiScSiO_4$				
a, Å	4.81939(6)	4.8168	4.8168(9)	4.82200(4)	4.8214(7)
b, Å	10.43893(4)	10.4317	10.4317(8)	10.4392(8)	10.444(1)
c, Å	5.970541(6)	5.9650	5.9650(9)	5.9720(4)	5.9729(8)
V, Å^3	300.37(5)		299.72(8)	300.76(6)	
Space group	*Pbnm*			*Pbnm*	*Pbnm*
Reference	This study.	[5]	[6]	[7]	[8]

Table 3. Comparison of experimental heat capacities of $LiScGeO_4$ and $LiScSiO_4$ with calculated heat capacities in various models ($J \cdot K^{-1} \cdot mol^{-1}$). Deviation, % is shown in brackets

Oxide	$C_{p,298}$, exp.	NK	KIM	Kel
$LiScGeO_4$	132.53	125.37 (−5.4)	131.7 (−0.63)	134.5 (1.48)
$LiScSiO_4$	118.13	118.54 (0.34)	120.9 (2.34)	126.5 (7.1)



Temperature dependences of molar heat capacity *a*) $LiScSiO_4$, *b*) $LiScGeO_4$. *1* — calculation by the Neumann–Kopp method, *2* — experiment.

that is written as follows or $LiScGeO_4$ and $LiScSiO_4$, respectively:

$$C_p = (150.40 \pm 0.56) + (26.84 \pm 0.60) \cdot 10^{-3} T - (23.00 \pm 0.57) \cdot 10^5 T^{-2}, \quad (2)$$

$$C_p = (160.40 \pm 0.43) + (11.17 \pm 0.50) \cdot 10^{-3} T - (40.50 \pm 0.44) \cdot 10^5 T^{-2}, \quad (3)$$

The correlation coefficients for equations (2) and (3) are equal to 0.9990 and 0.0098, while the maximum deviations from the fitting curves are 0.68 and 0.53%.

Table 4. Thermodynamic properties $LiScGeO_4$ and $LiScSiO_4$

T, K	C_p, $J \cdot K^{-1} \cdot mol^{-1}$	$H^\circ(T){-}H^\circ(320\,K)$, $kJ \cdot mol^{-1}$	$S^\circ(T){-}S^\circ(320\,K)$, $J \cdot K^{-1} \cdot mol^{-1}$	$-\Delta G/T^*$, $J \cdot K^{-1} \cdot mol^{-1}$
		$LiScGeO_4$		
320	136.6	–	–	–
350	141.1	4.16	12.44	0.538
400	146.8	11.37	31.67	3.25
450	151.2	18.82	49.22	7.80
500	154.7	26.47	65.34	12.40
550	157.6	34.28	80.22	17.89
600	160.1	42.22	94.04	23.67
650	162.4	50.29	106.9	29.58
700	164.5	58.46	119.1	35.55
750	166.5	66.74	130.5	41.50
800	168.3	75.11	141.3	47.40
850	170.1	83.57	151.5	53.23
900	171.7	92.12	161.3	58.97
950	173.4	100.7	170.6	64.60
1000	175.0	109.4	179.6	70.13
1050	176.5	118.2	188.2	75.54
		$LiScSiO_4$		
320	124.4	–	–	–
350	131.3	3.84	11.46	0.49
400	139.6	10.62	29.57	3.01
450	145.4	17.76	46.36	6.91
500	149.8	25.14	61.92	11.64
550	153.2	32.72	76.37	16.88
600	155.9	40.45	89.81	22.40
650	158.1	48.30	102.4	28.07
700	160.0	56.25	114.2	33.81
750	161.6	64.29	125.3	39.54
800	163.0	72.41	135.7	45.23
850	164.3	80.59	145.6	50.84
900	165.5	88.83	155.1	56.38
950	166.5	97.14	164.1	61.81
1000	167.5	105.5	172.6	67.14
1050	168.5	113.9	180.8	72.36

Note. * — $(\Delta G/T) = (H(T){-}H(320\,K))/T{-}(S(T){-}S(320\,K))$.

It was not possible to compare our findings for the heat capacity of $LiScGeO_4$ and $LiScSiO_4$ with the data provided by other authors due to the absence of such data. Therefore, $C_p = f(T)$ was calculated for the oxides of interest by the Neumann–Kopp method [16,17]. The results are shown in the Figure. Coincidence of the experimental and calculated C_p at low temperatures. At $T > 600\,K$, their difference is observed, which increases with temperature growth. According to [18], both positive and negative deviations from the Neumann–Kopp additive rule are observed, which are associated with atomic oscillation frequency variations in a complex oxide compound compared with simple oxides. The $C_p = f(T)$ values of the feed oxides required for the Neumann–Kopp calculations were taken from the literature: Li_2O — [19], Sc_2O_3 — [20], GeO_2 — [21], SiO_2 — [22]. In addition, $C_{p,298}$ values may be compared with the calculated values by other model representations: Neumann–Kopp (NK) [16,17], Kumok incremental method (KIM) [23], Kellogg method (Kel) [16,24,25]. These results are listed in Table 3. The Table shows that the best agreement with the experiment for $LiScGeO_4$ is provided by the Kumok method, and for $LiScSiO_4$ — by the Neumann–Kopp method.

Using relations (2) and (3), the main thermodynamic properties of the studied oxides compounds were calculated using the known thermodynamic equations. The obtained data is also given in the Table 4. It is shown that C_p values for $LiScGeO_4$ at all studied temperatures (for $LiScSiO_4$ — up to 1000 K) do not exceed the Dulong–Petit $3Rs$ limit, where R is the universal gas constant, s is the number of atoms per formula unit of the corresponding oxide.

4. Conclusion

The temperature effect on the molar heat capacity of $LiScGeO_4$ and $LiScSiO_4$ prepared by the solid-phase method was studied. It was found that $C_p = f(T)$ within 320−1050 K are well described by the Mayer−Kelly equation. Thermodynamic properties of the prepared compounds were calculated.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] T. Lyu, P. Dorenbos. Chem. Eng. J. **400**, 124776 (2020).

[2] Z. Zhou, P. Xiong, H. Liu, M. Peng. Inorg. Chem. **59**, *17*, 12920 (2020).

[3] M. Sharonov, C. Petricevic, A. Bykov, R.R. Alfano. Opt. Lett. **30**, *8*, 851 (2005).

[4] M. Sharonov, A.B. Bykov, P. Rojas, V. Petricevic, R.R. Alfano. Phys. Rev. B **72**, *11*, 115111 (2005).

[5] X. Sun, R. Tripathi, G. Ponov, M. Balasubramanian, L.F. Nazar. Inorg. Chem. **56**, *16*, 9931 (2017).

[6] R.M. Hasen, R.T. Downs, L.W. Finger. Am. Mineralogist. **81**, *2*, 327 (1996).

[7] J. Ito. Am. Mineralogist. **62**, *3–4*, 356 (1977).

[8] I. Steele, J. Pluth, J. Itô. Zt. Kristallogr. **147**, *1–2*, 119 (1978).

[9] E.A. Genkina, V.A. Timofeeva, A.B. Bykov. ZhSKh **27**, *3*, 167 (1986).

[10] Bruker AXS TOPAS V4: General profile and structure analysis sowtwere for powder diffraction data. — User's Manual Bruker AXS. Karlsruhe, Germany (2008).

[11] Z. Ye, Z. Wang, Q. Wu, X. Huo, H. Yang, Y. Qang, D. Wang, J. Zhao, H. Suo, P. Li. Dalton Trans. **50**, *29*, 10092 (2021).

[12] S. Miao, Y. Liang, Y. Zhang, D. Chen, X.-J. Wang. ACS Appl. Mater. Interfaces. **13**, *30*, 36011 (2021).

[13] V.M. Denisov, L.T. Denisova, L.A. Irtyugo, V.S. Biront. Phys. Solid State **52**, *7*, 1362 (2010).

[14] L.T. Denisova, L.A. Irtyugo, Yu.F. Kargin, V.V. Beletsky, V.M. Denisov. Neorgan. materialy **53**, *1*, 71 (2017). (in Russian).

[15] C.G. Maier, K.K. Kelley. J. Am. Chem. Soc. **54**, *8*, 3243 (1932).

[16] J. Leitner, P. Chuchvalec, D. Sedmidubský, A. Strejc, P. Abrman. Thermochim. Acta. **395**, *1–2*, 27 (2003).

[17] J. Leitner, P. Voňka, D. Sedmidubský, P. Svoboda. Thermochim. Acta. **497**, *1–2*, 7 (2010).

[18] A.A. Reznitsky. Kalometriya tverdogo tela (strukturnye, magnitnye, elektronnye prevrashcheniya). Izd-vo MGU, M. (1981). (in Russian). 184 p. (in Russian).

[19] T. Tanifuji, K. Shiozawa, S. Nasa. J. Nucl. Mater. **78**, *2*, 422 (1978).

[20] M. Zinkevich. Progress. Mater. Sci. **52**, *4*, 597 (2007).

[21] P. Richet, D. de Ligny, E.F. Westrum Jr. J. Non-Cryst. Solids **315**, *1–2*, 20 (2003).

[22] P. Gillet, A. Le Cléach, M. Madon. J. Geophys. Res. **95**, *B13*, 21635 (1990).

[23] V.N. Kumok. Pryamye i obratnye zadachi khimicheskoy termodinamiki. Nauka, Novosibirsk (1987). P. 108. (in Russian).

[24] O. Kubashevsky, S.B. Olkokk. Metallurgicheskaya termokhimiya. Metallurgiya, M., (1982). (in Russian).

[25] P.J. Spencer. Thermochim. Acta. **314**, *1-2*, 1 (1998).

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