CALCULATING THE TEMPERATURE DEPENDENCE OF THE SPECIFIC HEAT FOR RARE-EARTH ARSENATES

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Equations have been derived for the temperature dependence of the specific heat for 14 rare-earth arsenates. The standard specific heats of some of them have also been calculated by Debye's and Ivanova's methods.

The rare-earth arsenates are promising materials as they have semiconducting, ferroelectric, and other valuable properties [1]. They also have high melting points (1800-2000°C) [2, 3], but up to now, no measurements have been made on the thermophysical and thermodynamic characteristics.

We have calculated the temperature dependence of the specific heat $C_p \sim f(T)$ by Landiya's method [4], which is the most reliable published one. The standard entropies of the $MeAsO_4$ needed to calculate the specific heats were derived by means of entropy increments for Me^{3+} (rare-earth cations) and AsO_4^{3-} [5]. The melting points of the $MeAsO_4$ were taken from [2]. Table 1 gives the calculated specific heats. The standard entropies and specific heats vary periodically in the sequence from La to Lu. The values of S_{298}^0 and C_{p298}^0 initially increase from La to Pr, have a minimum at Nd, rise to Ho, and fall to Lu.

The specific heats of some arsenates were also calculated by Debye's method [6, 7]. The characteristic temperatures of the elements Θ'_D for the elements in the arsenates were calculated from Coref's formula [6, 7]:

$$\Theta'_D = \Theta_D \sqrt{T'_m / T_m}, \quad (1)$$

while conversion from the isochoric specific heat to the isobaric was by means of the Nernst–Lindeman equation [6, 7]:

$$C_p = C_v + 0.0051 C_p^2 / T_m. \quad (2)$$

TABLE 1. Arsenate Specific Heats

Arsenate	S^0_{298}, J/mole·K	C^0_{p298}, J/mole·K			Coefficients in $C_p = a + bT - cT^{-2}$, J/mole·K			Temperature range, K
		Debye	Ivanova	Landiya	a	$b \cdot 10^{+3}$	$-c \cdot 10^{-5}$	
$LaAsO_4$	127,9	95,89	116,59	112,49	121,78	35,86	17,8	298—2103
$CeAsO_4$	135,5	97,22	116,58	111,24	133,64	20,4	22,8	298—2110
$PrAsO_4$	142,9	98,59	116,53	115,90	131,40	23,3	20,05	298—2128
$NdAsO_4$	136,7	98,59	116,51	114,75	131,51	22,99	21,10	298—2133
$SmAsO_4$	137,5		116,50	115,05	131,52	23,0	20,8	298—2138
$EuAsO_4$	136,8		116,48	114,93	131,55	22,94	20,9	298—2143
$GdAsO_4$	141,2		116,46	116,08	131,38	23,11	19,8	298—2151
$TbAsO_4$	146,5		116,44	115,97	131,65	23,15	20,2	298—2158
$DyAsO_4$	146,4		116,46	116,46	131,82	22,77	19,8	298—2153
$HoAsO_4$	147,6	92,86	116,43	116,57	131,51	23,19	19,5	298—2163
$ErAsO_4$	145,6		116,38	116,27	131,57	23,01	19,8	298—2183
$TmAsO_4$	142,1		116,28	115,73	131,77	22,52	20,3	298—2223
$YbAsO_4$	138,6		116,20	115,17	131,80	22,30	20,8	298—2253
$LuAsO_4$	124,0		116,15	112,56	132,09	21,45	23,1	298—2273

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The C_{p298}^0 from Debye's method are lower than from Landiya's because Debye's theory gives a good description of the specific heats for crystals of high symmetry but not for medium and low ones. Debye's method could not be applied to estimate C_p for the other arsenates because there are no published Θ_D for those metals.

The standard specific heats were also calculated from Ivanova's scheme [7]

$$C_{p298}^0 = m(22{,}14 + 8{,}32T/T_t). \quad (3)$$

The C_{p298} from that method agree satisfactorily with Landiya's, but the method does not enable one to trace the periodic variation in C_p in the series. Also, all the C_p for the $MeAsO_4$ are approximately the same. We thus consider that Landiya's method gives the most reliable C_p for the arsenates, which are close to the measured values.

NOTATION

C_p isobaric specific heat; $MeAsO_4$ rare-earth arsenate; Me^{3+} rare-earth cation; AsO_4^{3-} arsenate ion; S_{298}^0 standard entropy; C_{p298}^0 standard specific heat; Θ'_D characteristic temperatures of the elements for the arsenates; T' melting point of arsenate; T_m melting point of element, C_v isochoric specific heat; m number of atoms in compound; T_t temperature of the first phase transition; T temperature at which the corresponding C_p^0 is determined.

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