

CALORIMETRIC INVESTIGATION OF THERMODYNAMIC PROPERTIES AND IONS ROTATION OF SOME PERBROMATES

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Low temperature heat capacity of ammonium, rubidium and cesium perbromates has been studied by method of adiabatic calorimetry. Anomaly of the heat capacity of cesium perbromate has been found, which corresponds to a structural phase transition. The separation of heat capacity into components has been carried out by the additive scheme. The torsion oscillation of BrO_4^- anions in solid perbromates at low temperatures has been found. Ammonium ions retardedly rotate around C_2 axes in the crystal lattice of NH_4BrO_4 .

Keywords: adiabatic calorimetry, heat capacity of perbromates

Introduction

Among the ionic crystals there is a group of compounds with isolated tetrahedral anions of XO_4^{k-} type. Distinguishing features of substances containing these anions include such properties as superionic conductivity, 'cold superconductivity', spontaneous electrical polarization etc., and manifestation of these properties as temperature varies is accompanied by different types of phase transitions [1-3]. Among such crystals we find perbromates, i.e. compounds, which include a BrO_4^- anion. Unlike perchlorates and periodates, the perbromates have been synthesized rather lately, so information available on their properties is very limited. Data on IR and R spectra of solid perbromates in the range of characteristic frequencies have been obtained only for the room temperature [4]. During the analysis of thermal decomposition of alkali metal perbromates it has been found that their thermal stability increases from lithium to cesium [5]. Investigation of KBrO_4 heat capacity in the low temperature range revealed two small anomalies at 245 K and 275 K at $C_p(T)$ curve [6]. The X-ray structural analysis of monocrystals showed, that KBrO_4 [7], RbBrO_4 [8]

and NH_4BrO_4 [8] crystallize in orthorhombic system with the space group P_{nma} and CsBrO_4 -in tetragonal system with the space group $I_{41/a}$. Parameters of unit lattice cells and their volume is shown in Table 1.

Table 1 Parameters of unit lattice cells of perbromates

Compound	Space group	Parameters of unit lattice cells, /Å			$V / \text{Å}^3$	Z
		a	b	c		
NH_4BrO_4	P_{nma}	9.270	6.071	7.657	430.9	4
KBrO_4	P_{nma}	8.930	5.921	7.488	395.93	4
RbBrO_4	P_{nma}	9.34	6.11	7.71	439.99	4
CsBrO_4	$I_{41/a}$	5.751	—	14.821	490.20	4

The earlier studies [7–9] has shown, that in perbromate crystals BrO_4^- anion has a shape of slightly distorted tetrahedron and the maximum distortion is observed in ammonium perbromate, where the angles O–Br–O are almost the same, but the length of bonds Br–O (1.603(7) Å and 1.623(5) Å differ essentially. In perbromates of potassium, rubidium and cesium the perbromate anion features has a slightly angular distortion and similar average length of bonds 1.610(12) Å for KBrO_4 , and 1.591(6) Å for CsBrO_4 . Distortions of perbromate anions in the crystal lattice of NH_4BrO_4 and CsBrO_4 are also evidenced by $^{79,81}\text{Br}$ nuclear magnetic resonance [10–12].

It is natural to suppose, that in crystalline perbromates of alkali metals and ammonium, as in perchlorates and periodates [13–17] as well, phase transitions are likely, with the nature of transitions being connected with orientational ordering of ions.

A study of the character of motion of tetrahedral ions in crystal lattice of perhalates is of considerable interest. It is well known, that perhalate ions perform the rotational motion around the axes of symmetry. As the energy of gyration increases, the oscillations around the axis pass to retarded rotation and then into a free rotation (for example, NH_4^+ ions in ammonium halogenides exhibit almost isotropic rotation). The fact that space groups are similar both for ammonium perbromate on the one hand, and for potassium and rubidium perbromates, on the other, may be interpreted as a consequence of a considerable disordering of ammonium ion, due to which its shape approaches sphere.

Application of data on the temperature dependence of the heat capacity allows to estimate potential energy of retarded rotation barriers and to establish the character of anions motion. For this purpose we used an additive scheme proposed by Sakamoto [18]. The method is based on the fact, that due to a dif-

ference in frequencies of translational and librational oscillations of crystal lattice and frequencies of internal oscillations of ions, vibrations are excited consecutively.

Experimental

The samples of perbromates have been prepared by neutralization of perbromic acid (content above 99%) with solutions of respective hydroxides (reagent grade) according to the procedure described in [8]. The samples were identified with IR-spectroscopy and X-ray methods. BrO_4^- content was analysed by iodometric titration. The samples were carefully dried under vacuum and heating. The main substances content was 99.9 mass%. Impurities were represented by carbonates, fluorides and bromides of ammonium and respective alkali metals. The analysis showed the presence of small amount of water (0.08 mass%), which did not decrease even after prolonged drying. All operations with loading the samples into the calorimeter were performed in a box with an atmosphere of dry inert gas.

Heat capacity of ammonium, rubidium and cesium perbromates has been studied in a vacuum adiabatic calorimeter with a 2 cm^3 stainless steel container [19]. The temperature dependence of C_p for each of the salts was plotted on the basis of more than 100 experimental points. Smoothing of $C_p(T)$ curve was performed according to the spline-approximation method with the help of a program, which is a part of the software of Ivtanthermo Data Base [20]. The curves have been extrapolated to Kelvin scale zero according to formula $C_p = AT^3$. The values of thermodynamic properties of rubidium, cesium and ammonium perbromates are given in Table 2.

Table 2 Thermodynamic properties of perbromates at 298.15 K

Compound	$C_p^\circ /$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$S^\circ /$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$H^\circ(T)-H^\circ(0) /$ $\text{J}\cdot\text{mol}^{-1}$	$-(G^\circ(T)-H^\circ)/T /$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
RbBrO ₄	122.0	182.8	24210	101.6
CsBrO ₄	123.7	196.0	25430	110.8
NH ₄ BrO ₄	143.4	200.1	27930	106.4

Results and discussion

The curve of temperature dependence of the heat capacity of perbromates studied featured anomalies in the form of maxima. In cases of ammonium and

rubidium salts only a small peak has been observed in the range of 265–280 K, while in the case of cesium salt in addition to this anomaly quite a few peaks have been observed (Fig. 1). Study of the heat capacity of samples cooled down slightly below the temperature of C_p maximum, showed that under such conditions some of the anomalies do not appear. The shape of the $C_p(T)$ curve in this case reflects a 'normal' heat capacity, it is shown in Fig. 1 by dashed line.

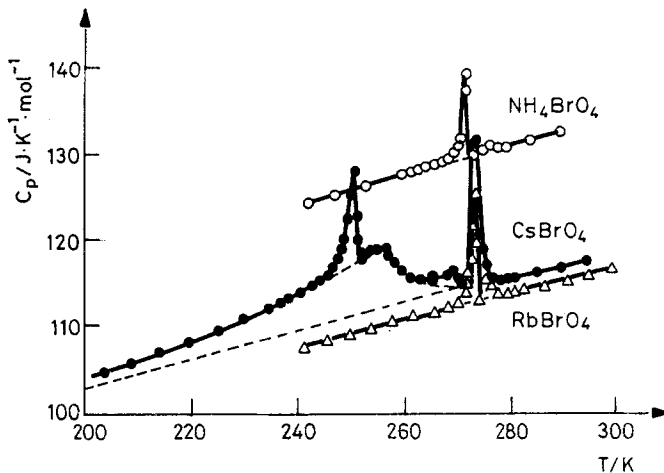


Fig. 1 Anomalies of the heat capacity on $C_p(T)$ curves of ammonium, rubidium and cesium perbromates

Earlier Schreiner *et al.* [6] investigated the heat capacity of potassium perbromate in the range of low temperatures. $C_p(T)$ dependences for $KBrO_4$ and $CsBrO_4$ in the interval below and above γ anomaly are practically symptic (Fig. 2), which allowed us to evaluate parameters (enthalpy and entropy) of the anomalous process. For other anomalies estimation of ΔS and ΔH has been done with the help of points obtained during supercooling of samples below T_{max} . Enthalpy and entropy values of anomalous processes are given in Table 3. The table shows the parameters of all anomalies, but the nature of these anomalies has not been established. It is possible, that some of these anomalies are caused by the presence of impurities in the samples. In particular, we suppose, that α and β anomalies are related to processes in crystallohydrates of perbromates.

In order to determine the nature of anomalies of perbromates of alkali metals and of ammonium, a study of nuclear magnetic resonance spectra in solid state at low temperature has been carried out with the 'Brüker' MLS-300 and WP-80 Fourier-spectrometers. Nuclear magnetic resonance spectra $^{79, 81}Br$, ^{39}K , ^{133}Cs ,

^{87}Rb , ^{14}N and ^1H have been recorded in pulse duty. The study of spectra, their analysis and interpretation have been carried out by Tarasov and Privalov [21].

In the temperature dependence of constants of quadrupole bonds $^{79,81}\text{Br}$ and ^{133}Cs variations in the range 200–260 K have been noted, which correspond to a structural phase transition in the crystal of CsBrO_4 . No variations of this kind have been observed in potassium, rubidium and ammonium perbromates. Ammonium ions in the crystal lattice of respective perbromate rotates anisotropically. Perbromate anion perform rotational oscillations (librations).

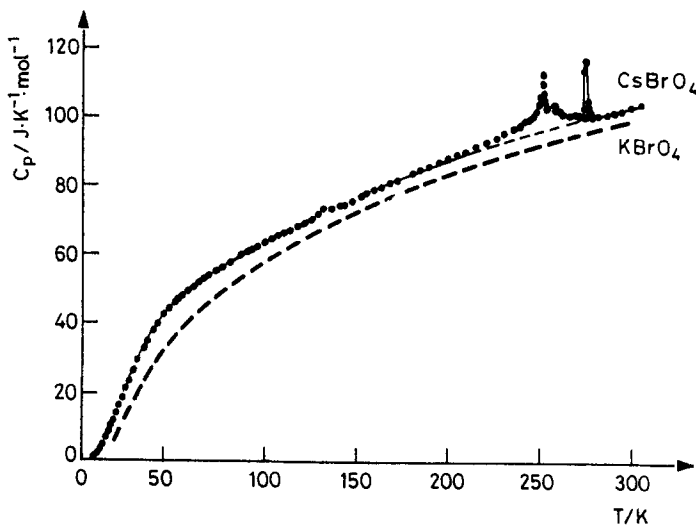


Fig. 2 $C_p(T)$ curves of cesium and potassium perbromates

Earlier works on research of low temperature heat capacity of perchlorates allowed us to conclude that perchlorate ion librates in the crystals of alkali metals perchlorates [22] and ammonium perchlorate [23], while the ammonium ion rotates retardedly, the barrier being $V_0 = 4 \text{ kJ}\cdot\text{mol}^{-1}$.

In order to evaluate the character of rotational motion of BrO_4^- anion, we have carried out separation of heat capacity of potassium [6], rubidium [24] and cesium [25] perbromates into components according to an additive scheme, which has been used earlier for alumino- [26] and borohydrides [27], as well as for perchlorates of alkali metals:

$$C_p = C_{\text{tr}} + C_i + C_{\text{rot}} + (C_p - C_v) + C_{\text{anom}} \quad (1)$$

(where C_p : experimental value of the heat capacity; C_{tr} : heat capacity attributed to translational oscillations of crystal lattice, calculated in accordance with the Debye's model; C_i : heat capacity, attributed to the internal oscillations of BrO_4^- anions, calculated in accordance with the Einstein's model; C_{rot} : heat capacity, attributed to rotational oscillations of the anion, ($C_p - C_v$): contribution of the work of expansion of the crystal lattice). Calculation results were used to evaluate frequencies of translational and rotational oscillation (Table 4).

Table 3 Parameters of anomalies

Compound	Anomaly	Temperature range / K	T_{max} / K	ΔS / $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	ΔH / $\text{J}\cdot\text{mol}^{-1}$
NH_4BrO_4	β	265–172	271.0	0.06	18
	α	272–276	273.5	0.01	2
RbBrO_4	β	262–274	273.2	0.08	21
	α	274–276	275.2	0.01	4
CsBrO_4	ε	126–136	130.6	0.08	10
	δ	240–252	250.5	0.10	24
	γ	160–272	251.1	1.51	349
	β	262–271	268.5	0.03	8
	α	270–278	273.4	0.17	56

Table 4 Frequencies of translational and rotational oscillation of lattice

Substance	Frequency of translational oscillation	Frequency of libration of BrO_4^- anions
KBrO_4	135	198
RbBrO_4	113	178
CsBrO_4	102	100

Assuming that BrO_4^- ion oscillates around the axes of the second order the calculation energy of potential barriers have been made according to the formula:

$$v_0 = \pi^2 I \frac{V^2}{2} \quad (2)$$

where ν -frequency of rotational oscillations, I -inertia moment of BrO_4^- ($1.81 \cdot 10^{-39} \text{ g/cm}^2$), which gave about 40 kJ for potassium and rubidium perbromates and about 7 kJ for CsBrO_4 . Such a considerable difference in barrier may be attributed to the fact that cesium perbromate has a scheelite structure, while KBrO_4 and RbBrO_4 have a baryte structure.

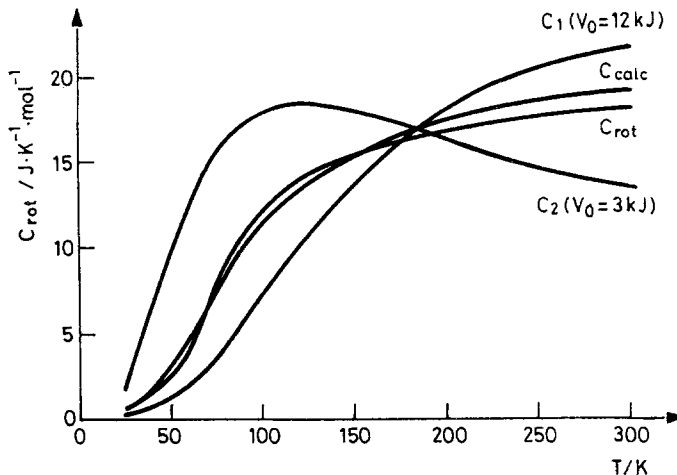


Fig. 3 Rotational heatcapacity of ammonium ions for different barriers. $C_{\text{calc}}=2/3C_1+1/3C_2$; C_{rot} -heat capacity from expression (3)

In order to determine the character of motion of ammonium ion in NH_4BrO_4 lattice, we had to use another procedure. The matter is, that the heat capacity of NH_4BrO_4 has already not five, but seven components (there comes additionally heat capacity attributed to internal oscillations of NH_4^+ ion and to its rotational oscillations). Rotational oscillations of tetrahedral ions NH_4^+ and BrO_4^- are excited at very close grade marks and we have not managed to draw a qualitative separation of their contributions. We used an approximation procedure, proposed in [23], where the heat capacity, attributed to rotational oscillations of NH_4^+ was determined as the difference:

$$C_{\text{rot}} = C_p(\text{NH}_4\text{ClO}_4) - C_p(\text{KClO}_4) - C_i(\text{NH}_4^+) \quad (3)$$

assuming that the frequencies of translational oscillations of ammonium and potassium salts are very near to each other. Contribution of internal oscillations of ammonium ion has been calculated according to the Einstein's model, proceeding from the frequencies given in [28]. The shape of resulting curve of the dependence of heat capacity of rotational oscillations upon temperature (Fig. 3)

and the analysis of the $C_p(T)$ dependences has showed, that ammonium ion rotates retardedly and maximum similarity of the theoretical curve to the experimental one is obtained if we assume that the rotational barriers are different: for two axes the value of the barrier is $12 \text{ kJ}\cdot\text{mol}^{-1}$, while for the third axis it makes $3 \text{ kJ}\cdot\text{mol}^{-1}$. It confirms the conclusion that the rotation of ammonium ion is anisotropic, drawn from the results of study of its nuclear magnetic resonance spectra.

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Zusammenfassung — Mittels adiabatischer Kalorimetrie wurde die Tieftemperatur-Wärmekapazität von Ammonium-, Rubidium- und Zäsiumberbromat untersucht. Man fand eine Anomalie für die Wärmekapazität von Zäsiumberbromat, in deren Hintergrund eine Phasenumwandlung steht. Anhand eines Additivschema wurde die Wärmekapazität in Komponenten gespalten. In festen Perbromaten fand man bei tiefen Temperaturen eine Torsionsschwingung der BrO_4^- -Anionen. Die Ammoniumionen zeigen eine verlangsamte Rotation um die C_2 -Achsen im Kristallgitter von NH_4BrO_4 .