79.81Br and 133Cs Nuclei Quadrupole Interactions and Phase Transitions in Crystalline Caesium Perbromate

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Introduction

There is little information about the properties of the alkali perbromates since those have been synthesized only recently [11]. Room temperature infra-red and Raman data in the region associated with perbromate ion were obtained to allow identification of the perbromate ion [2, 3]. Thermal decomposition studies of the alkali metal perbromates found caesium perbrom ate to be the most stable [4]. Recently heat capacity (c_p(T)) measurements on CsBrO_4 using adiabatic calorimetry between 10 K and 320 K have been obtained [5, 6]. c_p(T) shows a characteristic S-like curve apart from three anomalies between 250 K and 278 K associated with impurity water molecules that are present and a broad peak between 160–272 K due to a structural phase change.

According to single crystal X-ray diffraction at 297 K CsBrO_4 crystallizes in a tetragonal form with space group 14/4/a and cell parameters a = 5.751(6) Å and c = 14.871(12) Å. The BrO_4^- ions have a tetrahedral configuration with a small angular distortion. The Br–O distance is 1.591(6) Å. The BrO_4^- tetrahedra are arranged in the lattice in such a fashion that for each face of a particular tetrahedron there is only one parallel face on each of the neighbouring tetrahedra [7]. Such “parallelism” of faces is supposed to be the reason of the observed plasticity of the CsBrO_4 crystals.

The 12 oxygen nearest neighbours of the caesium cation form a truncated tetrahedron with Cs–O bond lengths approximately equal to oxygen-cation internuclear distances in perchlorates of all the other alkali metals in the high temperature phase (cubic form, space group F4 3 m [7, 8]. Usually in scheelite-type structures with space group 14/4/a the cations and anions occupy distinct positions 4b and 4a, respectively. For this arrangement the principal component q of the electric field gradient (EFG) tensor in the positions 4a and 4b are related by the inequality (9):

\[ |q|_{4a} > |q|_{4b}. \]  

CsBrO_4 is anomalous in that the occupation of sites 4b and 4a by anions and cations is reversed. Despite this reversal ineq. (1) remains valid indicating that lattice contributions to q are dominant rather then nearest neighbour effects. The uniqueness of the CsBrO_4 structure and its structural modification encouraged a study of local structural parameters, such as q NMR has been used to measure the EFG at both the anion and cation positions as a function of temperature particularly near the phase transition.

Experiment

Caesium perbromate was synthesized from Cs(OH) (special purity) and HBrO_4 (not less than 99% by mass) using the method described in [7]. The BrO_4^- content was analyzed iodometrically by precipitation of the tetraphenylammonium salt. The water content was determined from sample
weight loss upon desiccation at constant temperature in a vacuum with monitoring by IR and $^1$H NMR spectra. The X-ray diffraction pattern agrees with that of the previously synthesized CsBrO$_4$ [7]. CsBrO$_4$ is only weakly hygroscopic and the water content of a powder sample held in a moist atmosphere (90% humidity) did not exceed 0.17(3) wt%. The base sample corresponded to 99.8(1)% CsBrO$_4$ which increased upon desiccation to 99.9 wt% with the remaining crystal water corresponding to 0.08% and the other impurities (carbonate, fluoride, bromate) to less than 0.1%.

NMR spectra were recorded at magnetic fields of 1.88 T and 7.04 T, where the corresponding frequencies are $^{79}$Br (-75.2 MHz), $^{81}$Br (21.64 MHz, 81.02 MHz) and $^{133}$Cs (10.51 MHz, 39.35 MHz) on Bruker WP 80 and MSL 300 spectrometers respectively. Spectra were accumulated using excitation pulses of 1-4 $\mu$s corresponding to 10 degree pulse angle with 2 sec delays.

Results and Discussion

The $^{81}$Br NMR spectrum at 297 K recorded using $B_0 = 1.88$ T shows a second order quadrupole lineshape for the central (1/2 $\leftrightarrow$ -1/2) transition characterized by a splitting $\Delta v = 10.33$ KHz (eq. (2)). $\Delta v$($^{81}$Br) shows a steady increase with decreasing temperature both at 1.88 T (Fig. 1a) and 7.04 T (Fig. 1c) as does $\Delta v$($^{79}$Br) at 7.04 T (Fig. 1b). The lineshapes are all characterized by $\eta = 0$ as is confirmed by comparing at the two fields. The measured splitting, which at 297 K and 7.04 T corresponds to $\Delta v$($^{81}$Br) = 1.81(1) KHz and $\Delta v$($^{79}$Br) = 2.74(1) KHz, for the powder pattern of the central (1/2 $\leftrightarrow$ -1/2) transition can be related to the quadrupole parameters by:

$$
\Delta v = \frac{v_0^2}{144 \nu_{1L}} \left[ I(I + 1) - \frac{3}{4} \right] f(\eta)
$$

where $f(\eta) = 16(1 - \eta) + (3 - \eta)^2$

and $v_0 = \frac{e^2qQ}{h} \frac{3}{2I(2I - 1)}$; $C_Q = \frac{e^2qQ}{h}$.

For $\eta = 0$ and $I = 3/2$:

$$
\Delta v = \frac{25}{48} \nu_{1L} v_0 = \frac{25}{192} C_Q^2 \nu_{1L} \text{ with } C_Q = 2 v_0.
$$

The ratio of $\Delta v$ for the bromine isotopes at constant field

$$
\frac{\Delta v$($^{79}$Br)}{\Delta v$($^{81}$Br)} = \frac{v_1$($^{81}$Br)}{v_1$($^{79}$Br)} = 1.50
$$

which can be compared to the experimental value of

$$
\frac{\Delta v$($^{79}$Br)}{\Delta v$($^{81}$Br)} = \frac{2.74}{1.81} = 1.50.
$$

This remains constant for all temperatures. This value is indicative of the lineshapes being dominated by the second-order quadrupole interaction allowing spectral simulation by the “POWDER” program available within the Bruker software. Values of $C_Q$ deduced from $\Delta v$ agree with the values obtained from spectral simulation. It should be noted that the ratio of $\Delta v$ at 1.88 T and 7.04 T for $^{81}$Br (eq. (2)) from theory does not agree with the experimental value

$$
\frac{\Delta v$($^{81}$Br)}{\Delta v$($^{79}$Br)} = \frac{21.64}{81.02} = \frac{3.74}{5.71}.
$$

Fig. 1a

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1a.png}
\caption{Na$^{11}$BrO$_3$ + H$_2$O}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1b.png}
\caption{Cs$^{85}$BrO$_4$}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1c.png}
\caption{Cs$^{85}$BrO$_4$}
\end{figure}
time of the spectrometer. By variation of the parameters of the quadrupole interaction in the “POWDER” program, we practically adjust the calculated lineshape to fit the distorted experimental lineshape. Thereby the degree of distortion is significantly greater at the lower Larmor resonance frequency of the $^{81}\text{Br}$ nuclei (21.64 MHz).

$^{133}\text{Cs}$ NMR spectra at 1.88 T and 7.04 T (Fig. 2) show seven lines from first-order quadrupole splitting of the nuclear transitions. This splitting
and hence QCC increase monotonously from 0.100(1) MHz at 120 K to 0.119(1) MHz at 297 K. Over the same temperature range $\eta$ drops from 0.23 to zero as deduced from Fig. 3.

Fig. 3 and 4 summarizing changes of the quadrupole parameters for $^{133}$Cs and $^{79,81}$Br respectively, clearly show that the most marked changes occur between 200 - 260 K. The temperature depend-

\begin{equation}
\nu_Q(T) = \nu_Q^0 \left(1 - \frac{3 kT}{8\pi^2 Jv_{\text{libr.}}^2}\right)
\end{equation}

where $J$ is the moment of inertia of the BrO$_4^-$ anion which is equal to $179.7 \cdot 10^{40}$ g cm$^2$ relative to the

Fig. 3. Temperature dependence of $^{133}$Cs QCC and asymmetry parameter $\eta^{(133)}$Cs in caesium perbromate.

Fig. 4. Temperature dependence of $^{79,81}$Br QCC in crystalline CsBrO$_4$. 
C₃-axis of the tetrahedron. This shows a linear temperature dependence, which is observed at either side of the phase transition, and a weak parametric dependence on νlibr. This cannot explain the variation of νQ (79Br) at the phase transition (200–260 K). The change of νQ association with the phase transition can be explained in terms of changes in the lattice structure resulting from reorientation of BrO₄ tetrahedra.

From the two linear regions at either side of the phase transition the libration frequency may be deduced as

a) high-temperature range (T = 297 K),

\[ 2 \nu_Q = 1.85 \text{ MHz} \]

\[ \nu_{libr} = 3.5 \cdot 10^{-11} \text{ sec}^{-1} \]

b) low-temperature range (T = 180 K),

\[ 2 \nu_Q = 2.35 \text{ MHz} \]

\[ \nu_{libr} = 2.9 \cdot 10^{-11} \text{ sec}^{-1} \]

These values of νlibr (≈10 cm⁻¹) correspond to the lowest frequency lattice modes observed by IR spectra of similar crystals (10–200 cm⁻¹).

The decrease of QCC for bromine with increasing temperature indicate that BrO₄ tetrahedra must become more regular as the structure changes. Simultaneously for ¹³³Cs QCC increases and η drops to zero. As changes in QCC are dominated by lattice effects they have to explain the opposing behaviour for bromine and caesium. The orientational phase transition can be observed on temperature variation of the unit cell parameters.

In CsBrO₄ at 297 K the “c/a” ratio is 2.58 [7] which is considerably larger than the typical value 2.15–2.24 (8), characteristic of compounds with scheelite structure and space group I4₁/a. With decreasing temperature “c” decreases and “a” may increase. The equilibrium position and is characterized by the orientation of the BrO₄ tetrahedra relative to the c-axis. This orientation axis corresponds to a characteristic direction of the EFG. The smooth break of νQ(T) for 79Br and 8¹Br can be associated with a change of the relative orientation of the BrO₄ tetrahedra within the lattice framework. The positive temperature coefficient of \( \partial cQ / \partial T \) and change of η for ¹³³Cs could be related to lattice effects from anisotropic changes of the “a” parameter.

It has to be mentioned, that the anomalous increase of the effective quadrupole coupling constant with rising temperature was observed for the central ¹²⁷I and ¹⁸⁸Re nuclei of the tetrahedral IO₄ and ReO₄ ions with different cations (AsR₄, NR₄, NH₄, PR₄) in the lattice structure [11–13]. Such anomalous behaviour of the quadrupole coupling constants have been explained by the increase of the orientational mobility of tetrahedral ions in the lattice structure with rising temperature [14].

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