Raman Investigations on Potassium Hexabromostannate. Crystal Structure and Phase Transition

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The Raman spectra of K_2SnBr_6 have been recorded at different temperatures and found to be in agreement with tetragonal symmetry at room temperature and cubic symmetry at 140 °C. Crystals of the compound appear to be polysynthetic twins at temperatures below the phase transition point and behave as single crystals at temperatures above the transition point.

Earlier X-ray investigations seem to be in conflict concerning the symmetry of potassium hexabromostannate, K_2SnBr_6 . Ketelaar *et al.*¹ have determined the compound to be cubic with space group $Fm\bar{3}m = O_h$.⁵ Markstein *et al.*² have, on the other hand, determined it to be tetragonal with space group $P4_2,2 = D_4$ and found the deviation from cubic symmetry to be small and give the axial ratio c/a as 1.009 ± 0.002 . On the basis of microscopic investigations between -80 and 250 °C Galloni *et al.*³ have reported a phase transition at 126.5 °C. Above this temperature the compound should be cubic and below tetragonal.

Infrared and Raman spectra of polycrystalline samples of potassium hexabromostannate have been reported by several authors.⁴⁻⁶ Debeau *et al.*^{4,5} mention, that though the compound is tetragonal at room temperature the deviation from cubic symmetry must be so slight that it cannot be observed in the vibration spectra because the spectra of potassium hexabromostannate are similar to spectra of other compounds of this type with cubic symmetry. The observed wavenumbers are therefore assigned to the point group O_h : $\nu_1(A_{1g})$ 190 cm^{-1} , $\nu_2(E_g)$ 144 cm^{-1} , $\nu_3(F_{1u})$ 224 cm^{-1} , $\nu_4(F_{1u})$ 118 cm^{-1} , $\nu_5(F_{2g})$ 109 cm^{-1} and an external vibration $\nu_7(F_{1u})$ 78 cm^{-1} .

EXPERIMENTAL

Polycrystalline potassium hexabromostannate was prepared as described by Nakamura *et al.*⁸ Larger crystals with an edge length of approximately 3 mm were grown from saturated solutions. The compound was pale yellow.

The Raman spectra were recorded with a spectrometer equipped with a Jarrell-Ash model 25-101 double grating monochromator. The exciting lines used were 4880 Å and 5145 Å obtained from a Spectra-Physics model 165 Argon-ion laser.

X-RAY INVESTIGATION

Examination of the compound under a polarizing microscope showed that potassium hexabromostannate cannot be cubic at room temperature, because the crystals were birefringent. To determine the crystallographic axes in order to orientate the crystals on the Raman spectrometer, a large crystal, mounted on a goniometerhead, was investigated by a X-ray precession camera. From the X-ray photos the axial ratio c/a was determined to 1.012. This is in agreement with the tetragonal structure proposed by Markstein *et al.*²

SELECTION RULES

The free $SnBr_6^{2-}$ ion belongs to the point group O_h (Ref. 9) and the normal vibrations may be classified as follows (Table 1): $A_{1g} + E_g + F_{2g} + 2 F_{1u} + F_{2u}$.

The X-ray investigation indicates, that the deviation from cubic symmetry is small. If it is assumed that the crystalline compound from a spectroscopic point of view can be treated as cubic, as done by Debeau *et al.*,^{4,5} the space

group $Fm\bar{3}m=O_h^5$ and a primitive unit cell containing one formula unit have to be used. In cubic K_2SnBr_6 the complex ion occupies a site with O_h symmetry and the two K^+ ions are situated at a pair of sites with T_d symmetry.¹⁰ Figs. 1 and 2 show parts of the correlation diagrams for cubic potassium hexabromostannate.

Free ion group	Site group	Unit cell group
O_h	O_h	O_h
A_{1g}	A_{1g}	A_{1g}
E_g	E_g	E_g
F_{1g}	F_{1g}	F_{1g}
F_{2g}	F_{2g}	F_{2g}
F_{1u}	F_{1u}	F_{1u}
F_{2u}	F_{2u}	F_{2u}

Fig. 1. Correlation diagram for the $SnBr_6^{2-}$ ion in the cubic structure.

Site group	Unit cell group
T_d	O_h
F_2	F_{1u} F_{2g}

Fig. 2. Correlation diagram for the K^+ ions in the cubic structure.

It can be seen from the correlation diagrams, that the internal and external vibrations, respectively, may be classified as follows: $A_{1g} + E_g + F_{2g} + 2 F_{1u} + F_{2u}$ and $F_{1g} + F_{2g} + F_{1u}$. Modes of the symmetry species A_{1g} , E_g , and F_{2g} are allowed in the Raman spectrum. Hence observation of three internal and one external vibration in the Raman spectrum of cubic potassium hexabromostannate can be expected.

However, the selection rules given above can only be expected to be valid above 126.5 °C. At room temperature the compound should be treated as tetragonal with space group $P4_21_2 = D_4^2$ and with two formula units in the primitive unit cell. In tetragonal K_2SnBr_6 the two complex

Fig. 3. Correlation diagram for the $SnBr_6^{2-}$ ion in the tetragonal structure.

Site group	Unit cell group
D_2	D_4
B_1	A_2
B_2	B_1
B_3	E

Fig. 4. Correlation diagram for the K^+ ions in the tetragonal structure.

ions occupy a pair of sites with C_4 symmetry and the four K^+ ions are situated on sites with D_2 symmetry.¹⁰ Figs. 3 and 4 show the necessary part of the correlation diagrams for tetragonal potassium hexabromostannate.

From the correlation diagrams it can be seen that the internal and external vibrations, respectively, may be classified as follows: $4A_1 + 4A_2 + 3B_1 + 3B_2 + 8E$ and $2A_1 + 3A_2 + 2B_1 + 7E$. Here modes of the symmetry species A_1 , B_1 , B_2 , and E are allowed in the Raman spectrum.

This means that the Raman spectrum should consist in not more than 18 components of the internal vibrations and 11 external vibrations. Because the deviation from cubic symmetry is small it is assumed that the splitting in the internal vibrations caused by the dynamic coupling is small, if observed at all. As a consequence of these selection rules all the fundamentals of the complex ion are allowed in the Raman spectrum, but it is expected, that the intensity of the vibrations, which are forbidden in the cubic case, will be weak.

Table 1. Observed Raman spectra.

Internal vib.	Free ion ^a	Crystals		$T \sim 20^\circ\text{C}$		$T \sim 140^\circ\text{C}$	
	ν cm^{-1}	ν cm^{-1}	rel. int.	ν cm^{-1}	rel. int.	ν cm^{-1}	rel. int.
$\nu_1 (A_{1g})^a$	184	190	vs	190	vs	188	vs
$\nu_2 (E_g)$	140	144	s	144	s	142	m
$\nu_3 (F_{1u})$	—	—	—	—	—	—	—
$\nu_4 (F_{1u})$	—	116	(sh)	—	—	—	—
$\nu_5 (F_{2g})$	101	110	s	109	s	106	m
$\nu_6 (F_{2u})$	—	—	—	—	—	—	—
External vib.							
	—	88	w	~ 82	w(sh)	—	—
	—	80	w	—	—	—	—
	—	75	w(sh)	—	—	—	—
	—	57	vw	—	—	—	—
	—	47	w	41	vw	—	—
	—	33	w	23	w	—	—

^a The symmetry species given in the table refer to the assignment of the free ion fundamentals.

OBSERVED RAMAN SPECTRA

The observed bands in the Raman spectra of potassium hexabromostannate at three different temperatures and the wavenumbers of the Raman active vibrations of the free ion are given in Table 1.

The wavenumbers of the internal vibrations at room temperature found in this investigation agree with the wavenumbers given by Debeau *et al.*^{4,5} Furthermore three bands are observed in the spectrum which are assigned to external vibrations. This agrees with the tetragonal and not the cubic structure at room temperature. These three bands have not been reported by Debeau *et al.*^{4,5} The fact that no splitting of the internal vibrations or any of the ungerade vibrations are observed agrees with the assumption of small coupling, even though the deviation from cubic symmetry is obvious because there is observed more than one external vibration.

The Raman spectrum at low temperature shows, as expected, no appreciable wavenumber shift concerning the internal vibrations. The band at 116 cm^{-1} is assigned to a component of ν_4 rather than of ν_5 because ν_4 is found at 118 cm^{-1} in the infrared spectrum of the compound^{4,5} and because there is not observed more than one component of the other internal vibrations.

At low temperature the half-width of the

bands is expected to diminish and it may then be possible to observe very weak bands which cannot be observed at room temperature or which may be covered by other bands with a large half-width. Furthermore a shift towards higher wavenumber is expected for the external vibrations at low temperature. The observation of six external vibrations at -178°C is in accordance with these assumptions.

Galloni *et al.*³ have reported that potassium hexabromostannate has no phase transitions between -80 and 126.5°C , but transitions below -80°C cannot be excluded. However, the observation of six external vibrations and a component of ν_4 is in accordance with the tetragonal structure.

When the compound is heated the external vibrations can be followed to approximately 110°C . At higher temperatures only the internal vibrations can be observed. This is in accordance with the phase transition from tetragonal to cubic symmetry at 126.5°C observed by Galloni *et al.*³ but could also be due to line broadening.

POLARIZED RAMAN SPECTRA

Polarized spectra of orientated crystals have been recorded at room temperature and at about 140°C .

The X-ray investigation showed that the crystallographic axes pass through the corners of the crystal. To avoid rotation of the polariza-

tion direction of the exciting beam when it enters the crystal, faces were polished parallel to the (100), (010), and (001) planes. In some cases these faces have already been developed under the crystal growth. All measurements were carried out with scattered light of the same polarization achieved by mounting a half-wave plate between the analyzer and the entrance slit.

For tetragonal potassium hexabromostannate single crystals, it can be seen from the character table of the unit cell group, that fundamentals of the symmetry species A_1 , B_1 , B_2 , and E should be observed only in polarized spectra of the types (XX), (YY), (ZZ) – (XX), (YY) – (XY) and (YZ), respectively.

Polarized spectra of the types listed above were recorded at room temperature, but no changes of wavenumber or intensity of any bands were observed in comparison with spectra of polycrystalline samples.

This means that the crystal, though it looks like a single crystal, must be considered as a kind of polysynthetic twin consisting of domains which build up the crystal with random distribution of the a and c axes in a given direction. Above the phase transition temperature at 126.5 °C one can imagine that the crystal will act like a genuine single crystal because the axial ratio then will be exactly 1. If this is the case it should be possible to obtain polarized spectra above this temperature.

For cubic single crystals it can be seen from the character table of the unit cell group, that fundamentals of the symmetry species A_{1g} and E_g should be observed in polarized spectra of the type (ii), $i = X, Y, Z$ and fundamentals of the F_{2g} species should be observed in polarized

Table 2. Intensity ratios in the polarized Raman spectra.

	$\frac{\nu_5}{\nu_2}$	$\frac{\nu_5}{\nu_1}$	$\frac{\nu_2}{\nu_1}$
(XX)	$\frac{0.84}{1}$	$\frac{0.10}{1}$	$\frac{0.12}{1}$
(XZ)	$\frac{3.52}{1}$	$\frac{0.42}{1}$	$\frac{0.13}{1}$

spectra of the type (ij), $i \Delta j = X, Y, Z$, $i \neq j$.

The polarized Raman spectra of the two types are sketched in Fig. 5, and in Table 2 are given the relative intensity ratios between the lines.

Though it was not possible to obtain complete extinction of the contribution to the detected light intensity from the vibrations in a forbidden species, the spectra strongly indicate that the crystal behaves like a single crystal with cubic symmetry above the transition temperature. It is evident that ν_1 and ν_2 follow each other in intensity and have their largest intensity in the (XX) spectra. This is in accordance with the assignment of ν_1 and ν_2 to the A_{1g} and E_g symmetry species, respectively. Moreover ν_5 clearly separates from ν_1 and ν_2 and its intensity is approximately four times larger in polarized spectra of the (XZ) type than in polarized spectra of the (XX) type measured relative to ν_1 and ν_2 (Table 2). This agrees with the assignment of ν_5 to the F_{2g} symmetry species.

Upon repeated temperature cycling over the phase transition point the crystal has returned to the initial state with respect to spectra and with respect to the single crystal/twin transformation. This indicates that the transition is reversible.

CONCLUSION

All the lines in the Raman spectra of potassium hexabromostannate at room temperature and at –178 °C can be explained by assuming tetragonal crystal symmetry with space group D_4^2 . At 140 °C the lines can be explained by assuming cubic symmetry with space group O_h^5 . The phase transition at 126.5 °C observed by Galloni *et al.*³ is confirmed by the Raman spectra and

Fig. 5. Polarized Raman spectra of K_2SnBr_6 at 140 °C.

found to be reversible. Furthermore, there is some evidence that the crystal is a polysynthetic twin below the transition temperature and behaves as a single crystal above this temperature.

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REFERENCES

1. Ketelaar, A. A., Rietdijk, A. A. and van Stavern, C. H. *Rec. Trav. Chim. Pays-Bas* 56 (1937) 907.
2. Markstein, G. and Nowotny, H. Z. *Kristallogr.* 100 (1938) 265.
3. Galloni, E. E., de Benyacar, M. R. and de Abeledo, M. J. Z. *Kristallogr.* 117 (1962) 470.
4. Debeau, M. and Poulet, H. *Spectrochim. Acta A* 25 (1969) 1553.
5. Debeau, M. and Krauzman, M. C. R. *Acad. Sci. B* 264 (1967) 1724.
6. Greenwood, N. N. and Straughan, B. P. J. *Chem. Soc. A* (1966) 962.
7. Brown, D. H., Dixon, K. R., Livingston, C. M., Nuttall, R. H. and Sharp, D. W. A. *J. Chem. Soc. A* (1967) 100.
8. Nakamura, D., Ito, K. and Kubo, M. *Inorg. Chem.* 1 (1962) 592.
9. Woodward, L. A. and Anderson, L. E. *J. Chem. Soc.* (1957) 1284.
10. Wyckoff, R. W. G. *Crystal Structures*, Wiley, New York 1965, Vol. 3, pp. 339, 344.

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