Internal Vibrations of the Antimonate Octahedron in Ordered Perovskites

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Vibrational Spectra, Antimonates

The infrared and Raman spectra of the perovskites SrLaMgSbO$_6$ and Ba$_4$LiSb$_3$O$_{12}$ are reported and discussed in terms of antimonate internal modes.

We have shown that the vibrational spectra of oxides with ordered perovskite structure reveal the internal vibrational modes of octahedra containing highly charged central cations$^{1-3}$. This is due to their simple crystal structure. In this note we report the vibrational spectra of SrLaMgSbO$_6$ and Ba$_4$LiSb$_3$O$_{12}$. The former has the 1:1 ordered perovskite structure with SbO$_6$ octahedra with site symmetry O$_h$ and one SbO$_4$ group per primitive cell; the latter has a 1:3 ordered perovskite structure with SbO$_6$ octahedra with site symmetry D$_{4h}$ and three corner-sharing octahedra per primitive cell: each SbO$_6$ octahedron shares corners with four other SbO$_6$ octahedra (in a plane) and two LiO$_6$ octahedra (along one of the axes).

Experimental procedures and performance of the measurements have been described before$^{1-3}$. The more important results are given in Table I.

Table I. Internal modes of Sb$^{5+}$O$_6$ octahedron in ordered perovskites$^{*}$.

<table>
<thead>
<tr>
<th>Mode</th>
<th>$O_h$</th>
<th>$D_{4h}$</th>
<th>SrLaMgSbO$_6$</th>
<th>Ba$_4$LiSb$<em>3$O$</em>{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1$</td>
<td>$A_1g$</td>
<td>$A_1g$</td>
<td>745 (R)</td>
<td>720 (R)</td>
</tr>
<tr>
<td>$v_2$</td>
<td>$E_g$</td>
<td>$A_1g + B_1g$</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$v_3$</td>
<td>$T_{1u}$</td>
<td>$A_2u + E_u$</td>
<td>670 (ir)</td>
<td>715, 580 (ir)</td>
</tr>
<tr>
<td>$v_4$</td>
<td>$T_{1u}$</td>
<td>$A_2u + E_u$</td>
<td>380 (ir)</td>
<td>345, 300 (ir)</td>
</tr>
<tr>
<td>$v_5$</td>
<td>$T_{2g}$</td>
<td>$B_{2g} + E_g$</td>
<td>425 (R)</td>
<td>425 (R)</td>
</tr>
</tbody>
</table>

* All values in cm$^{-1}$; R: observed in Raman spectrum; ir: observed in infrared spectrum.

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The spectra of SrLaMgSbO$_6$ are exactly as is to be expected for the given symmetry. The intensity of the $v_5$ mode is probably too weak to be measurable. All bands are rather broad which can be ascribed to disorder of Sr$^{2+}$ and La$^{3+}$ ion on the larger cation sites$^1$.

The spectra of Ba$_4$LiSb$_3$O$_{12}$ are also very simple and can be ascribed to the internal modes of an SbO$_6$ octahedron with D$_{4h}$ symmetry. The $T_{1u}$ triplets are split and show the more intense component at the low-energy side. If we take this value (580 cm$^{-1}$ for $v_2$ and 300 cm$^{-1}$ for $v_4$) as the $E_u$ mode the centre of gravity is 625 cm$^{-1}$ for $v_2$ and 315 cm$^{-1}$ for $v_4$.

The $v_4$ mode in SrLaMgSbO$_6$ is situated at much higher wavenumbers than in Ba$_4$LiSb$_3$O$_{12}$. This is probably connected with the fact that the $v_4$ mode of the SbO$_4$ group couples with La–O and/or Mg–O stretching vibrations. The stretching modes of the SbO$_4$ group ($v_1$, $v_5$) lie also at higher wavenumbers in SrLaMgSbO$_6$ than in Ba$_4$LiSb$_3$O$_{12}$, but the difference is less pronounced than in the case of the $v_2$ mode. As argued before$^3$ differences of this type can be related with the total electrostatic bond strength of the oxygen ions of the SbO$_4$ group. In SrLaMgSbO$_6$ this amounts to 2 for each of the six O$^{2-}$ ions; in Ba$_4$LiSb$_3$O$_{12}$ we have four times 2$1/2$ and twice 1$1/2$, so that the average is much higher than 2. As a consequence the Sb–O bond is weaker and the stretching frequency lies at lower wavenumbers. We realize that this interpretation of the spectra of Ba$_4$LiSb$_3$O$_{12}$ is too simple, but on the other hand it accounts for the greater lines. This agrees with earlier observations$^{3,4}$.

The difference between the two compounds is small, viz. a different superstructure. This difference, however, brings about a strong difference between the chemical surroundings of the antimonate group in the two compounds.