

Internal Vibrations of the Antimonate Octahedron in Ordered Perovskites

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The infrared and Raman spectra of the perovskites SrLaMgSbO_6 and $\text{Ba}_4\text{LiSb}_3\text{O}_{12}$ 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 cations¹⁻³. This is due to their simple crystal structure. In this note we report the vibrational spectra of SrLaMgSbO_6 and $\text{Ba}_4\text{LiSb}_3\text{O}_{12}$. The former has the 1:1 ordered perovskite structure with SbO_6 octahedra with site symmetry O_h and one SbO_6 group per primitive cell; the latter has a 1:3 ordered perovskite structure⁵ 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 before¹⁻³. The more important results are given in Table I.

Table I. Internal modes of Sb^{5+}O_6 octahedron in ordered perovskites*.

Mode	Representation		SrLaMgSbO_6	$\text{Ba}_4\text{LiSb}_3\text{O}_{12}$
	O_h	D_{4h}		
ν_1	A_{1g}	A_{1g}	745 (R)	720 (R)
ν_2	E_g	$A_{1g} + B_{1g}$	—	—
ν_3	T_{1u}	$A_{2u} + E_u$	670 (ir)	715, 580 (ir)
ν_4	T_{1u}	$A_{2u} + E_u$	380 (ir)	345, 300 (ir)
ν_5	T_{2g}	$B_{2g} + E_g$	425 (R)	425 (R)

* 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 ν_2 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 sites⁴.

The spectra of $\text{Ba}_4\text{LiSb}_3\text{O}_{12}$ 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 ν_3 and 300 cm^{-1} for ν_4) as the E_u mode the centre of gravity is 625 cm^{-1} for ν_3 and 315 cm^{-1} for ν_4 .

The ν_4 mode in SrLaMgSbO_6 is situated at much higher wavenumbers than in $\text{Ba}_4\text{LiSb}_3\text{O}_{12}$. This is probably connected with the fact that the ν_4 mode of the SbO_6 group couples with La-O and/or Mg-O stretching vibrations. The stretching modes of the SbO_6 group (ν_1, ν_3) lie also at higher wavenumbers in SrLaMgSbO_6 than in $\text{Ba}_4\text{LiSb}_3\text{O}_{12}$, but the difference is less pronounced than in the case of the ν_4 mode. As argued before⁶ differences of this type can be related with the total electrostatic bond strength⁷ of the oxygen ions of the SbO_6 group. In SrLaMgSbO_6 this amounts to 2 for each of the six O^{2-} ions; in $\text{Ba}_4\text{LiSb}_3\text{O}_{12}$ we have four times $2\frac{1}{3}$ and twice $1\frac{2}{3}$, 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 $\text{Ba}_4\text{LiSb}_3\text{O}_{12}$ is too simple, but on the other hand it accounts for the greater lines. This agrees with earlier observations^{3,6}.

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.

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