The vibrational spectrum of Nd$_2$BaCuO$_5$

E. J. BARAN*
Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, CC 962, 1900 La Plata, Argentina

A. E. LAVAT
Area de Química, Facultad de Ingeniería, Universidad Nacional del Centro de la Provincia de Buenos Aires, 7400 Olavarria, Argentina

R. SAEZ PUCHE, A. SALINAS SANCHEZ
Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, E28040 Madrid, Spain

Compounds of general composition Ln$_2$BaCuO$_5$ (Ln=lanthanide) adopt different structural types [1, 2]. Two series of structures have been reported for Ln$_2$BaCuO$_5$ compounds [2-4]. For lanthanide ions smaller than Nd(III) (Y and Sm–Lu) the so-called “green phases” (orthorhombic, space group Pbnm) are stabilized [2, 3]. They are one of the main impurities generated during the synthesis of the LnBa$_2$Cu$_3$O$_7-x$-type high-\(T_c\) superconducting oxides [5]. A different structural type (tetragonal, space group P4/mmb) becomes stabilized for Ln = La or Nd [2, 4, 6, 7], although in the case of the lanthanum-containing material the totally stoichiometric composition does not seem to be attainable [4].

Recently we have investigated the vibrational [8] and magnetic [9, 10] properties of the “green phases”. In this work, in order to extend these studies to the second structural type, we studied the vibrational spectrum of Nd$_2$BaCuO$_5$. Some aspects of the magnetic behaviour of this material have been advanced in one of our previous studies [10].

Powdered samples of Nd$_2$BaCuO$_5$ were obtained by solid-state reactions starting from 1:1:1 mixtures of Nd$_2$O$_3$, CuO and BaCO$_3$. The ground and well-mixed reagents were treated in air, progressively at 750, 850 and 950 °C, with several intermediate grindings, and finally heated at 1000–1020 °C. The colour of the compound after these treatments was brown. X-ray powder diffractometry [6] confirmed the formation of a pure single-phase material.

The infrared spectra were recorded with a Perkin–Elmer 580B spectrophotometer, using the KBr pellet technique. Raman spectra were obtained with a Dilor spectrometer, using the 488 nm line of an argon-ion laser for excitation. The spectra obtained are shown in Fig. 1.

The Nd$_2$BaCuO$_5$ framework is built from edge- and face-sharing BaO$_{10}$ and NdO$_4$ polyhedra, and the Cu(II) ions are present in the form of isolated square-planar units [7]. Therefore, it seems possible to attempt an approximate assignment of the CuO$_4$ vibrations in this lattice on the basis of the irreducible representation of a square-planar \(D_{4h}\) molecule [11, 12], i.e.

\[
\Gamma_{\text{D}_{4h}} = A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2E_u
\]

Three of these components (\(A_{1g}, B_{1g}\) and \(B_{2g}\)) are Raman-active, another three (\(A_{2u}\) and \(2E_u\)) are infrared-active and the remaining one (\(B_{2u}\)) is inactive.

Table I gives the proposed assignment, based on these arguments. Interestingly, the antisymmetric
TABLE I Assignment of the vibrational spectrum of 
Nd$_2$BaCuO$_5$

<table>
<thead>
<tr>
<th>Band position (cm$^{-1}$)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>626</td>
<td>A$_{1g}$($v_3$-CuO$_4$)</td>
</tr>
<tr>
<td>592</td>
<td>E$_g$($v_5$-CuO$_4$)</td>
</tr>
<tr>
<td>430</td>
<td>B$_{2g}$($v_6$-CuO$_4$)</td>
</tr>
<tr>
<td>~430 sh</td>
<td>u(Nd-O)</td>
</tr>
<tr>
<td>348</td>
<td>E$_g$(δ$_s$-CuO$_4$)</td>
</tr>
<tr>
<td>275</td>
<td>B$<em>{1g}$($\delta</em>\parallel$ in-plane-CuO$_4$)</td>
</tr>
<tr>
<td>242</td>
<td>External modes</td>
</tr>
</tbody>
</table>

sh, Shoulder.

B$_{2g}$-CuO$_4$ stretching vibration is also seen as a weak shoulder in the infrared spectrum, probably activated by correlation field effects. On the other hand, the strong infrared band located at 350 cm$^{-1}$ can undoubtedly be assigned to Nd–O stretchings of the NdO$_8$ units (cf. [13] and references therein). Finally, it should be pointed out that the A$_{2g}$ infrared-active mode (an out-of-plane deformation [12]) is not observed because it probably lies below 100 cm$^{-1}$ (cf. [12]).

A comparison of the present spectra with those of the "green phases" [8] shows that both types of materials present a very different and distinctive vibrational behaviour. It is also interesting to emphasize the similarity between the infrared spectrum of Nd$_2$BaCuO$_5$ and those of Nd$_2$CuO$_4$ and Pr$_2$CuO$_4$ [14] and of the n-type Nd$_{2-x}$Ce$_x$CuO$_4$ superconductors [15], materials which also possess square-planar CuO$_4$ co-ordination polyhedra in their structures.

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References

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