

## The vibrational spectrum of $\text{Nd}_2\text{BaZnO}_5$

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Materials of stoichiometry  $\text{Ln}_2\text{BaM}^{\text{II}}\text{O}_5$  ( $\text{M}^{\text{II}} = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$ ) belong to four different structural types, depending on the  $\text{Ln}(\text{III})$  and/or  $\text{M}(\text{II})$  cations present in the lattice [1, 2]. In the case of  $\text{M}(\text{II}) = \text{Zn}$ , the phases containing Y and  $\text{Ln}(\text{III}) = \text{Sm}$  to Ho adopt the orthorhombic  $\text{Pbnm}$  structural type, in which the  $\text{Zn}(\text{II})$  ions are present as isolated square-pyramidal units [3]. Phases with  $\text{Ln}(\text{III}) = \text{La}$  or Nd adopt a tetragonal structure, space group  $\text{I4/mcm}$  and  $Z = 4$ , with isolated tetrahedral  $\text{ZnO}_4$  moieties present in the lattice [4, 5].

In a previous paper we presented a general analysis of the infrared spectra of the different  $\text{Ln}_2\text{BaM}^{\text{II}}\text{O}_5$  structural types [2]. As the tetragonal  $\text{I4/mcm}$  structure is only present in  $\text{La}_2\text{BaZnO}_5$  and  $\text{Nd}_2\text{BaZnO}_5$  we have now attempted to obtain a deeper insight into its vibrational behaviour by careful analysis of the Raman and infrared spectra of  $\text{Nd}_2\text{BaZnO}_5$ , for which a detailed structural analysis has been published recently [5].

Samples of  $\text{Nd}_2\text{BaZnO}_5$  were obtained by solid state reactions starting from 1:1:1 mixtures of  $\text{Nd}_2\text{O}_3$ ,  $\text{BaCO}_3$  and  $\text{ZnO}$ . The well mixed powders were treated in air, progressively at 700, 800 and 900 °C, with several intermediate grindings, and finally heated for 24 h at 950–1000 °C. The formation of a single phased material was confirmed by X-ray powder diffractometry.

The infrared spectra were recorded using a Perkin-Elmer 580B spectrophotometer, using the KBr pellet technique. Raman spectra were obtained using a Jovin-Yvon U-1000 instrument, using the 488.0 nm line of an  $\text{Ar}^+$  laser (Spectra Physics, model 165) for excitation. The obtained spectra are shown in Fig. 1.

The investigated material is built up by eightfold coordinated  $\text{Nd}(\text{III})$  ions and  $\text{BaO}_{10}$  bicapped antiprisms, whereas the  $\text{Zn}(\text{II})$  ions are present in the form of isolated tetrahedral units [5]. Therefore, it seems possible to attempt an approximate assignment of these  $\text{ZnO}_4$  vibrations on the basis of a factor group analysis of the lattice [6, 7].

The correlation between the point group of the "free" ion ( $T_d$ ), its site-symmetry ( $D_{2d}$ ) and its factor group ( $D_{4h}$ ) is shown in Table I, and Table II presents the proposed assignment based on this analysis.

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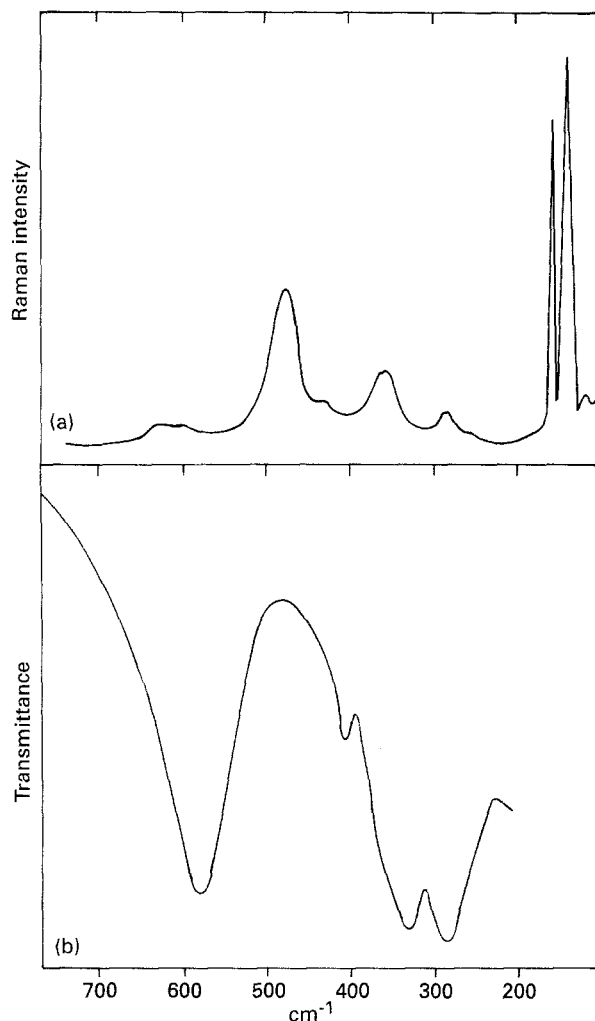


Figure 1 (a) Raman and (b) infrared spectra of  $\text{Nd}_2\text{BaZnO}_5$ .

The general spectral pattern points to important coupling effects, probably related to the weakness of the  $\text{Zn-O}$  bonds. This is also probably one of the reasons for the relatively low intensity and broadening of the Raman line assigned to the  $\nu_1(A_{1g})$  mode. It is also evident that in the region below  $350 \text{ cm}^{-1}$ , coupling between  $\text{ZnO}_4$ -deformational modes and  $\text{Nd-O}$  motions becomes important, as some  $\text{Ln-O}$  modes are predicted to lie in this region [2, 8, 9]. A weak Raman line located at  $434 \text{ cm}^{-1}$  cannot be assigned with certainty.

A comparison of the infrared spectrum of  $\text{Nd}_2\text{BaZnO}_5$  with that of the respective lanthanum compound,  $\text{La}_2\text{BaZnO}_5$  [2], clearly shows that all of the bands are displaced to higher wavenumbers in

TABLE I Factor group analysis of the internal vibrations of the  $\text{ZnO}_4$  groups in the  $\text{Nd}_2\text{BaZnO}_5$  lattice ( $14/m\bar{c}m$  and  $Z = 4/2$ )

Free ion ( $T_d$ )	Site-symmetry ( $D_{2d}$ )	Factor group ( $D_{4h}$ )
$\nu_1 A_1$	$A_1$	$A_{1g} + B_{2u}$
$\nu_2 E$	$A_1 + B_1$	$A_{1g} + B_{2u} + B_{2g} + A_{1u}$
$\nu_3 F_2$	$B_2 + E$	$B_{1g} + A_{2u} + E_g + E_u$
$\nu_4 F_2$	$B_2 + E$	$B_{1g} + A_{2u} + E_g + E_u$

Activity of the factor group modes:  
 $A_{1g}, B_{1g}, B_{2g}, E_g$  = Raman active  
 $A_{2u}, E_u$  = infrared active  
 $B_{2u}, A_{1u}$  = inactive

TABLE II Assignment of the vibrational spectrum of  $\text{Nd}_2\text{BaZnO}_5$  (values in  $\text{cm}^{-1}$ )

Infrared	Raman	Assignment
	636	$\nu_3(E_g)$
	602	$\nu_3(B_{1g})$
582		$\nu_3(E_u + A_{2u})$
	488	$\nu_1(A_{1g})$
406		$\nu_4(A_{2u})$
	363	$\nu_4(E_g + B_{1g})$
333		$\nu_4(E_u) + \nu(\text{Nd}-\text{O})$
277		$\nu(\text{Nd}-\text{O})$
	288	External modes
	160	
	143	

the neodymium material, in agreement with its smaller unit cell volume, and following a trend usually observed in isostructural lanthanide compounds [2, 10–13].

It was also interesting to compare the spectra of  $\text{Nd}_2\text{BaZnO}_5$  with those of  $\text{Nd}_2\text{BaCuO}_5$ , in which square planar  $\text{CuO}_4$  units are present [9]. Both materials show very similar infrared spectra but the Raman spectra are totally different. The overall comparison indicates that the square-planar  $\text{CuO}_4$  units may present slightly stronger metal–oxygen bonds than the tetrahedral  $\text{ZnO}_4$  moieties.

Finally, we have made a rough estimation of the force constant of the Zn–O bonds, using a modified valence force field [14] and the Raman values for the two stretching vibrations. A force constant of 250 N/m can be determined for the metal–oxygen bonds, whereas the bond/bond interaction constant lies around 8 N/m. Using the value of the principal force constant we have also estimated the bond order (according to Siebert [15]) for the Zn–O

bonds and found a value slightly below unity, a result which supports the presumption of weak Zn–O bonds in this material and shows again that the tetrahedral  $\text{ZnO}_4$  units are subjected to great couplings with the motions of the other building units present in the lattice.

## Acknowledgements

This work was supported by CONICET (Argentina). C.O.D.V. thanks Professor O. Sala valuable contributions and the Universidade de São Paulo for financial support.

## References

1. J. K. BURDETT and J. F. MITCHELL, *J. Amer. Chem. Soc.* **112** (1990) 6571.
2. A. E. LAVAT, E. J. BARAN, R. SAEZ PUCHE, A. SALINAS SANCHEZ and J. M. MARTIN-LLORENTE, *Vibrat. Spectrosc.* **3** (1992) 291.
3. C. MICHEL and B. RAVEAU, *J. Solid St. Chem.* **49** (1983) 150.
4. C. MICHEL, L. ER-RAKHO and B. RAVEAU, *ibid.* **42** (1982) 176.
5. M. TAIBE, J. ARIDE, J. DARRIET, A. MOQUINE and A. BOUKHARI, *ibid.* **86** (1990) 233.
6. S. D. ROSS, "Inorganic infrared and raman spectra" (McGraw-Hill, London, 1972).
7. A. MULLER, E. J. BARAN and R. O. CARTER, *Struct. Bonding* **26** (1976) 81.
8. S. L. HERR, K. KAMARAS, D. B. TANNER, S. W. CHEONG and G. R. STEWART, *Phys. Rev. B* **43** (1991) 7847.
9. E. J. BARAN, A. E. LAVAT, R. SAEZ PUCHE and A. SALINAS SANCHEZ, *J. Mater. Sci. Lett.* **11** (1992) 1087.
10. E. J. BARAN, G. P. CICLEO, G. PUNTE, A. E. LAVAT and M. TREZZA, *ibid.* **7** (1988) 1010.
11. A. E. LAVAT, M. TREZZA, I. L. BOTTO, D. I. RONCAGLIA and E. J. BARAN, *Spectrosc. Lett.* **21** (1988) 355.
12. E. J. BARAN, E. G. FERRER, I. BUENO and C. PARADA, *J. Raman Spectrosc.* **21** (1990) 27.
13. I. L. BOTTO, E. J. BARAN, C. CASCALES, I. RASINES and R. SAEZ PUCHE, *J. Phys. Chem. Solids* **52** (1991) 431.
14. A. MULLER and B. KREBS, *J. Molec. Spectrosc.* **24** (1967) 180.
15. A. FADINI and F. M. SCHNEPEL, "Vibrational spectroscopy: methods and applications" (Ellis Horwood, Chichester, 1990).

Received 11 August  
and accepted 11 October 1993