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Letter

A Raman study of neodymium(III) oxide peroxide, $Nd_2O_2(O_2)$, at ambient and high pressures*

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1. Introduction

Neodymium(III) oxide peroxide, $Nd_2O_2(O_2)$, is formed at very high oxygen pressures and contains O^{2-} ions as well as $O_2{}^{2-}$ ions. It is remarkably stable at atmospheric pressure [1]. A thermal decomposition to neodymium(III) sesquioxide, Nd_2O_3, takes place only at 420 °C and 1 bar.

The structure of $Nd_2O_2(O_2)$ shows a striking resemblance to the fluorite (CaF_2)-type structure, which would be expected for $Nd^{4+}O_2$ (Fig. 1). If the coordination of the neodymium ion is considered, seven of its eight oxygen neighbours are located at the corners of an only slightly distorded cube. The eighth oxygen is shifted away from the eighth corner along a cubic

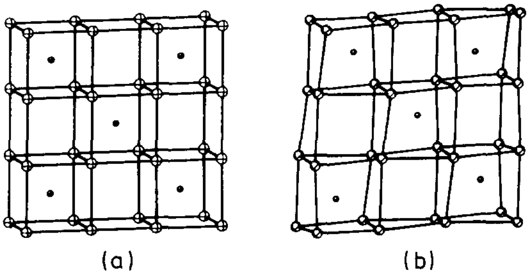

Fig. 1. Comparison of (a) the CaF_2 structure with (b) that of $Nd_2O_2(O_2)$. The small circles represent the metal atoms.

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*Dedicated to Professor Otto Wilhelm Flörke on the occasion of his 65th birthday.

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edge to form the $(O-O)^{2-}$ peroxide group (O-O distance 1.474 Å) [1] (Fig. 2).

The molar volume of a hypothetical $Nd^{4+}O_2$ with a fluorite structure, extrapolated from the data for CeO_2 and PrO_2, is about 9% less than that of 0.5 $Nd_2O_2(O_2)$ (corresponding to a composition "NdO_2"). It has therefore been speculated that at higher pressures a transformation $Nd_2{}^{3+}O_2(O_2) \rightarrow 2Nd^{4+}O_2$ might be possible [1]. From a structural point of view, such a transformation could easily proceed by moving the eighth oxygen back towards the eighth corner of the coordination cube around neodymium, thereby eventually breaking the O-O bond in $(O-O)^{2-}$ and forming two O^{2-} ions. For the sake of electroneutrality, Nd^{3+} would at the same time be forced to change to Nd^{4+} according to an intracrystalline redox reaction, namely

$$O_2^{2-} + 2Nd^{3+} \rightarrow 2O^{2-} + 2Nd^{4+}$$

If such a reaction did indeed take place at higher pressures, it would imply a rather high compressibility for $Nd_2O_2(O_2)$.

We present in this paper the Raman spectrum of $Nd_2O_2(O_2)$. Its pressure dependence up to 30 kbar seems at least not to be contradictory to the reaction discussed above.

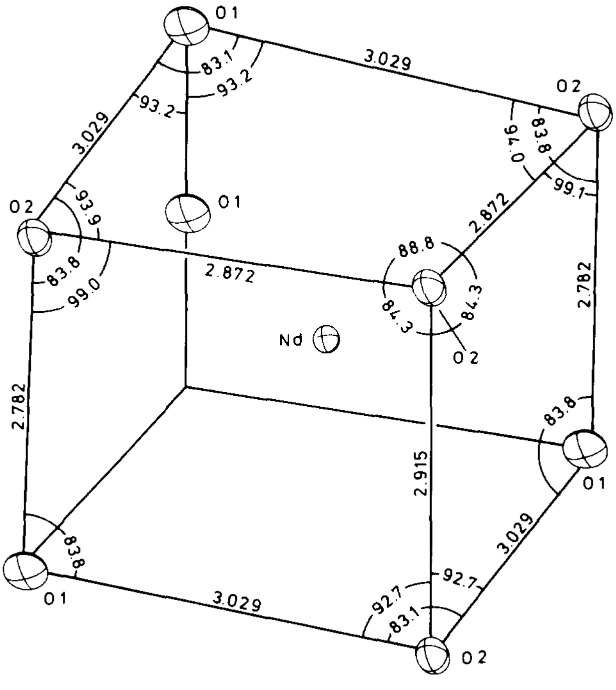

Fig. 2. Environment of Nd^{3+} in $Nd_2O_2(O_2)$. Seven of the eight neighbours of the Nd^{3+} ion are located at the comers of a slightly distorted cube, while the eighth oxygen is shifted away from this position to form the peroxide ion.

2. Experimental details

Nd$_2$O$_2$(O$_2$) has been prepared [1] by means of a reaction of an Nd$_2$O$_3$–KO$_2$ mixture at 40 kbar and 1500 °C for 30 min in a platinum capsule using a modified "Belt"-type apparatus [2]. After quenching to ambient conditions, the dichroitic compound (light blue to pink) can easily be recovered by leaching the reaction product with water, thereby removing the excess KO, and/or other potassium oxides formed during the reaction. Nd$_2$O$_2$(O$_2$) is stable against water.

The high pressure Raman equipment used has been described in the literature [3]. While it was relatively easy to obtain the Raman spectra of Nd$_2$O$_2$(O$_2$) under ambient conditions, especially using the 488.0 nm line of an Ar' laser, its spectra in a diamond anvil cell were not of a good quality, particularly since there are only a few lines of higher intensity. We therefore only report the pressure dependence of a limited number of Raman-active modes.

3. Results and discussion

The Raman spectrum of Nd$_2$O$_2$(O$_2$) under ambient conditions is shown in Fig. 3. The Raman bands in this figure can be correlated with those of Nd$_2$O$_3$ with the trigonal A structure, as well as those of rare earth sesquioxides having the cubic C structure or the monoclinic B structure [4]. A full assignment, of these modes of monoclinic Nd$_2$O$_2$(O$_2$), which belongs to the space group C2 /m (C^3_{2h}) with $Z = 2$ [1], will be published elsewhere [5]. The

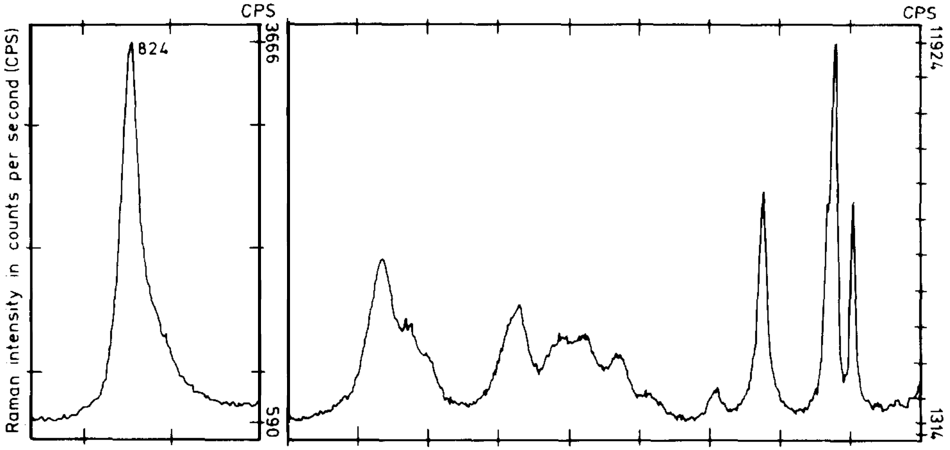

Fig. 3. Raman spectrum of Nd$_2$O$_2$(O$_2$) under ambient conditions. The ν(O—O) band at 824 cm^{-1} is shown in more detail on the left-hand side of the figure. ν(O—O) is slightly less intense than ν(Nd—O(2)) at 434 cm-'.

$\nu(O-O)$ band at 824 cm^{-1} in $Nd_2O_2(O_2)$ is, however, unique compared to other rare earth sesquioxides and clearly indicates the presence of peroxide groups in this crystal. If the bond distance of 1.474 Å is compared with those of other peroxide groups in which a side-on coordination of the metal to the peroxide ion occurs (η' type) [6], then it is perfectly clear that this bond distance represents a very average value for these bonds. The $\nu(O-O)$ stretching band can provide definite evidence about the bound dioxygen and is very characteristic of the bond order [6]. In this regard the value of 824 cm-' represents once again an average value and it can therefore be said without any doubt that the peroxide binds to the neodymium ion in a side-on way, as was also shown in the X-ray study of $Nd_2O_2(O_2)$[1]. It is evident from Fig. 3 that ν_1 is asymmetrical, and since there is only one (O-O) group in the primitive unit cell and an isotopic splitting of this band can be ruled out [7], the asymmetrical nature of $\nu(O-O)$ cannot be explained at this stage.

The presence of peroxo groups in the lattice of $Nd_2O_2(O_2)$ being confirmed unambiguously, it is of interest to observe frequency shifts of this band with the application of pressure. The results obtained from the compression of $Nd_2O_2(O_2)$ samples in a diamond anvil cell are summarized in Fig. 4. The decomposition of the samples after long exposure to the laser light could be detected in the first instance by the disappearance of the $\nu(O-O)$ band, the almost featureless spectrum obtained in the frequency range where the Nd-0 stretching modes occur, and eventually the disappearance of the intense Nd-0 bending modes at low frequencies. However, the results in Fig. 3 indicate quite clearly that in contrast to the Nd – O(2) (oxygen belonging to the oxide ion) stretching mode at 436 cm^{-1} and the Nd-O(l) (oxygen belonging to the peroxide ion) stretching mode (which is not shown in Fig. 4), $\nu(O-O)$ is rather insensitive towards pressure. At a first glance this appears to be highly unusual for $\nu(O-O)$ of a peroxide group. However, it must be considered that any shortening of the 0 – 0 bond will further distort

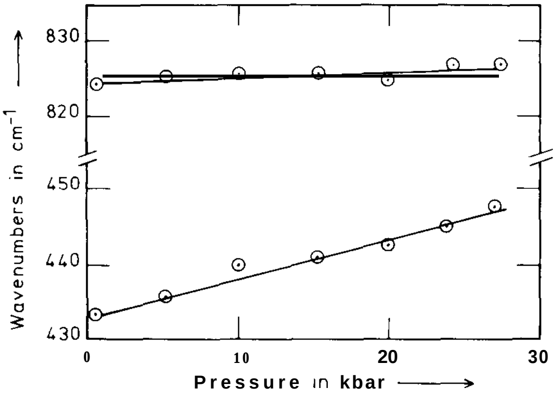

Fig. 4. Pressure dependence of (a) $\nu(O-O)$ (top) in $Nd_2O_2(O_2)$ and (b) one of the Nd-O(2) (neodymium-oxide) stretching modes (bottom).

the lattice from a fluorite lattice. The pressure dependence of $\nu(O-O)$ can therefore be understood in terms of two opposing mechanisms, namely the normal compression of the (O-O) bond, which should under other circumstances be rather compressible, and the increasing destabilization of the lattice when it further distorts from the "ideal" fluorite lattice. A transformation to $Nd^{4+}O_2$ has not been observed in the present measurements. A detailed study of the vibrational spectra of $Nd_2O_2(O_2)$ is in progress, including measurements at very low temperatures.

Acknowledgments

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References

1 K.-J. Range, M. Stadler, F. Rau and U. Klement, *Angew. Chem., 99* (1987) 1 176; *Angew. Chem. Int. Edn. Engl.*, 26 (1987) 1174.

2 K.-J. Range and R. Leeb, *Z. Naturf. B, 30* (1975) 889.

3 A. M. Heyns and J. B. Clark, *J. Raman Spectrosc., 14* (1983) 342.

4 J. Gouteron, D. Michel, A. M. Lejus and J. Zarembowitch, *J. Solid State Chem., 38* (1981) 288.

5 A. M. Heyns and K.-J. Range, submitted to *J. Phys. Chem. Solids.*

6 M. H. Gubclman and A. F. Williams, *Struct. Bonding, 55* (1983) 1.

7 R. Guilard, J. M. Latour, C. LeComte, J-C. Marchon, J. Protas and D. Ripoll, *Inorg. Chem.*, 17 (1978) 1228.