

Supporting Information

***Ab initio* assignments of FIR, MIR, and Raman bands of bulk Ba species relevant in NO_x storage-reduction**

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Ba(NO₃)₂

The crystal structure of Ba(NO₃)₂ was debated in the 1960's and 70's. After several authors^{1,2} assigned Ba(NO₃)₂ to *Pa3* space group already, Birnstock³ observed *hk0* reflections violating the assignment of *Pa3* space group. In the following years Brooker^{4,5} reported detailed spectroscopic work on the crystal structure, finally concluding that the best description for Ba(NO₃)₂ at room temperature is the T_h⁶ space group.⁶ Another very detailed spectroscopic work on the structure of Ba(NO₃)₂ was published by Bon et al.⁷ in 1976, while the authors assigned all observed modes to an incorrect space group (T₄). Still, the assignment of vibrational modes to observed band is mainly based on a proper factor group analysis. Therefore the chosen crystal symmetry is of critical importance and will strongly influence the reliability of these results.

The unit cell of $\text{Ba}(\text{NO}_3)_2$ includes 4 formula units, where NO_3^- ions are located on C_3 sites and Ba^{2+} ions are located at S_6 sites. These 36 atoms give rise to 105 fundamental vibrations, which could be further divided in 48 internal and 57 external modes (24 librational and 33 lattice modes):

$$\Gamma_{\text{int}} = 2A_g + 2E_g + 6F_g + 2A_u + 2E_u + 6F_u$$

$$\Gamma_{\text{ext}} = 2A_g + 2E_g + 6F_g + 3A_u + 3E_u + 8F_u$$

Within these vibrations, the components F_u are IR-active, while A_g , E_g and F_g are Raman-active. From the calculation 108 modes were obtained, while three of them refer to trivial translations of the unit cell. Due to this site symmetry the fundamental vibrations of the nitrate ion in $\text{Ba}(\text{NO}_3)_2$ split up into several modes. The asymmetric stretching and the in-plane bending mode, which belong to E' symmetry (IR+R active) in the free nitrate ion, will split into 6 modes (E_u , E_g , $2F_u$, $2F_g$), while symmetric stretching and out-of-plane bending show 4 modes (A_u , A_g , F_u , F_g) in the crystal. In the lattice mode region the assignment of experimentally obtained bands and calculated vibrations is not straightforward. On one side lattice imperfectness and delocalized modes make it difficult to resolve all bands, while on the other side the calculated intensities are small in comparison to the internal modes, so that their differences are at the convergence limit.

Furthermore, in order to prove whether the measured samples of this study could resemble the behavior of single crystals, as assumed by the calculation, highly resolved X-ray diffraction measurement were performed at the Swiss Norwegian Beamline (SNBL) with the same $\text{Ba}(\text{NO}_3)_2$ sample. The diffraction pattern of $\text{Ba}(\text{NO}_3)_2$ is shown in Figure SA. With the

Scherrer equation $\bar{D}_{hkl} = \frac{K\lambda}{\beta \cos \Theta}$, where the crystallite size \bar{D}_{hkl} is given by the Scherrer

factor K (~ 1), the wavelength $\lambda = 0.498 \text{ \AA}$, the reflection width β (full width at half-maximum) and the scattering angle Θ , the average size of the crystallites was calculated to be 190 nm.

BaCO₃

BaCO₃ is described very often in the mineralogical literature, due to its structural similarity with aragonite (CaCO₃), one of the most extensively studied minerals. However, the structure of BaCO₃ is often only slightly discussed or experimental data are given for completeness without details. In 1974 White published a review of carbonate minerals, including also data for BaCO₃. A detailed theoretical assignment of lattice vibrations for an aragonite structure model is reported by Jayasooriya et al., while complete factor group assignments were presented by Ferraro et al.⁸, Frech et al.⁹ and Griffith¹⁰. Cerussite (PbCO₃), another member of the aragonite group, is described by a very detailed paper of Martens et al. Based on the factor group analysis of the aragonite structure the latter authors show a precise assignment of internal and external Raman modes for cerussite. Unfortunately the data for IR measurements and assignments are not reported precisely.

The unit cell of BaCO₃ contains four formula units, where CO₃²⁻ ions are located on C_{2v} sites and Ba²⁺ ions are located at D₂ sites. In general, these 20 atoms in an aragonite like structure will show a total of 57 vibrations (+3 trivial translations), which could be divided into 24 internal and 33 external modes (12 librational and 21 translational):

$$\Gamma_{\text{int}} = 4A_g + 2B_{1g} + 2B_{2g} + 4B_{3g} + 2A_u + 4B_{1u} + 4B_{2u} + 2B_{3u}$$

$$\Gamma_{\text{ext}} = 5A_g + 4B_{1g} + 5B_{2g} + 4B_{3g} + 4A_u + 4B_{1u} + 3B_{2u} + 4B_{3u}$$

Within these modes all B_u type modes will be IR active, while all g-modes are Raman active. This crystal symmetry leads to a split of the carbonate asymmetric stretching and the in-plane bending to 8 different modes (A_u, A_g, B_{1u}, B_{1g}, B_{2u}, B_{2g}, B_{3u}, B_{3g}), while symmetric stretching and out-of-plane bending are split to 4 modes (A_g, B_{3g}, B_{1u}, B_{2u}). Within the external region

the assignment of librational and translational modes is less complicated in comparison to $\text{Ba}(\text{NO}_3)_2$. (Table 2)

The BaCO_3 sample used in this study was also investigated by X-ray diffraction measurements at the SNBL. The data are shown in Figure S-2 together with the diffraction pattern observed for witherite by DeVilliers.¹¹ Analogues to $\text{Ba}(\text{NO}_3)_2$ the average crystallite size was calculated to be 260 nm.

BaO

Due to the high sensitivity of BaO towards CO_2 and water in air, fresh BaO samples were prepared by two routes, namely decomposition of (A) BaO_2 or (B) BaCO_3 . The decomposition was carried out under He (PanGas, >99.999%) flow in a NETZSCH STA449C thermogravimetric cell and the effluent gas was analyzed by a mass spectrometer (PFEIFFER VACUUM OMNISTAR).

(A) BaO_2 was isothermally decomposed at 870 K for 2 h. From a decomposition run up to 1470 K, it is known that the used BaO_2 contains at least 16 % BaCO_3 which is not decomposed at this low temperature. The completeness of the BaO_2 decomposition reaction was confirmed by reoxidation at 750 K in a 20 % oxygen flow in He after the decomposition. The measured mass uptake of O_2 fitted exactly with the mass loss during the decomposition, confirming the formation of BaO and BaO_2 after the decomposition and reoxidation, respectively.

(B) BaCO_3 was ground with an equimolar amount (w.r.t. Ba) of active carbon (ABCR) and placed in the thermogravimetric cell. With a temperature ramp of 10 K min^{-1} the sample was heated up to 1120 K and kept for 2 h. The onset of the decomposition of BaCO_3 (1) occurs at 1010 K and is promoted by the Boudouard equilibrium (2), which removes CO_2 and hinders therefore the reformation of BaCO_3 :



The carbon addition accelerates the reaction and decreases the necessary temperature for complete decomposition from above 1570 to 1120 K. After the evolution of CO, the evolved gas contained CO₂ and H₂O, which further changed to H₂ and CO above 920 K. After all gas evolutions had completed, the sample contained less than 5% of BaCO₃, calculated from the mass of evolved CO₂ and CO.

Although these efforts were spent to obtain spectroscopic pure BaO, no well resolved spectra was obtained within this work. This is partly caused by the strong differences in the absorption coefficient of BaO and the impurity BaCO₃, which is assumed to be 100 times higher.

Figure S-1. X-ray diffraction pattern of the used $\text{Ba}(\text{NO}_3)_2$ samples ($\lambda=0.498 \text{ \AA}$). The crosses mark diffraction data from Nowotny and Heger (recalc. from $\lambda=1.5406 \text{ \AA}$).¹²

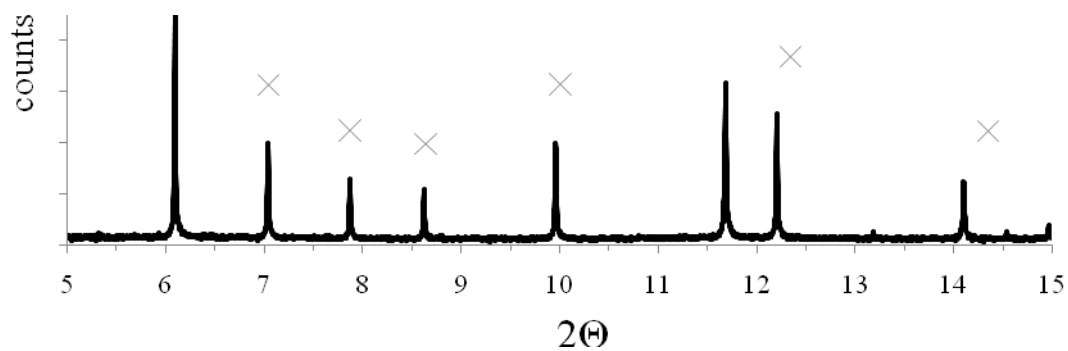
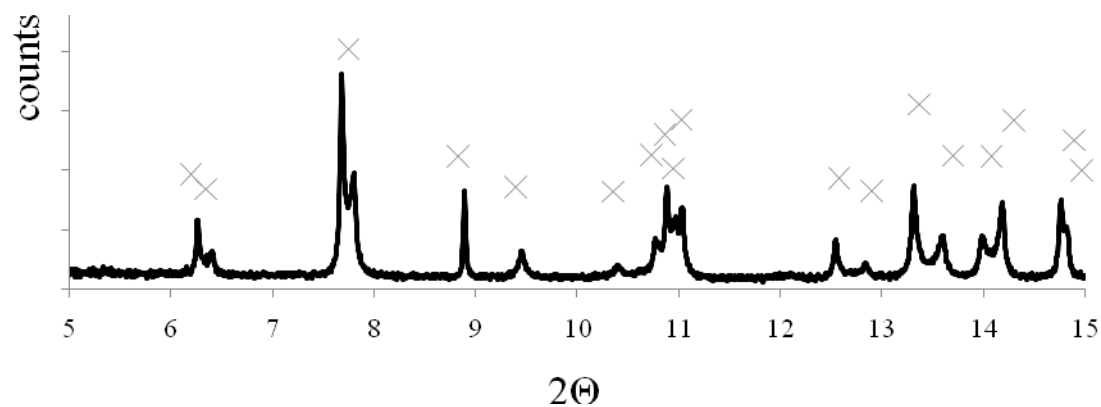


Figure S-2. X-ray diffraction pattern of the used BaCO_3 samples ($\lambda=0.498 \text{ \AA}$). The crosses mark diffraction data from DeVilliers (recalc. from $\lambda=1.5406 \text{ \AA}$).¹¹



References

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