



GdBO₃ and YBO₃ crystals under compression

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ABSTRACT

High-pressure X-ray diffraction studies on nanocrystals of the GdBO₃ and YBO₃ rare-earth orthoborates are herein reported up to 17.4(2) and 13.4(2) GPa respectively. The subsequent determination of the room-temperature pressure-volume equations of state is presented and discussed in the context of contemporary publications which contradict the findings of this work. In particular, the isothermal bulk moduli of GdBO₃ and YBO₃ are found to be 170(13) and 163(13) GPa respectively, almost 50% smaller than recent findings. Our experimental results provide an accurate revision of the high-pressure compressibility behaviour of GdBO₃ and YBO₃ which is consistent with the known systematics in isomorphic borates and previous ab initio calculations. Finally, we discuss how experimental/analytical errors could have led to unreliable conclusions reported elsewhere.

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1. Introduction

Rare-earth orthoborates exhibit useful luminescent properties when doped with lanthanide ions. They demonstrate a strong chemical stability and optical damage resistance making them desirable for optics applications [1–6]. The luminescent properties, such as intensity and chromaticity, can be tuned via the external control parameters of pressure [7]. A natural extension of such high pressure studies is to investigate the isothermal pressure-volume compressibility, or its inverse, the fundamental thermodynamic parameter of the isothermal bulk modulus.

The primary objective of this work is to clarify the bulk modulus of GdBO₃ by performing high pressure powder X-ray diffraction on nanocrystal samples. YBO₃ nanocrystals were also investigated for comparison. Certainly, single crystal diffraction measurements would have facilitated the refinement of atomic positions, however

the structure of the GdBO₃ and YBO₃ orthoborates is already well known [8–10]. For the purpose of determining lattice parameters as a function of pressure, and subsequently the isothermal bulk modulus, powder XRD measurements at high pressure are more than suitable. The choice of nano-crystalline samples offers a route to optimise the polycrystallinity of the sample (see [Supplementary Fig. 1](#)) without affecting the observed compressional behaviour, as discussed below. (N.B.: When no 'nano-' or 'micro-' prefix is stated, the article refers to the nanocrystal samples which are the focus of this work.)

The bulk modulus of a material is a fundamental thermodynamic parameter. The secondary objective of this paper is, more generally, to draw attention to the fact that the accurate and reliable determination of compressibility values requires careful data acquisition and analysis which is not always performed. Recently, the bulk modulus of GdBO₃ was reported by Woźny et al. in Ref. [11] to be 326 GPa, which the authors allege supports the earlier reported value of 321 GPa by Wang et al. in Ref. [12]. In our previous work, Ref. [13], we commented on the reliability of the bulk modulus alleged in Ref. [12] pertaining to the isomorphic borate YBO₃, and the

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reader is referred there for more details. The focus of the current article is the reported bulk moduli of GdBO₃, although nanocrystal YBO₃ samples were investigated in parallel for comparison. The experimental results of Ref. [12] pertaining to GdBO₃ attracted close criticism from Ref. [14], which provided ab initio calculations and arguments based on the systematics of isomorphous borates to suggest that the actual isothermal bulk modulus of GdBO₃ is in fact closer to 135 GPa. In this work, through careful data acquisition and analysis, whereby non-hydrostatic data are identified and disregarded, the bulk modulus of GdBO₃ was determined to be 170(13) GPa, which is in good agreement expected values based on compressibility systematics of orthoborates and with the predicted value of 135 GPa of Ref. [14], and is approximately 50% of the overestimated value of 326 GPa of Ref. [11], and of 321 of Ref. [12].

2. Methods

2.1. Sample preparation

Undoped nanocrystals of monoclinic YBO₃ and GdBO₃ were synthesised according to, and by the authors of, Ref. [8], via a sol-gel Pechini method using 900 °C annealing as reported in Ref. [8]. The average crystalline domain size was determined to be 31 nm for YBO₃, and 40 nm for GdBO₃, using the Scherrer formula on the X-ray diffraction (XRD) data. The average particle size, according to Ref. [8], is 350 nm. Therefore, the average grain size must be between 30 and 350 nm.

2.2. Measurements

GdBO₃ and YBO₃ nanocrystals were loaded into membrane-driven diamond anvil cells (DACs) to achieve gigapascal (GPa) pressures. Pure Cu powder was included in an isolated sample area for use as a pressure gauge in the XRD experiments [15]. Tungsten gaskets were pre-indented to 30 µm prior to loading the nanocrystals, and diamond anvils with culet sizes ~300 µm were used. The pressure transmitting medium (PTM) was a 16:3:1 methanol-ethanol-water mixture [16].

Angle-dispersive synchrotron powder XRD data were acquired at ALBA Synchrotron [17] (Barcelona, Spain) on the Materials Science and Powder Diffraction beamline (BL04-MSPD) using a monochromatic beam $\lambda = 0.4246$ Å focused to a spot size of 20 × 20 µm. A SX165 Rayonix Mar CCD detector was used to record the data. The nanocrystal samples were typically rotated about the axis perpendicular to the X-ray beam over a range of $\pm 3^\circ$ with a typical acquisition time of 10 s. The XRD patterns were masked and integrated in Dioptas [18]. Refinement of the calculated Le Bail profiles against the observed data was performed in JANA2006 [19]. The lattice parameters of the refined Le Bail were then used to calculate the unit cell volumes of YBO₃ and GdBO₃ as functions of increasing pressure. Equations of state (EOS) were fitted to the volume-pressure data using EOSFit7 [20] using second-order ($B_0' = 4$) Birch-Murnaghan equations [21], the validity of which was checked via the gradient of associated F_E vs. f_E plots [22] provided in the [Supplementary Material](#).

3. Results

3.1. X-ray crystallography and bulk moduli

The GdBO₃ and YBO₃ nanocrystals were compressed at ambient temperature up to 17.4(2) and 13.4(2) GPa respectively. (The numbers in parentheses are the standard errors in the least significant digit.) Representative integrated XRD patterns for both compounds are provided in Fig. 1. All XRD patterns are consistent with the monoclinic C2/c structure previously determined via neutron

diffraction [9] for YBO₃, and subsequently confirmed for GdBO₃ via X-ray diffraction [8]. No phase transition is observed in either compound over the full pressure range. The lattice parameters and residual values for both compounds at each pressure increment are provided in [Supplementary Tables 1 and 2](#). Example raw diffraction images of nano-GdBO₃ and nano-YBO₃ are shown in [Supplementary Fig. 2](#). We note that although the C2/c space group symmetry was unambiguously determined via neutron diffraction [9], numerous subsequent articles have continued to use older, although similar, structural models which can now be discarded, in particular the $P6_3/m$, $P6_3/mmc$ or $P6_3/mcm$ space groups which do not account for a number of low intensity low angle reflections observed via synchrotron XRD. Additionally, these orthoborates in fact appear to be pseudo-wollastonites rather than the commonly referenced 'pseudo-vaterites' [10].

The lowest pressure GdBO₃ XRD pattern (Fig. 1b) indicated trace amounts of a triclinic GdBO₃ phase which were detected via extremely low-intensity low-angle reflections (marked with red asterisks). The triclinic GdBO₃ phase is well documented in Ref. [8]. The trace impurity was not detectable using in-house XRD techniques and it is present in such small amount that it does not affect subsequent compressional data analysis of the pure monoclinic phase. Indeed, the reflections from the triclinic GdBO₃ phase are not observable at higher pressures even with the high-sensitivity of synchrotron XRD.

The integrated XRD patterns for GdBO₃ and YBO₃ shown in Fig. 1 are of the lowest and highest pressures observed within the quasi-hydrostatic pressure range. The onset of non-hydrostaticity in the GdBO₃ and YBO₃ samples was identified by observing the evolution of the full-width half maximum (FWHM) of the 002 reflection with increasing pressure (shown in [Supplementary Fig. 3](#)). The clear discontinuity in the rate of change of FWHM at 6.5 GPa for YBO₃ and 9 GPa for GdBO₃ indicate the loss of quasi-hydrostaticity and all data above these pressures have been omitted from further analysis, although they are still included in Fig. 2(a) to illustrate that the onset of non-hydrostaticity is also observed in the calculated unit cell volumes as a function of pressure. Integrated XRD patterns for GdBO₃ and YBO₃ at the maximum investigated pressures in non-hydrostatic range, 17.4(2) and 13.4(2) GPa respectively, are shown in [Supplementary Fig. 4](#).

The unit cell volumes of GdBO₃ and YBO₃, determined by Le Bail analysis, are plotted in Fig. 2 as a function of increasing pressure. As shown in Fig. 2(a), second-order Birch-Murnaghan (BM) equations of state (EOS) provide excellent fits to the data below the aforementioned quasi-hydrostatic limits, providing isothermal bulk moduli [22] of $B_0 = 170(13)$ and $163(13)$ GPa for GdBO₃ and YBO₃ respectively, where the bulk modulus, B , is given by, $B = -V\delta P/\delta V$. The data above the quasi-hydrostatic limit (shown with empty symbols) clearly diverge from the second-order BM EOS. Using the same input data and type of EOS, the PASCAL principal axis strain calculator [23] calculates very similar bulk moduli of 170(2) and 163(1) GPa for GdBO₃ and YBO₃ respectively. Fig. 2(b) shows the normalised unit cell volume for both compounds, emphasising the quasi-hydrostatic data only. The EOS fits were constrained to second-order ($B_0' = 4$) to limit the number of fitting parameters and to thereby facilitate comparison. The F_E vs. f_E plots provided [Supplementary Fig. 6](#) provide a useful visual assessment of the quality of the fitted equations of state. The excellent suitability of the second-order EOS truncation is demonstrated via the essentially zero gradient in those plots. The reader is referred to Ref. [22] for more details regarding F_E vs. f_E plots. In addition to the bulk modulus of GdBO₃, we also calculated for the first time the individual axial compressibilities via the isothermal compressibility tensor [24] (see [Supplementary Table 3](#)) which reveals an anisotropic compressibility in GdBO₃ essentially identical to that exhibited by YBO₃ in our previous work [13] and which we rationalised in terms of the compressibilities of the constituent BO₄-

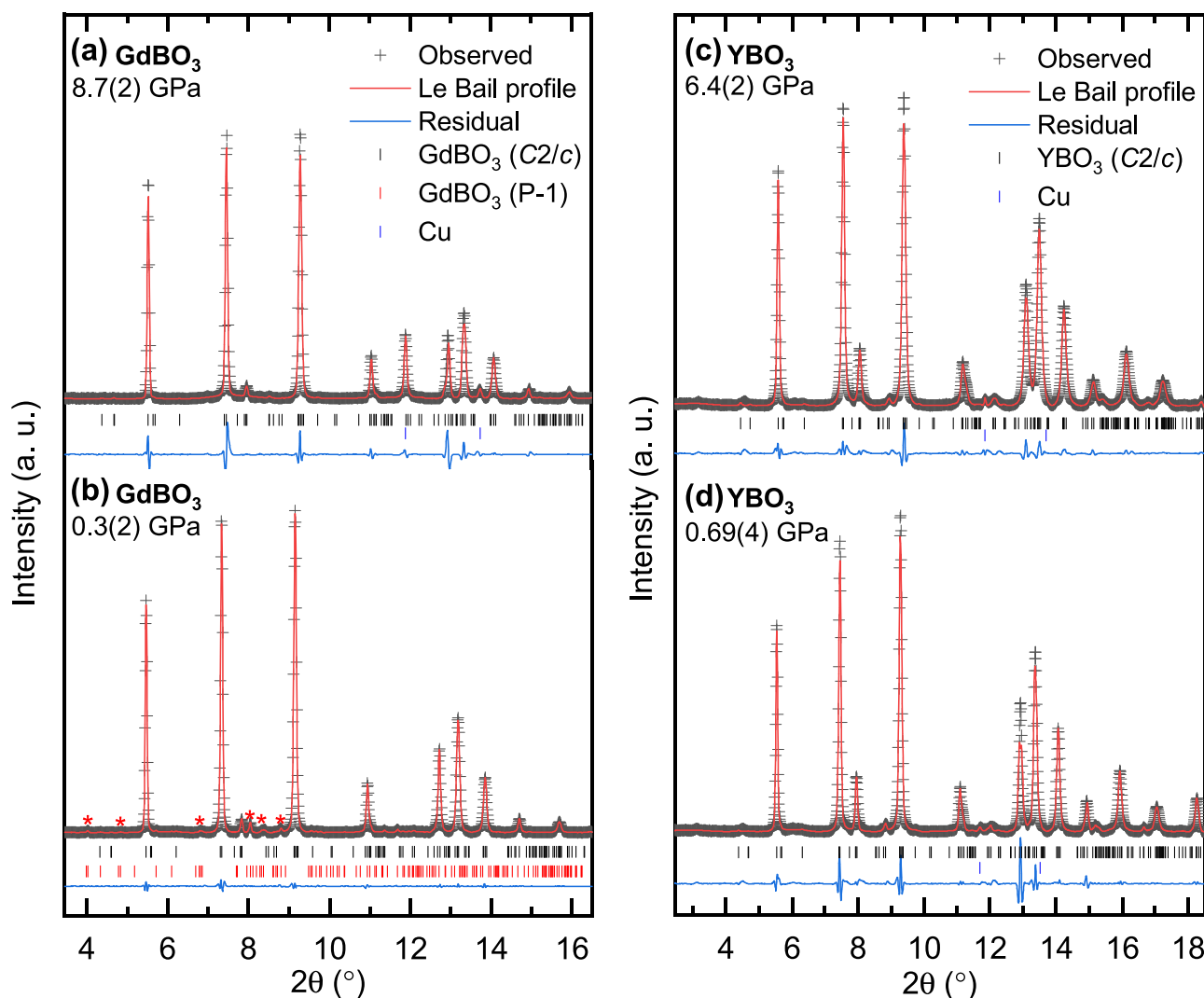


Fig. 1. Integrated XRD patterns for (a and b) nano-GdBO₃ and (c and d) nano-YBO₃. Observed data points are shown with black crosses. The calculated Le Bail profiles are shown with red lines. The difference between the observed and calculated profiles is shown in blue. Tick marks below the profiles correspond to reflections from the compounds indicated in the legends. In the nano-GdBO₃ pattern at lowest pressure, (b), the extremely low-intensity reflections from the triclinic phase are labelled with red asterisks. The lattice parameter data for the GdBO₃ and YBO₃ over the full pressure range are provided in [Supplementary Tables 1 and 2](#) and they are plotted individually in [Supplementary Fig. 5](#). The lattice parameters for the triclinic (*P*-1) GdBO₃ only observed at the lowest pressure are: $a = 6.4820(9)$, $b = 6.4682(7)$, $c = 6.2589(5)$ Å and $\alpha = 108.37(1)$, $\beta = 107.00(1)$ and $\gamma = 93.15(1)^\circ$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

tetrahedra and AO₈-dodecahedra. We note that the anisotropic compressibility is compatible with the constraint of the EOS to second-order ($B_0' = 4$) because the physical meaning of the constraint is only that, to a first approximation, the pressure derivative of the bulk modulus is constant.

3.2. Critical comparison of bulk moduli with reported values

Two important points must be made before commencing with the following discussion. Firstly, we are able to make a direct comparison between the compressional properties of GdBO₃ of this work, and the GdBO₃:Eu³⁺ of Ref. [11] because eightfold-coordinated Gd³⁺ and Eu³⁺ ions have very similar ionic radii of 1.053 and 1.066 Å, respectively, according Ref. [25]. Therefore, the bulk moduli of GdBO₃ and GdBO₃:Eu³⁺ can be expected to be essentially identical. Secondly, we are also able to make a direct comparison between powder samples consisting of nano-crystals and micro-crystals. This is shown in Fig. 3(a) where the nano-YBO₃ data of this work are compared with the micro-YBO₃ data of our previous work, Ref. [13]. The bulk modulus of the micro-YBO₃ samples in our previous work was determined to be 164(8) GPa. This is in excellent agreement

with the bulk modulus determined here for the nano-YBO₃ sample of 163(13) GPa. The nano-YBO₃ and micro-YBO₃ data in Fig. 3(a) perfectly agree to within the displayed errors. (The data of Wang et al. Ref. [12] are included in Fig. 3(a) for comparison, a detailed discussion of which is available in Ref. [13].)

The main focus of Woźny et al. in Ref. [11] is the high-pressure luminescence properties of GdBO₃:Eu³⁺, however, Section 3.2 of the paper discusses the high-pressure structural properties of GdBO₃:Eu³⁺, in particular the bulk modulus, which they allege to be 326 GPa, and which they state contradicts the ab initio calculations of Errandonea et al. [14] and supports the findings of Wang et al. [12]. We limit our critique of Ref. [11] to the results presented in their Section 3.2. The pressure-volume data of Refs. [11–14] are displayed in comparison the data of this work in Fig. 3.

In Fig. 3(b) the GdBO₃ data of the present work, shown in black, are very well fitted with a bulk modulus of 170(13) GPa. The data of Wang et al., shown in blue, are well described by their alleged equations of state, however for reasons previously discussed (see Ref. [13]) their bulk moduli for YBO₃ and GdBO₃ are likely to be an over-estimation by a factor of approximately 2. The data of Woźny et al., shown in red, have here been refitted with a bulk modulus of 95(13)

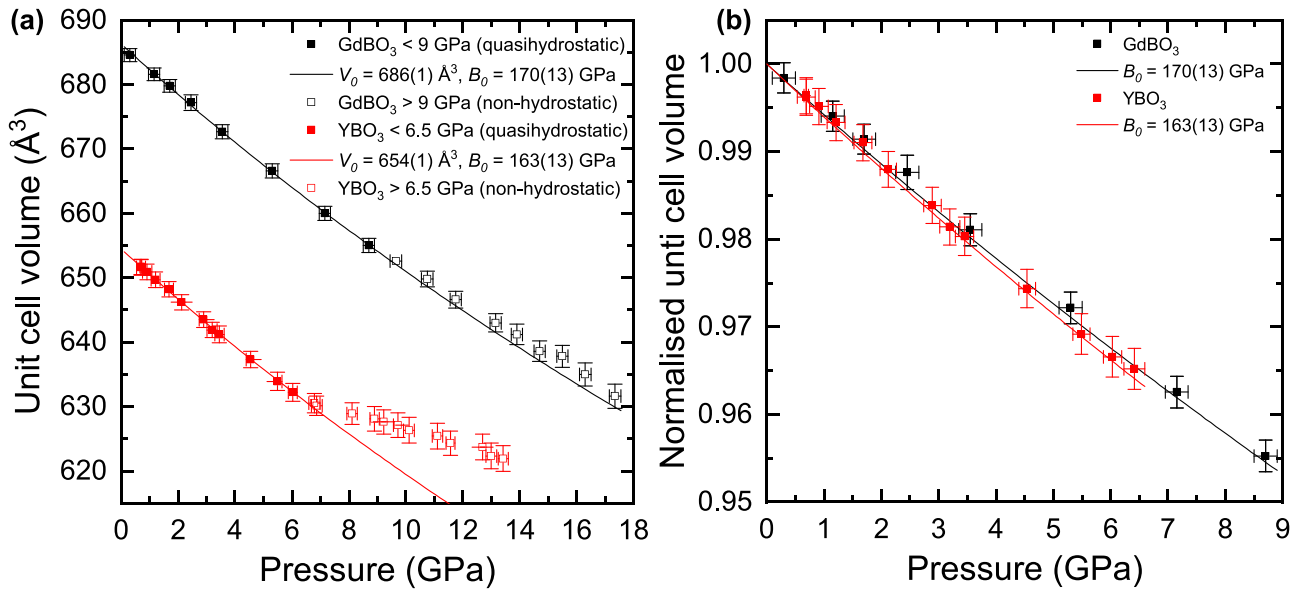


Fig. 2. GdBO₃ and YBO₃ unit cell volume as function of increasing pressure. Black symbols correspond to GdBO₃ and red symbols to YBO₃. Solid symbols correspond data acquired under quasi-hydrostatic conditions, and empty symbols to data acquired under non-hydrostatic conditions. The lines correspond to second-order Birch-Murnaghan equations of state. The error bars were determined from the Le Bail refinements of the powder X-ray diffraction patterns. The pressure was determined from the copper equation of state. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

GPa. There are three important remarks: firstly that the alleged GdBO₃ bulk modulus of 326 GPa is not compatible with their data; secondly, that in any case such a large bulk modulus is not compatible with the known compressibility systematics of isomorphic borates [26]; and thirdly, that the low bulk modulus of 95(13) GPa re-fitted here drastically underestimates the bulk modulus of GdBO₃. Therefore, the data of Woźny et al. do not agree with those of Ref. [12] (shown in blue) as they claim. Their result is potentially the product of problems either with their experimental data or the analysis thereof, however it is not possible to say based on the data they present, for example: not a single XRD refinement is presented and only integrated patterns are

provided; no details are provided of how the XRD fits were made; no details are provided of how the equations of state were fitted, such as the type or order; the XRD patterns exhibit gasket reflections from the very lowest pressure; and, the XRD reflections are broad/exhibit low-intensity at low pressures (compare for example to the data in Fig. 1). For their XRD experiments Daphne 7575 oil was used, which has a hydrostatic limit at ambient temperature of ~ 4 GPa, so it is not clear why the XRD peaks are so broad at low pressure, although it is possible that the sample chamber was too densely packed to allow room for sufficient PTM, therefore leading to bridging of the sample between diamonds.

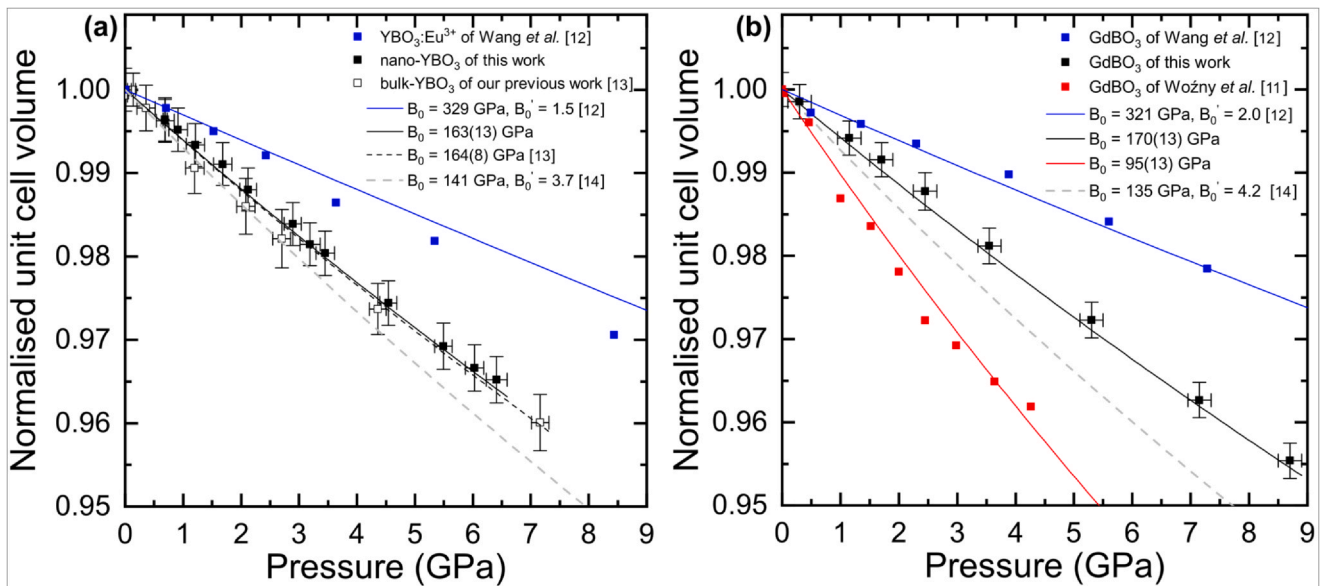


Fig. 3. Comparison of the reported normalised volumes of (a) YBO₃ and (b) GdBO₃. The black data correspond to data acquired by the authors of this article here and in Ref. [13]. Blue data are reported by Wang et al. in Ref. [12]. Red data are reported by Woźny et al. in Ref. [11]. Lines correspond to second-order Birch-Murnaghan equations of state when B_0' is not stated. The blue EOS are reported in Ref. [12]. The red EOS was fitted by the present authors with a drastically lower bulk modulus (95(13) GPa) than reported in Ref. [11] (326.09(4) GPa). The dashed grey EOS are from the ab initio calculations of Ref. [14]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Regarding the triclinic GdBO₃ phase reported on by Woźny et al., we cannot recreate the equation of state shown in their Fig. 2(c). Numerous different equation of state have been fitted to their data using their reported values of $V_0 = 230.77 \text{ \AA}^3$ and $B_0 = 27.09 \text{ GPa}$ as fixed parameters, as shown in Supplementary Fig. 7, however we were not able to reproduce the reported EOS. Relaxing the fixed parameters results in converged fit with a very low bulk modulus of 19(3) GPa, which describes the data very closely but still raises concerns. For example, a bulk modulus of 19(3) GPa would suggest that the triclinic GdBO₃ compound is as compressible as a rare-gas solid, which cannot be the case. This points to unexplained experimental errors which have led to underestimations in both monoclinic and triclinic GdBO₃ bulk moduli. The essential difference between the triclinic and monoclinic GdBO₃ phases is that the BO₄-tetrahedra in the monoclinic phase open to up form triangular BO₃-units in the triclinic phase. Therefore, although a lower bulk modulus is indeed expected for the triclinic phase, the fact that the triclinic structure contains GdO₈-octahedra and BO₃-trigonal-units certainly indicates a compound more rigid than a rare-gas solid. Therefore, further high-pressure experiments are required on the triclinic GdBO₃ structure in order to clarify its isothermal compressional behaviour.

4. Conclusions

This experimental X-ray diffraction study of GdBO₃ and YBO₃ nanocrystals under compression, up to 17.4(2) and 13.4(2) GPa respectively, has provided an accurate revision of the compressional behaviour of monoclinic GdBO₃. In particular, the fundamental property of bulk modulus was found to be 170(13) and 163(13) GPa for GdBO₃ and YBO₃ nanocrystals respectively, thereby revealing that the compressional behaviour of both compounds is consistent with the family of borate compounds. The ab initio calculations of Ref. [14] predicted a GdBO₃ bulk modulus of 135 GPa, which consistent with the results presented here, and those expected based on observed compression systematics based on metallic cationic radius [26]. The previously alleged bulk moduli [11,12] suggested that GdBO₃ would be less compressible than all known ultra-incompressible nitride and carbides [28] which is not expected for such a layered structure [29]. This study concludes that the claims of GdBO₃ incompressibility made by other authors are not correct, in particular that the GdBO₃ bulk modulus values of 326 GPa reported in Ref. [11], and of 321 GPa in Ref. [12], are overestimated by a factor of approximately 2. In this work, comparison of the compressional behaviour of GdBO₃ with structurally analogous YBO₃ provides very similar results for both compounds as expected. The YBO₃ bulk modulus determined here (163(13) GPa) agrees very closely with our previous result [13] on YBO₃ micro-powders of 164(8) GPa, and shows that in the case of these rare-earth orthoborates optimisation of powder XRD experiments is possible through the use of nanopowder samples without affecting the observed compressional behaviours. The results of this work highlight that careful data acquisition and analysis are necessary for the accurate and reliable determination of the fundamental thermodynamic value of the isothermal bulk modulus.

CRedit authorship contribution statement

Robin Turnbull: Conceptualization, Writing - original draft, Formal analysis, Visualization. **Daniel Errandonea:** Conceptualization, Writing - review & editing, Supervision, Funding acquisition, Formal analysis, Resources. **Juan Ángel Sans:** Writing - review & editing, Investigation. **Vanesa Paula Cuenca-Gotorb:** Investigation. **Rosario Isabel Vilaplana:** Investigation. **Jordi Ibáñez:** Investigation. **Catalin Popescu:** Methodology, Investigation, Resources. **Agata Szczeszak:** Investigation. **Stefan Lis:** Investigation.

Francisco Javier Manjón: Conceptualization, Writing - review & editing, Supervision, Funding acquisition, Formal analysis, Resources.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jallcom.2021.158962.

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