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Structural and thermal stability of Czochralski grown GdCOB oxoborate single crystals

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Properties such as chemical and structural stability, thermal expansion and thermal conductivity are investigated, with the purpose of better characterizing the behaviour of Czochralski grown GdCOB [$Ca_4GdO(BO_3)_3$], oxoborate single crystals, to be used in optical devices.

Introduction

The linear and non-linear optical properties of $Ca_4GdO(BO_3)_3$ (GdCOB) single crystals have been previously reported.[1] Owing to the non-linear characteristics[2] and the Nd^{3+} laser action[3] evidenced in GdCOB, this material is already quite an efficient crystal for frequency conversion (SHG) and for use as a self frequency doubling (SFD) laser.[4] For both applications, the crystal has to be optically perfect and very stable with regard to the laser exciting beam. Therefore, a number of parallel investigations were performed in order to explore the real behaviour of GdCOB in use. This concerns the structural stability and homogeneity of single crystals and their thermal behaviour, mainly for pure GdCOB crystals elaborated at the Crismatec firm.

The compound $Ca_4GdO(BO_3)_3$ crystallises with a monoclinic acentric structure,[5] the space group is *Cm* (Fig. 1). In previous structural investigations,[6] Iliukhin *et al.* reported some disorder in the distribution of Ca and Gd ions with respect to their theoretical sites. Such disorder in crystals designed for optical purposes could result in inhomogeneities in the crystal growth (and in the Nd^{3+} crystal field, for doped GdCOB crystals). Therefore, it is necessary to be able to check for such disorder in large sized single crystals. The compound belongs to the $M_4LnO(BO_3)_3$ family and shows congruent melting at 1480 °C, which allows the crystals to be grown from the melt by a vertical pulling method (Czochralski method). The crystallisation occurs during the very slow extraction of a seed from the molten charge, contained in a radio-frequency heated iridium crucible. A typical run lasts about one week and crystals grown thus may reach 10 cm in length and 30–50 mm in diameter when produced by the Crismatec company.[2] The very first, small, crystals of GdCOB were obtained in the laboratory by the same process.

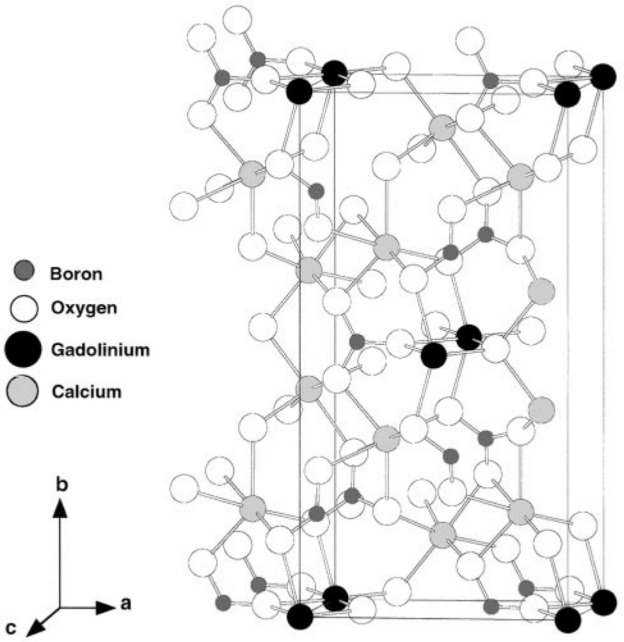

Fig. 1 Crystal structure of GdCOB

One question is whether the crystals produced are quite identical from successive experiments, since the crucible is refilled for each new run. Any variation in composition or structure of the crystals would influence the mechanical and optical properties (*e.g.* refractive indices) of samples designed for specific applications. Another point is the effect of temperature, *i.e.* thermal behaviour of a charge submitted to prolonged melting (stability), thermal gradient while cooling the high temperature elaborated crystals (thermal expansion and thermal conductivity), effect of temperature on the birefringence which could induce modification in the phase matching angles, thermal effect of incident laser beam for second harmonic generation or self frequency doubling. Some answers to these questions are reported herein, with the purpose of better characterizing the chemical and thermal stability of Czochralski grown GdCOB single crystals.

Chemical composition

The chemical composition of several crystals grown by the Czochralski process by Crismatec, was tested; in addition, the composition of a crystal obtained in the laboratory, by the same method, was also determined. Starting materials are $CaCO_3$, (R.P. normapur 99.5), B_2O_3 (R.P. ultrapur) and Gd_2O_3 (R.P. 4N).

An ICP analysis was performed to determine the proportions of Ca, Gd and B, in various runs of crystal elaboration. The results (weight ratios) are gathered in Table 1, together with theoretical ratios in the stoichiometric compound.

As oxygen content cannot be determined, one may assume that either Ca or Gd have the theoretical value, and this leads to various formulations of the chemical composition. However, the ratios Ca/Gd and B/Gd keep intrinsic values, reported in Table 2, for the various crystals.

Differential thermal analysis and thermogravimetry show that no weight losses occur during the thermal treatment. The results suggest that, within the accuracy of the method, the

Table 1 Chemical analysis (ICP) for selected Czochralski grown crystals

crystal growth run number	weight ratio		
	calcium (%)	gadolinium (%)	boron (%)
Crismatec crystal 1	31.2(0.6)	30.4(0.1)	6.43(0.1)
5	31.0	30.2	6.40
10	32.1	30.9	6.45
11	32.2	30.7	6.47
12	31.7	30.5	6.35
13	31.5	30.4	6.33
lab. crystal	32.1	30.7	6.55
theoretical values	31.4	30.8	6.36

Table 2 Cation ratios in GdCOB crystals from various growth cycles

growth run	Ca/Gd	B/Gd
Crismatec crystal 1	4.0(0.2)	3.1(0.1)
5	4.0	3.1
10	4.1	3.0
11	4.1	3.1
12	4.1	3.0
13	4.1	3.0
lab. crystal	4.1	3.1

composition of Czochralski grown crystals remains quasi-constant during the production and it is stoichiometric. Further investigations will confirm the reliability of the elaboration process.

Structural stability

As mentioned above, GdCOB melts congruently which implies that no transformation or decomposition occurs during the thermal treatment. As the kinetics of crystal growth is very slow, these points have been checked in several ways.

Lattice stability

Data collection was performed with a scanning step of 0.01° in 2*θ*, and counting time of 10 s per step, on a Siemens D5000 X-ray diffractometer (Co-Kα radiation), equipped with a graphite back-monochromator set on the diffracted beam, in front of the detector. X-Ray data collection and treatment were monitored by the Siemens DIFFRACT-AT routine, the U-FIT set of routines was used for lattice constants least-square fitting.

X-Ray diffraction patterns of several crystals arising from several crystal growths were recorded and the inferred lattice constants are given in Table 3. These parameters show very small variations and the resulting volume of the unit cell remains constant, within the accuracy range.

In spite of a slight modification of diffracted intensity for some lines, it can be assumed that the successive cycles of crystal growth do not affect the resulting crystal structure.

Table 3 Refined lattice constants for several powdered crystals of GdCOB

growth run	a/Å	b/Å	c/Å	β/°	V/Å^3
Crismatec initial batch 1	8.0991(6)	16.024(1)	3.5583(3)	101.24(1)	452.9(7)
5	8.0971(6)	16.019(1)	3.5590(3)	101.26(1)	452.7(6)
10	8.0968(5)	16.017(1)	3.5588(2)	101.27(1)	452.6(5)
11	8.0941(6)	16.012(1)	3.5581(2)	101.27(1)	452.2(7)
12	8.0967(4)	16.017(1)	3.5584(1)	101.26(1)	452.6(4)
lab. crystal	8.0966(3)	16.016(1)	3.5585(1)	101.26(1)	452.5(4)

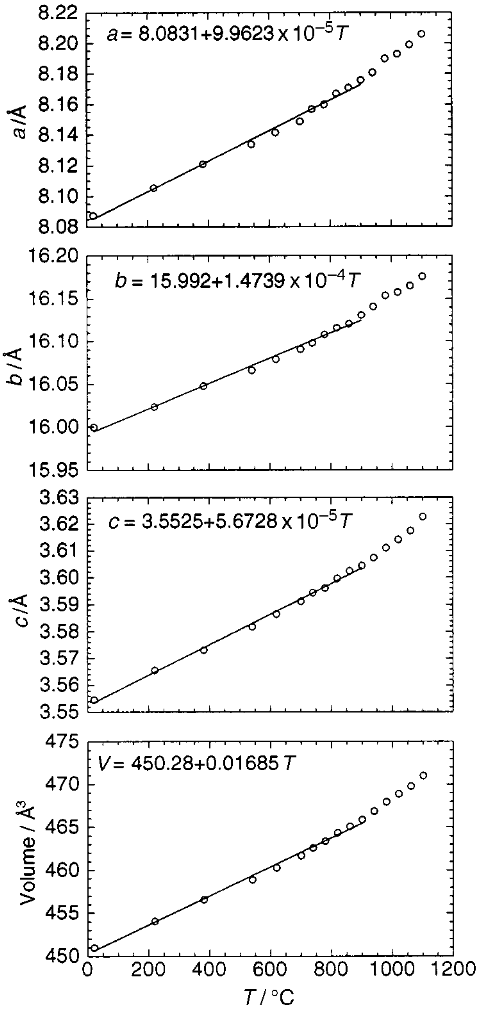

Fig. 2 Variation of lattice constants *a*, *b*, *c* and *V versus* temperature, in GdCOB

Thermal optical coefficient

The optical coefficient, d*n*/d*T*, gives the variation of birefringence *versus* temperature, and should be as low as possible, to keep quite stable non-linear optical properties over a wide temperature range. In a qualitative test performed in the laboratory, the intensity of the second harmonic of a YAG laser beam, obtained with a heated GdCOB crystal, was insensitive to temperature variations within the range 20–200 °C. A quantitative evaluation,[7] not reported here gives a d*n*/d*T* average value of 2×10^{-6} K^{-1} for GdCOB, one order of magnitude smaller than for BBO for instance, where d*n*/d*T* = 1.6×10^{-5} K^{-1}.

Thermal expansion

The thermal behaviour of GdCOB was examined in two ways: at the atomic scale, through the variation of lattice constants as a function of temperature and, at macroscopic scale, on oriented crystals, in order to determine the thermal expansion in all three directions.

(a) X-Ray diffraction powder patterns were recorded on a powdered Czochralski grown sample from Crismatec, between 20 and 1100 °C, in steps of 40 °C. This was performed on an Inel X-ray diffractometer, fitted with a high temperature device and linear detection, with λ(Cu-Kα) (at the Institut des Matériaux de Nantes). The scan step was 0.03° and the

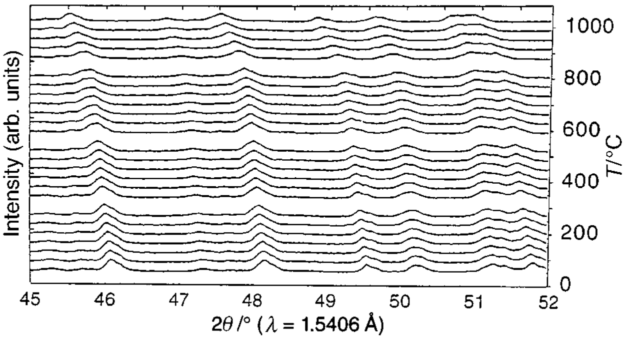

Fig. 3 XRD patterns of GdCOB for several temperatures [2θ range 45–52°, λ(CuKα)]

counting time was 40 s. Lattice constants calculated from the X-ray patterns (Diffract-AT + U-fit routines) were plotted *versus* temperature (Fig. 2). Up to 1100 °C, only the diffraction lines of a GdCOB single phase were present. However, a weak anomaly was detected, around 900 °C, in the linear variation of lattice constants which is also visible on the X-ray diffraction patterns (Fig. 3). The temperature range 800–1000 °C was carefully re-investigated with steps of 15 °C and this evolution was confirmed. Dilatometric coefficients have been deduced by linear regression, for the two ranges of temperature, apart from 860 °C, where the weak change in the slope was detected [$\alpha_a = (1/a)(\Delta a/\Delta t)$].

(b) Simultaneously, thermal expansion coefficients were determined on a single crystal cut along the *a, b* and *c* crystallographic directions, up to 1000 °C (at 20 °C h^{-1}). The curves, not presented here, showed a very weak change in the slopes around 850 °C, for axes *a* and *b*. As can be seen in Table 4, the coefficients of thermal expansion determined by X-ray diffraction for $T < 860$ °C fit quite well to those obtained on the crystalline sample. Evaluation of the lattice constants, after the crystal was returned to room temperature, showed coincidence with the initial set of lattice constants. There is no irreversible transformation during the thermal treatment.

Thermal conductivity

Evaluation of thermal conductivity is a fundamental point for developing a non-linear anisotropic material, such as GdCOB: first, this parameter will influence the result of crystal growth and secondly, poor conductivity could result in strong local thermal gradients, which would modify the refractive indices and hence affect the phase matching angles. An expensive temperature stabilisation device would then be required. The thermal conductivity, *k*, was determined along the *X*, *Y* and *Z* crystallophysic (or dielectric) directions of a crystal, according to the classical method described here and derived from Cowan's method:[8] $k = \text{density} \times \text{specific heat } (C_p) \times \text{thermal diffusivity } (D)$, as a function of temperature.

1. Specific heat, C_p. This was determined by differential calorimetry, between 20 and 800 °C (heating rate: 3 °C min^{-1}) on a cylinder cut from a single crystal. The resulting specific heat C_p is plotted in Fig. 4. The accuracy is within 3%. Between 300 and 500 °C, the experimental points are well fitted by a Debye model. Below 300 °C, the data are fitted by a third order polynomial: $C_p = \Sigma a_i T^i$, with $a_0 = 0.5661$, $a_1 = 1.391 \times 10^{-3}$, $a_2 = 3.655 \times 10^{-6}$, $a_3 = 4.51 \times 10^{-9}$.

Table 4 Thermal expansion coefficients of a GdCOB single crystal, along the crystallographic axes

thermal expansion coefficients/K^{-1}	from thermal expansion	from XRD determination	
		$T < 860$ °C	$T > 860$ °C
α_a	10.2×10^{-6}	$11.1(1) \times 10^{-6}$	$17.0(4) \times 10^{-6}$
α_b	8.3×10^{-6}	$8.3(2) \times 10^{-6}$	$13.3(3) \times 10^{-6}$
α_c	14.3×10^{-6}	$15.0(2) \times 10^{-6}$	$21.0(7) \times 10^{-6}$

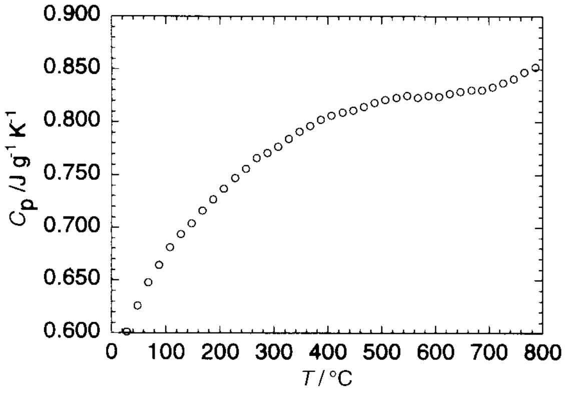

Fig. 4 Specific heat of GdCOB, as a function of temperature

2. Thermal diffusivity, *D*. This was obtained by the 'flash laser method': one face of a flat disk of material was submitted to a laser pulse and the temperature evolution was analysed on the back face with a chromel–alumel thermocouple fitted to it. The sample was in a furnace reaching 1000 °C under helium atmosphere, in order to measure the diffusivity as a function of temperature.

Owing to the rather low conductivity and the transparency of the samples to the incident laser beam (1.06 µm), a specific and complex coating had to be added, to improve the laser beam absorption by the sample: on the sample surface, a layer of graphite powder was deposited, covered by a 5 µm gold sheet. The corresponding values of the diffusivity, *D*, along the three crystallophysic directions were obtained with a precision of 5%. The volume and weight of the samples gave an average experimental density $d = 3.70(2)$ g cm^{-3}. Finally, the thermal conductivity, *k*, was obtained (accuracy of 8%), after correction for thermal expansion of the samples (Table 5). In the range of temperature explored, the thermal conductivity is low, although it is slightly higher along *X* or *Z* than along the *Y* direction. It is however weakly dependent on temperature.

The resulting average value of conductivity for GdCOB is in the same range as those of some recently developed non-linear crystals (Table 6),[9–11] even if this value is low with regard to laser crystals, such as YAG.

Structural refinement

As mentioned in introducing the GdCOB structure, structural investigations reported some disorder in the distribution of Ca and Gd ions with respect to their theoretical sites.[6] A departure from ideal structure would bring some calcium on the gadolinium site and *vice versa* and this was effectively found by Ilyukhin and Dzhurinskii who reported 0.86 Gd + 0.14 Ca on the Gd site. The ionic sizes of Gd^{3+} and Ca^{2+} allow such a disorder but it would result in point defects in the charge balance (colour centres) and in local variations of the crystal field of Nd^{3+} ions introduced for the laser effect. Therefore, a structural refinement was performed on a Czochralski grown GdCOB single crystal. Simultaneously, in order to check the stability of the elaboration process, crystals from different runs were examined under the same conditions ($n = 1$, 5, 12).

Experimental

The three crystalline samples were cut as spheres of a few tenths of millimetres, in order to get comparable results and to avoid any X-ray absorption effect, which is always difficult

Table 5 Thermal diffusivity, D, and conductivity, k (accuracy of 8%), as a function of temperature along X, Y and Z

T/°C	D/mm^2 s^{-1}	$k(\parallel X)$/W m^{-1} K^{-1}	T/°C	D/mm^2 s^{-1}	$k(\parallel Y)$/W m^{-1} K^{-1}	T/°C	D/mm^2 s^{-1}	$k(\parallel Z)$/W m^{-1} K^{-1}
14	0.982	2.173	18.0	0.603	1.32	16	0.917	2.401
24	1.123	2.539	130.2	0.473	1.22	72	0.758	1.880
51	0.938	2.227	271.9	0.419	1.18	121	0.683	1.799
80	0.812	2.016				172	0.656	1.807
151	0.835	2.237				223	0.650	1.852
201	0.820	2.277				252	0.618	1.789
253	0.702	2.009						

Table 6 Average thermal conductivity of selected materials, for non-linear optics or laser applications (room temperature)

material		conductivity/W m^{-1} K^{-1}	ref.
NLO:	GdCOB	2.0	this work
	BBO	1.6	8
	LBO	3.5	8
	KTP	3.0	9
Lasers:	YVO$_4$	5.0	Casix Society
	YAG	10.0	10

Table 7 Refinement of GdCOB crystal structure

crystal structure	
$Ca_4GdO(BO_3)_3$	
M	510
space group	Cm
Z	2
calculated density/g cm^{-3}	3.70

refined lattice constants on crystals:

	a/Å	b/Å	c/Å	β/°	V/Å^3
GdCOB1	8.078(1)	15.981(2)	3.5519(4)	101.26(1)	449.7(1)
GdCOB2	8.070(1)	15.971(2)	3.5474(5)	101.29(1)	448.4(1)
GdCOB3	8.078(1)	15.983(2)	3.5490(6)	101.28(1)	449.4(1)

data collection	
on Nonius CAD4 diffractometer	
radiation wavelength	Mo-Kα, $\lambda = 0.71069$ Å
temperature	room temp.
crystal size and shape	sphere, 0.7 mm
scan	ω–2θ
range of h, k, l	$-14 < h < 14$, $0 < k < 28$, $-6 < l < 6$
sin θ/λ range	$0.18 < \sin\theta/\lambda < 0.9$
absorption correction	none (spheres)
anisotropic thermal factors	for heavy cations Gd, Ca(1) and Ca(2)

refinement results	GdCOB1	GdCOB2	GdCOB3
number of significant reflections	1412	1281	1272
final R value (based on $\|\Delta F\|^2$)	0.021	0.025	0.022
final R_w	0.035	0.035	0.036
secondary extinction	0.15×10^{-4}	0.18×10^{-4}	0.13×10^{-4}
multiplicity factors for:			
Gd (theor. 0.5)	0.492	0.490	0.490
Ca(1) (theor. 1.0)	1.07	1.04	1.06
Ca(2) (theor. 1.0)	1.00	1.00	1.01

to account for. Diffracted intensities were collected at room temperature, on the same X-ray diffractometer, in the same period. Experimental conditions are gathered in Table 7. Data were collected over one half of the reciprocal space, owing to the acentric character of the structure. Lattice constants were fixed for each sample, by least square refinement over 20 reflections. Atomic coordinates and thermal factors were refined (anisotropic factors for the heavy ions Gd and Ca) and the occupancy factors of cations were allowed to vary from their theoretical values.

Results and comments

The main result is the very low degree of average disorder in all three samples of GdCOB, confirmed by several observations (Table 8). (i) Atomic coordinates show very small variations (within the accuracy range) from one crystal to the other. Therefore, only one set of refined parameters is given (from sphere no. 1). (ii) Thermal factors are low for all cations and their values do not suggest perturbations of Ca and Gd on their sites. The O(1) thermal factor is rather low, but this is related to the fact that O(1) is bound to heavy cations and is not allowed to strongly vibrate, as the oxygen atoms connected to boron do. (iii) The occupancy factors for cations, when allowed to vary from their ideal values, take modified values which suggest less than 3% cation exchange. This slight disorder concerns Gd and Ca(1) only. (iv) Finally, the effects of secondary extinction (reported in Table 7), introduced for all three samples in the last steps of refinement, have the same large magnitude (about 10^{-5}). It can clearly be attributed to the large size and high perfection of the samples. It strongly affects the few reflections with low sin θ/λ, which are therefore excluded from the refinement.

Bond strengths, σ, around the cations Gd and Ca were estimated, using the bond lengths Gd—O, Ca(1)—O and Ca(2)—O, deduced from the refined atomic positions. The sum Σ of σ values around a considered site gives the effective valence of the concerned atom.[12] The results gathered in Table 9 confirm the localisation of these atoms where they are expected, with a slight exchange of Gd and Ca(1) on their respective sites.

If one looks back to the disorder reported in ref. 6, it probably arises from the growing process employed by the authors to produce crystals (crystallisation from a PbO flux, between 1100 and 950 °C). Cooling speed and crystal size are completely different from the ones employed here and their resulting crystal structure looks much more disordered.

On a different scale, a local investigation on the possible disorder around the optically active ion has been carried out using absorption and emission spectroscopies, which are reported elsewhere.[2,3]

Conclusion

If one excepts the mechanical stress of the Czochralski rotation and the thermal shocks inherent to this elaboration process, the thermodynamical conditions seem quite stable throughout the crystal growth and produce quasi perfectly organised single crystals. Technical specifications are reviewed in Table 10.

The non-linear characteristics of GdCOB are quite comparable to those of the well known and developed BBO, LBO and KDP crystals, and less sensitive to the temperature. Moreover, GdCOB crystals are quite stable and can be obtained at very large sizes. Therefore GdCOB deserves further development as a non-linear optical medium and in self frequency doubling devices.

We want to acknowledge Dr P. Deniard (Institut des Matériaux de Nantes, France) for high temperature X-ray

Table 8 Refined atomic parameters in GdCOB Czochralski grown crystals

		mean atomic coordinates				anisotropic thermal factors $\times 10^4$					
atom	Wyckoff pos.	x	y	z	$B/\text{Å}^2$	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Gd	2a	0(0)	0(0)	0(0)	0.2	5	2	27	0	2	0
Ca(1)	4b	0.1415(1)	0.3873(1)	0.3263(3)	0.1	7	−1	40	−1	1	0
Ca(2)	4b	0.2618(1)	0.1816(1)	0.6521(3)	0.3	13	3	56	−1	10	−3
O(1)	2a	0.8259(7)	0(0)	0.4212(17)	0.15(6)						
O(2)	4b	0.4611(5)	−0.0746(3)	0.7490(12)	0.39(4)						
O(3)	4b	0.7925(5)	0.1724(3)	−0.1146(13)	0.53(5)						
O(4)	4b	0.0862(5)	0.1430(3)	0.0781(12)	0.37(4)						
O(5)	4b	0.9690(5)	0.2684(3)	0.2773(13)	0.58(5)						
O(6)	2a	0.2024(8)	0(0)	0.6087(20)	0.48(8)						
B(1)	2a	0.3762(9)	0(0)	0.7011(21)	0.47(8)						
B(2)	4b	0.9491(6)	0.1944(4)	0.0819(15)	0.54(6)						

From symmetry restrictions, $\beta_{12} = \beta_{23} = 0$, for atoms in 2a Wyckoff positions.

Table 9 Bond lengths around Gd, Ca(1) and Ca(2) atoms (in GdCOB1 refined structure)

	Gd—O	Ca(1)—O	Ca(2)—O
	2.245(6)	2.320(4)	2.327(5)
	2.253	2.323	2.327
	2.346	2.342	2.350
	2.390 × 2	2.352	2.465
	2.443	2.366	2.472
		2.368	2.631
Sum of bond strengths (effective valence/theoretical valence)	2.93/3	2.1/2	1.97/2

Table 10 Summary of GdCOB technical specifications

chemical formula	$Ca_4GdO(BO_3)_3$
crystal structure	monoclinic, biaxial crystal space group Cm, $Z = 2$
unit-cell constants	$a = 8.078$ Å, $b = 15.98$ Å, $c = 3.55$ Å, $\beta = 101.28°$
density	$3.70\ \text{g cm}^{-3}$
melting point	1480 °C
hardness	about 6.5 Mohs
hygroscopy	none
specific heat	$0.601\ \text{J g}^{-1}\ \text{K}^{-1}$ (at 28 °C)
thermal conductivity	$k_X = 2.18\ \text{W m}^{-1}\ \text{K}^{-1}$ (at 18 °C) $k_Y = 1.32\ \text{W m}^{-1}\ \text{K}^{-1}$ $k_Z = 2.40\ \text{W m}^{-1}\ \text{K}^{-1}$
thermal expansion coefficients	$\alpha_a = 10.5 \times 10^{-6}\ \text{K}^{-1}$ (below 900 °C) $\alpha_b = 8.3 \times 10^{-6}\ \text{K}^{-1}$ $\alpha_c = 14.7 \times 10^{-6}\ \text{K}^{-1}$
temperature derivative of refractive indices[7] ($\lambda = 1.064$ µm)	$dn_x/dT = 2.0 \times 10^{-6}\ \text{K}^{-1}$ $dn_y/dT = 2.5 \times 10^{-6}\ \text{K}^{-1}$ $dn_z/dT = 1.2 \times 10^{-6}\ \text{K}^{-1}$

diffraction patterns, Dr. B. Ferrand (LETI, CEA, Grenoble) for having the crystals polished as spheres, Dr J. Vaissermann (University P. et M. Curie, Paris, URA CNRS 419) for X-ray data collection facilities on single crystals and J. P. Sola (Crismatec) for preparing oriented samples for conductivity measurements.

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