JOURNAL OF Materials CHEMISTRY

Structural and luminescent properties of Eu^{3+} doped $Gd_{17.33}(BO_3)_4(B_2O_5)_2O_{16}$

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Crystal structure of gadolinium borate $Gd_{17.33}(BO_3)_4(B_2O_5)_2O_{16}$ has been refined by the Rietveld method from X-ray powder diffraction data. $Gd_{17.33}(BO_3)_4(B_2O_5)_2O_{16}$ crystallizes in the monoclinic space group *Cm* with lattice constants $a = 1841.70(3)$, $b = 374.08(1)$, $c = 1419.30(3)$ pm and $\beta = 119.85(1)°$. The structure contains two types of borate groups BO_3^{3-} and $B_2O_5^{4-}$, and nine independent gadolinium atoms. IR, Raman and HREM studies supported the presence of these two different borate groups in the structure. The luminescent spectra of the Eu^{3+} doped material consist of several sharp lines originating from the optical transitions within the f^6 configuration of the Eu^{3+} ions at different cation sites.

Introduction

Rare earth borates 'Ln_3BO_6', have been known for a long time from phase analysis of Ln_2O_3–B_2O_3 systems.[1,2] Recently we have established the crystal structures of La_3BO_6[3] and Y_3BO_6[4] and found that the compositions of these compounds are not as simple as those proposed previously. From the single crystal structure analysis, the composition of the lanthanum compound was found to be $La_{26}(BO_3)_8O_{27}$, which shows a slight La_2O_3 excess relative to La_3BO_6. The yttrium compound $Y_{17.33}(BO_3)_4(B_2O_5)_2O_{16}$, by contrast, was found to have an excess of borate and contains both isolated borate BO_3^{3-} and polyborate $B_2O_5^{4-}$ groups in the structure. Owing to the lack of suitable single crystals, the structure model of the yttrium compound was determined by direct methods from powder diffraction data. Although the Rietveld refinement results in a fairly satisfactory residual value ($R_p = 0.06$),[4] a couple of uncertainties remain, in particular for the light elements in the structure. To further understand the crystal structure of these compounds, we report here the structural studies of the gadolinium compound by X-ray powder diffraction and high resolution TEM (HREM), as well as by IR and Raman spectroscopy. Some of the light elements in the structure, such as borate groups, have been identified from HREM and from IR and Raman spectra. A preliminary study on the luminescent properties of the europium-doped materials is also presented.

Experimental

Polycrystalline samples of the gadolinium borate $Gd_{17.33}(BO_3)_4(B_2O_5)_2O_{16}$ were synthesized using stoichoimetric Gd_2O_3 and H_3BO_3 as the starting materials. After preheating at 850 °C for 6 h, the samples were ground and reheated from 1150 to 1350 °C for 8 h in air. The Eu^{3+} doped sample (0.5 atom%) luminescent materials were prepared in a similar way using Eu_2O_3 as the doping agent.

The X-ray powder diffraction measurements were carried out on a Rigaku D/MAX-2000 diffractometer using Cu-Kα radiation from a rotational anode. The HREM image and the electron diffraction were obtained with a Hitachi H-9000 electron microscope. The IR spectrum was measured with a Nicolet Magna 750 FT-IR spectrometer. The Raman spectrum was recorded with a Nicolet FT-Raman 910 spectrometer. The photoluminescent spectra, obtained with a Hitachi M-850 fluorescent spectrophotometer, have been corrected for the energy distribution of the light source and the sensitivity of the photomultiplier. The emission spectrum under excitation by X-rays was recorded on a home made X-ray fluorescent spectrophotometer without correction.

The X-ray powder diffraction pattern of $Gd_{17.33}(BO_3)_4(B_2O_5)_2O_{16}$ was carefully collected in the 2θ range 10–110° in θ–2θ fashion and is shown in Fig. 1. Fig. 2 shows the electron diffraction pattern of $Gd_{17.33}(BO_3)_4(B_2O_5)_2O_{16}$ along the *b*-axis. Careful inspection

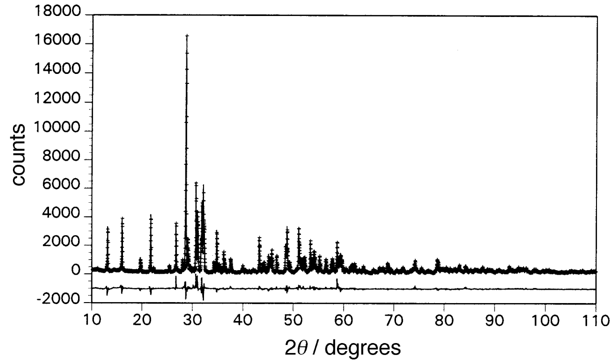

Fig. 1 Refined X-ray powder diffraction patterns of $Gd_{17.33}(BO_3)_4(B_2O_5)_2O_{16}$

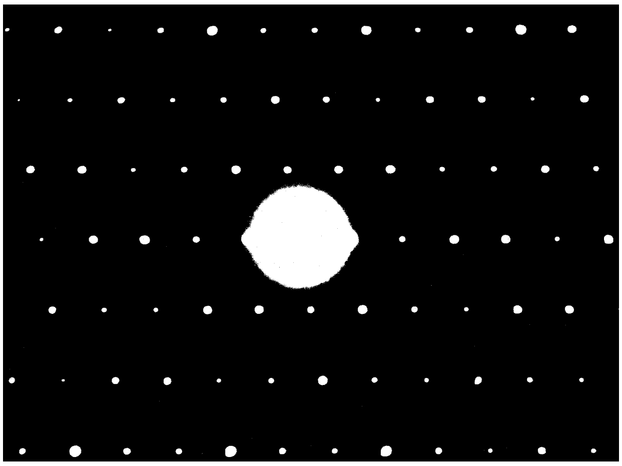

Fig. 2 Electron diffraction of $Gd_{17.33}(BO_3)_4(B_2O_5)_2O_{16}$ along the *b*-axis

of the electron diffraction and the X-ray powder diffraction pattern confirmed that the gadolinium compound crystallizes in the same structure type as the yttrium analogue.[4] The lattice constants, refined with the FINAX program, are $a=1841.70(3)$, $b=374.08(1)$, $c=1419.30(3)$ pm and $\beta=119.85(1)°$. The complete structure was refined by the Rietveld procedure with the FULLPROF program using the structure parameters of the yttrium compound $Y_{17.33}(BO_3)_4(B_2O_5)_2O_{16}$ as an initial set.[4] The boron and oxygen atoms within the borate groups have been treated with rigid body constraints throughout the refinement. Initially the occupation factors of the gadolinium atoms were fixed, but the refinement of temperature factors indicated that some of the gadolinium positions are not fully occupied. Therefore in the subsequent refinement, the occupation factors of the gadolinium atoms were refined with a constrained temperature factor. Three of the refined occupation factors are very close to unity, so they were fixed in the subsequent refinement. The occupation factors of the oxygen atoms can not be refined. From the refinement, the overall number of gadolinium atoms in the unit cell is 16.95, which is slightly lower than that required for the charge balance (17.33). The reason of this discrepancy may arise from partial occupancy of the oxygen positions or from under-estimation of the gadolinium occupancy. A similar composition has also been found in the yttrium compound $Y_{17.33}(BO_3)_4(B_2O_5)_2O_{16}$.[4] The final residues of the refinement are $R_p=0.084$, $R_{wp}=0.11$ and $R_{Bragg}=0.073$. The refined X-ray powder pattern of this compound is shown in Fig. 1. The atomic parameters of the structure are available upon request from the authors.

Results and Discussion

Structure of $Gd_{17.33}(BO_3)_4(B_2O_5)_2O_{16}$

The asymmetric unit of $Gd_{17.33}(BO_3)_4(B_2O_5)_2O_{16}$ consists of nine gadolinium, nineteen oxygen and four boron atoms. All of these atoms are located on the special Wyckoff position 2a (x, 0, z). This means that all of the atoms in the structure are located within the mirror planes at $y=0$ and 1/2. Fig. 3 shows a projection of the $Gd_{17.33}(BO_3)_4(B_2O_5)_2O_{16}$ structure along a direction close to the b-axis. In comparison with the lanthanum analogue $La_{26}(BO_3)_8O_{27}$,[3] this compound contains two different kinds of planar borate groups, *i.e.* BO_3^{3-} and $B_2O_5^{4-}$, and this leads to a more borate rich composition for $Gd_{17.33}(BO_3)_4(B_2O_5)_2O_{16}$. Table 1 lists the compositions of related compounds in terms of the $Ln_2O_3:B_2O_3$ ratio. Compared with Ln_3BO_6, the lanthanum compound contains excess La_2O_3, while an excess of B_2O_3 is present in the gadolinium compound. We have compared the X-ray powder patterns of these compounds with those of the major phases found for Ln_3BO_6 in the literature[1,2] and they are found to be identical. This means that the compound with the composition Ln_3BO_6 does not actually exist in the Ln_2O_3–B_2O_3 systems.

Table 1 Composition of related borates

compound	$La_2O_3:B_2O_3$ ratio	borate group
$La_{26}(BO_3)_8O_{27}$	3.25 : 1	isolated BO_3^{3-}
Ln_3BO_6	3.00 : 1	non existant
$Gd_{17.33}(BO_3)_4(B_2O_5)_2O_{16}$	2.17 : 1	BO_3^{3-} and $B_2O_5^{4-}$

According to the coordination environment, the nine gadolinium atoms may be divided into three categories. In Fig. 3 these three types of the coordination polyhedral are labeled A, B and C, respectively. The type A polyhedron is a monocapped octahedron, which is similar to that observed in the A-type rare earth sesquioxides Ln_2O_3.[5] Six out of the nine gadolinium atoms in the $Gd_{17.33}(BO_3)_4(B_2O_5)_2O_{16}$ structure are coordinated in this manner. The type B structure is a bicapped trigonal prism with a coordination number of eight and is shown by two gadolinium atoms. One gadolinium atom is of type C which is an irregular seven-coordinate polyhedron.

Since the unique b-axis is relatively short for this compound, the structure can be clearly visualized by high-resolution electron microscopy. Fig. 4 shows the high-resolution TEM image (HREM) of the gadolinium compound along the b-axis. Some of the atomic species can be identified by a close inspection of the HREM image and the crystal structure in Fig. 3. The largest bright points in the HREM image correspond to the $B_2O_5^{4-}$ groups and the less intense bright points correspond to the BO_3^{3-} groups. The remaining bright points can be attributed to areas between the gadolinium atoms where isolated oxygen atoms are located.

The presence of the BO_3^{3-} and $B_2O_5^{4-}$ borate groups is further supported by Raman and IR spectroscopy. Fig. 5 shows the Raman and IR spectra of the gadolinium borate at room temperature. The IR absorption and Raman peaks at wavenumbers <500 cm^{-1} originate mainly from the lattice dynamic modes, which will not be considered further. The assignment of the vibration modes for the remaining peaks is complicated by possible overlap of the different borate groups. Therefore only those vibration modes which could characterize the nature of the borate groups will be considered. The assignments of the IR and Raman peaks to the vibration modes of BO_3^{3-} and $B_2O_5^{4-}$ groups in this compound were derived by comparison with that of $LaBO_3$ and $Mg_2B_2O_5$,[6] which are listed in Table 2. There are a number of well defined peaks in the IR and Raman spectra, which we can assign. A broad IR absorption band at *ca.* 837 cm^{-1} can be assigned to a stretching mode of B–O–B in $B_2O_5^{4-}$ groups. In the Raman spectrum an isolated peak with a Raman shift of *ca.* 910 cm^{-1} is

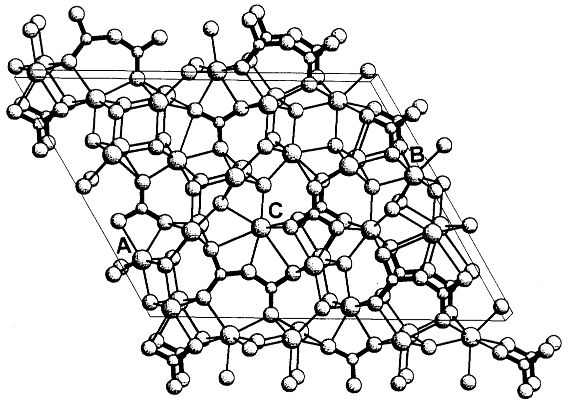

Fig. 3 A projection of the crystal structure of $Gd_{17.33}(BO_3)_4(B_2O_5)_2O_{16}$ along a direction close to b-axis

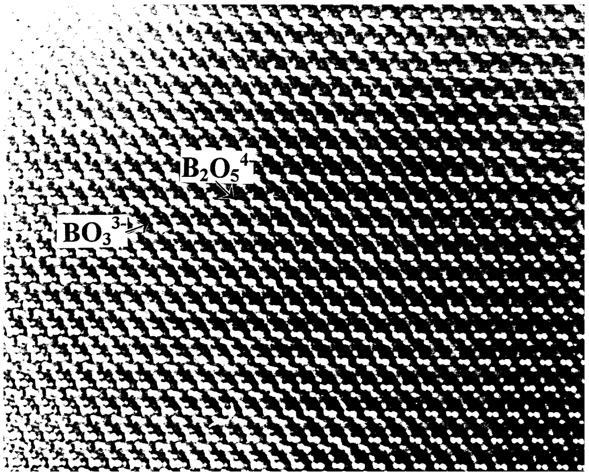

Fig. 4 HREM image of $Gd_{17.33}(BO_3)_4(B_2O_5)_2O_{16}$ along [010]

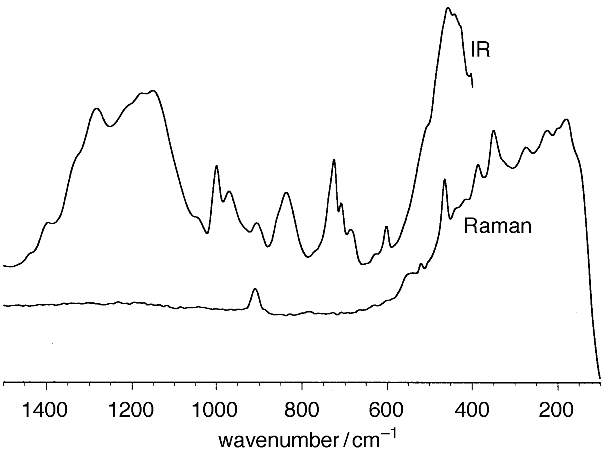

Fig. 5 IR and Raman spectra of $Gd_{17.33}(BO_3)_4(B_2O_5)_2O_{16}$

Table 2 Assignments of IR and Raman spectra for $Gd_{17.33}(BO_3)_4(B_2O_5)_2O_{16}$

IR absorption/cm^{-1}	Raman shift/cm^{-1}	possible assignment
1397		ν (BO)
1283		ν_{as} (BO_3^{3-})
1180		ν_s (BO_2)
1152		
999		ν_s (BO_2) in $B_2O_5^{4-}$
970		
906	910	ν_s (BO_3^{3-})
837		ν_s (BOB)
725		γ (BO_3^{3-}) and γ (BO_2)
709		
689		

associated with ν_s of BO_3^{3-}. These characteristic peaks in the IR and Raman spectra indicate the existence of these two borate groups in the structure.

Summarizing the structural studies, several techniques, *i.e.* Rietveld refinement of the powder diffraction pattern, HREM, IR and Raman spectra have been used in characterizing the structure of $Gd_{17.33}(BO_3)_4(B_2O_5)_2O_{16}$. Although there are still some uncertainties remaining in the structure refinement, the structural model of this compound appears to be correct. It is also worth pointing out that the structural characterization methods used in this study emphasize different parts of the structure. The Rietveld refinement of the X-ray powder diffraction is sensitive to the heavier atoms. Meanwhile, from the HREM image one can actually visualize the location of the light elements or groups. Finally the IR and Raman spectra confirm the presence of the two different borate groups in the structure.

Luminescent properties

The excitation and emission spectra of Eu^{3+} doped $Gd_{17.33}(BO_3)_4(B_2O_5)_2O_{16}$ are shown in Fig. 6. The excitation spectra consist of a broad band at *ca.* 270 nm and several sharp peaks at longer wavelength. These transitions originate from the charge transfer excitation (CT) and the excitation within the f^6 configuration respectively. The emission spectra, also shown in Fig. 6, can be attributed to the optical transitions from $^5D_0$ to ^7F_J ($J = 1$–6). It is known that $^5D_0$–$^7F_1$ and $^5D_0$–$^7F_2$, which are typical magnetic and electric dipole–dipole transitions, respectively, depend strongly on the local symmetry of the Eu^{3+} atoms. In this compound, all of the gadolinium atoms are located at mirror planes, but their coordination environments are quite different. Therefore the relative intensity of the electric and magnetic dipole–dipole transitions may vary for Eu^{3+} at different sites. It can be seen from Fig. 3 that the type A polyhedron, which is a monocapped octahedron, is the most symmetric polyhedron in this structure. The type B and C polyhedra, on the other hand, strongly deviate from central symmetry. Based on the selection rules, the magnetic dipole–dipole transition $^5D_0$–$^7F_1$ should be relatively strong for Eu^{3+} at type A sites. The electric dipole–dipole transition $^5D_0$–$^7F_2$ may predominate for Eu^{3+} at type B and C sites.

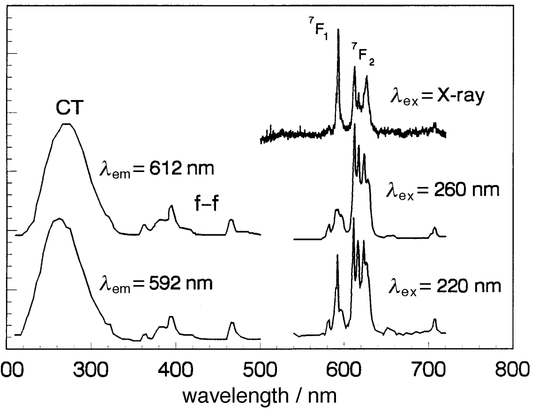

Fig. 6 Emission (right) and excitation (left) spectra of $Gd_{17.33}(BO_3)_4(B_2O_5)_2O_{16}$:$Eu^{3+}$, under different excitations; CT = charge transfer

Fig. 6 shows the excitation spectra obtained by monitoring respectively the emissions of $^5D_0$–$^7F_1$ and $^5D_0$–$^7F_2$. A small shift of the charge transfer bands (CT) can be seen. The CT band monitored by the electric dipole–dipole transition $^5D_0$–$^7F_2$ is located at longer wavelength in comparison with that of the magnetic dipole–dipole transition $^5D_0$–$^7F_1$. In the charge transfer excitation, O 2p electrons are excited into 4f levels, and the position of the CT excitation band is determined by the energy difference between the O 2p valence band and the 4f levels of Eu^{3+}. If the CT excitation can be considered as a local transition, we may use molecular orbital or cluster considerations to understand the shift of the CT bands in the excitation spectra. It is known that the 4f orbital is not involved in bonding between rare earth metals and ligands. However, the interaction between the Eu 5d and O 2p orbitals leads to bonding (2p) and anti-bonding (5d) molecular orbitals. One could, therefore, expect that the shorter the Gd—O bond, the larger the energy difference between the 4f and O 2p electrons. From the structure analysis it is known that the average Gd—O bond distance of type-A polyhedra (*ca.* 238 pm) is shorter than those of type B (250 pm) or C (263 pm), so that the CT excitation band of Eu^{3+} in type A sites should be at a higher energy than the others. This is consistent with the shift of the CT excitation bands observed. It is also expected that Eu^{3+} can be excited preferentially by different excitation sources. Fig. 6 shows the emission spectra of the Eu^{3+} in $Gd_{17.33}(BO_3)_4(B_2O_5)_2O_{16}$ excited by 220 and 260 nm UV light with an excitation bandwidth of 2 nm. The emission of $^5D_0$–$^7F_1$ is relatively weak under excitation at 260 nm and becomes stronger when excited at 220 nm. The emission spectrum under X-ray excitation shows a much stronger $^5D_0$–$^7F_1$ transition (Fig. 6), which is worth further study. It is seen that this localized picture, although maybe not very appropriate from the band-structure point of view, is helpful in understanding the CT excitation in this complicated compound.

In conclusion, the structure of $Gd_{17.33}(BO_3)_4(B_2O_5)_2O_{16}$, refined by Rietveld analysis, contains two types of borate groups, BO_3^{3-} and $B_2O_5^{4-}$, and nine gadolinium atoms. HREM, IR and Raman studies confirm the presence of two types of borate groups in the structure. The gadolinium atoms can be divided into three different types. The luminescence spectra of the Eu^{3+} doped material consist of several sharp lines originating from optical transitions within the f^6 configuration of Eu^{3+} ions at different cation sites.

The project is supported by National Natural Science Foundation of China under the contract No. 296525101.

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Paper 7/07896J; *Received* 3rd *November*, 1997