Journal of Optoelectronics and Advanced Materials Vol. 2, No. 5, 2000, p. 451-458

Section 1: Single crystal materials

CRYSTAL STRUCTURE, CRYSTAL GROWTH AND OPTICAL PROPERTIES OF PHASES IN THE TERNARY SYSTEMS Li_2O-M_2O_3-B_2O_3 (M=Ln,Y)

J. P. Chaminade, V. Jubera, A. Garcia, P. Gravereau, C. Fouassier

Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB-CNRS) [UPR 9048], Université Bordeaux I, Avenue du Dr Albert Schweitzer, 33608 Pessac Cedex (France)

Synthesis and crystal growth of pure and activated borates in the ternary phase diagram Li_2O-Ln_2O_3-B_2O_3 are described. $Li_6M_{1-x}Ce_x(BO_3)_3$ (M= Y, Gd) crystals were grown by the Czochralski technique. Single crystals obtained by the flux method allowed us to determine the crystal structure of the new oxyborates $Li_2Ln_5O_4(BO_3)_3$ with Ln = Yb-Lu and $LiLn_6O_5(BO_3)_3$ with Ln = Pr-Tm. Emission and excitation spectra, decay curves have been recorded for Ce^{3+}, Eu^{3+} and Tm^{3+} in these three types of matrices. Single crystals of $Li_6M_{1-x}Ce_x(BO_3)_3$ (M= Y, Gd) exhibit a high scintillation efficiency. An unusual red emission of Ce^{3+} has been observed in $LiY_6O_5(BO_3)_3$ compared to the blue in $Li_6Y(BO_3)_3$.. Eu^{3+}: $LiY_6O_5(BO_3)_3$. Eu^{3+}: $Li_2Yb_5O_4(BO_3)_3$ and Tm^{3+}: $LiY_6O_5(BO_3)_3$ present the color characteristics and decay time appropriate for red and blue in plasma display panels.

Keywords: Borates, Crystal structure, Crystal growth, Optical properties

1. Introduction

Borate compounds are currently very attractive for the scientific community owing to their wide range of applications [1-3]. They exhibit high transparency far in the UV, good chemical stability and for some of them crystals with high optical quality. Our interest in search of new phosphors and scintillators led us to investigate borate systems. Particularly, there is a renewed interest in improving neutron instrumentation available for existing neutron sources and for new neutron facilities in Europe and in United States.

Recently some of us have demonstrated the interest of $Li_6Ln_{1-x}Ce_x(BO_3)_3$ (*Ln*= Y, Gd) as neutron detectors [4-5]. An investigation of the Li_2O-Ln_2O_3-B_2O_3 ternary phase diagram was undertaken and led us to discover two new compositions $LiLn_6O_5(BO_3)_3$ with *Ln* = Pr-Tm [6] and $Li_2Ln_5O_4(BO_3)_3$ with *Ln* = Yb-Lu [7]. The aim of this work is to describe the synthesis, the crystal growth and the structure of $Li_6Ln_{1-x}Ce_x(BO_3)_3$ (*Ln*= Y, Gd) and of these two new borates. Their preliminary optical properties are discussed depending on the rare earth Ce^{3+}, Eu^{3+} and Tm^{3+} used as the activator.

2. Experimental

2.1 Powder preparation

The synthesis of powders was carried out by high temperature solid state reaction from the starting materials LiOH, H_2O, H_3BO_3, Ln_2O_3 (*Ln*= Gd, Y, Eu, Tm) and (or) $Ce(NO_3)_3,6H_2O$ of purity ≥ 99.99%, under controlled atmosphere (O_2, Ar or H_2 depending on the rare earth). The chemical reactions were respectively the following:

$$6LiOH,H_2O + 3H_3BO_3 + (1-x)/2\ Ln_2O_3 + xCe(NO_3)_3,6H_2O \rightarrow Li_6Ln_{(1-x)}Ce_xB_3O_9 + H_2O\uparrow + \text{nitric vapor}\uparrow$$

$5/2Ln_2O_3 + 3H_3BO_3 + 2LiOH,H_2O \rightarrow Li_2Ln_5O_4(BO_3)_3 + 15/2H_2O\uparrow$ and
$3Ln_2O_3+3H_3BO_3+LiOH,H_2O \rightarrow LiLn_6B_3O_{14}+6H_2O\uparrow$

The thermal process consists of several steps: first preheating at 400°C for 3h, and then, after grinding, a second step sintering at 750 - 900°C for 15h to 24h depending on the material composition.

In all cases the final products were controlled by X-ray powder diffraction analysis using CuKα radiation (XRD).

2.2 Crystal growth

Crystal growth of $Li_6Gd_{(1-x)}Ce_x(BO_3)_3$ and $Li_6Y_{(1-x)}Ce_x(BO_3)_3$ have been undertaken by the Czochralski method. A DTA performed on $Li_6Gd(BO_3)_3$ shows that congruent melting occurs at about 860°C with a high undercooling of about 200°C.

The pre-melted product was loaded in a conical vitreous carbon crucible of 150cm^3 and placed in a resistance furnace inside a water-cooled chamber of the pulling apparatus. The whole crystal growth assembly was first evacuated and then filled with dried and deoxygenated pure argon gas. The crucible was heated to a temperature slightly higher than the melting point until all the charge was melted and homogenized. The seed held on an alumina rod was dipped to touch the melt at a rotation rate of 5-7 pm. The typical pulling rate was 0.3-0.5mm/h with a duration of more than a week to obtain a boule of 30mm in diameter and 60mm long (Fig. 1). They sometimes show (010) facets and (10-2) cleavage planes. Details of the growth procedure will be published elsewhere [4].

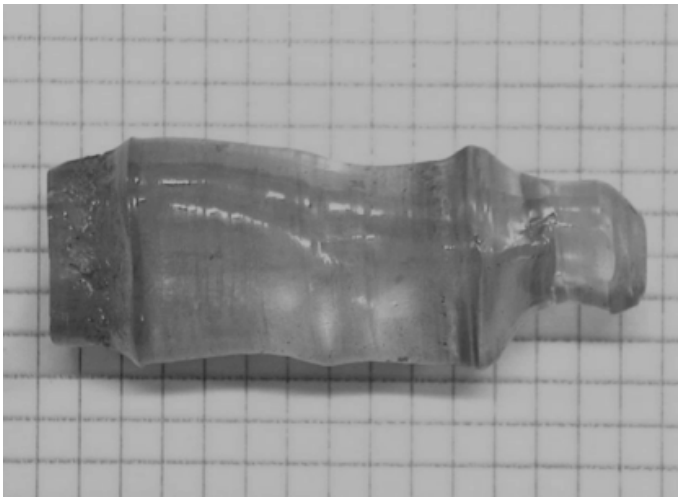

Fig. 1. As- grown single crystal of $Li_6Gd_{(1-x)}Ce_x(BO_3)_3$ (a division=5 mm).

These crystals have high-hardness, are nonhygroscopic, chemically stable and easy to polish.

Single crystals of the two oxyborates have been grown by the flux method in the Li-*Ln*-B-O system using Li_2O-B_2O_3 rich melt as $Li_2Ln_5O_4(BO_3)_3$ and $LiLn_6O_5(BO_3)_3$ do not melt congruently.

Different compositions in the ternary phase diagram were investigated. Appropriate thermal cycles were performed: - heating to 1200°C for 6h, then slowly cooling at 2°C/h to 900°C and finally at 50°C/h to room temperature in the first case, - heating to 950°C for 6h, then slowly cooling at 2°C/h to 800°C and finally at 50°C/h to room temperature in the second case.

Single crystals of $Li_2Yb_5O_4(BO_3)_3$ were selected by optical examination in the partially melted mixture, they grew as transparent colorless needles.

The $LiGd_6O_5(BO_3)_3$ crystals were recovered by leaching the flux with dilute hydrochloric acid. They grew as transparent colorless wedge-shape plates.

3. Results and discussion

3.1 Structural characteristics

$Li_6Gd(BO_3)_3$ is isostructural with $Li_6Yb(BO_3)_3$ [8] and $Li_6Ho(BO_3)_3$ [9].It crystallizes in the monoclinic system with the space group $P2_1/c$ with the refined parameters: a=7.224(3) Å, b= 16.510(5) Å, c= 6.694 (3) Å, β=105.37(5)°, Z=4.

The structure of $Li_6Gd(BO_3)_3$ can be described as made up of chains of edge-sharing GdO_8 polyhedra running along c axis connected by borate triangles and Li atoms (Fig. 2), giving rise to a chain with Gd-Gd distance of 3.84 Å. The shortest distance between two Gd^{3+} ions of parallel chains is equal to 7.15 Å, leading to a mono-dimensional character.

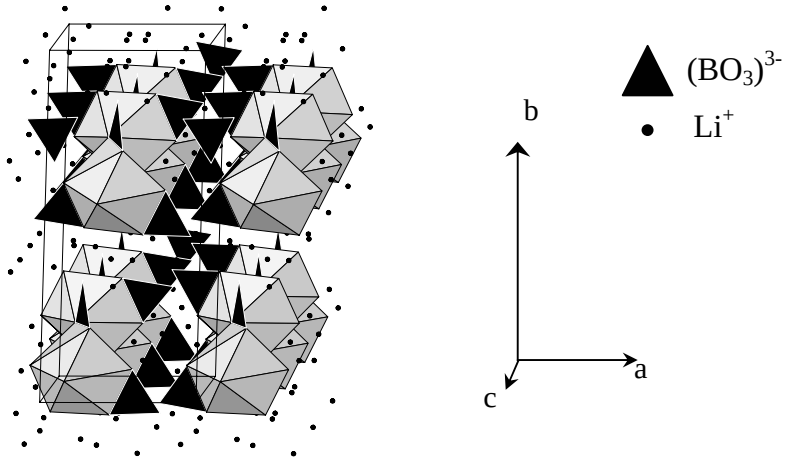

Fig. 2. Structure of $Li_6Gd(BO_3)_3$ showing the zigzag chain of Gd polyhedra.

The structure of the oxyborate $Li_2Yb_5O_4(BO_3)_3$ was solved using a data collection with a four circles automatic diffractometer (CAD-4) and with MoKα radiation. The cell is monoclinic (space group $P2_1/m$, Z= 2) with a= 10.095(2) Å, b= 3.519(2) Å, c= 15.647(11) Å, β= 105.45(3)°, V= 535.7(5) $Å^3$. Refinement of 86 parameters using 3298 independent reflections having intensity $I > 2\sigma(I)$ led to R= 0.037 (wR= 0.091) [7].

The structure of $Li_2Yb_5O_4(BO_3)_3$ can be described as a bi-dimensional framework, $(Yb_{10}O_8)_n^{14+}$ of Yb polyhedra connected by common edges and corners parallel to the (010) plane), connected by boron triangles forming cavities where are inserted Li atoms. Lithium polyhedra and borate groups constitute an $((Li_4B_6O_{18})^{14-})_n$ anionic chain developing in the b direction. Some oxygen atoms share only Yb polyhedra justifying the oxyborate label (Fig. 3).

The structure of the oxyborate $LiGd_6O_5(BO_3)_3$ was solved using a data collection with a four circles automatic diffractometer (CAD-4) and with MoKα radiation. The cell is monoclinic (space group $P2_1/c$, Z=4) with a= 8.489(4)Å, b= 15.706(3)Å, c=12.117(6)Å, β= 132.27(2)°, V=1195(1)$Å^3$. Refinement of 198 parameters using 4402 independent reflections having intensity $I > 3\sigma(I)$ led to R=0.037 (wR= 0.087)[6].

This structure can be described as a three-dimensional framework of Gd polyhedra, $(Gd_6O_{14})^{10-}$, connected by common edges and corners, forming cavities where are inserted Li and B atoms (Fig. 4).

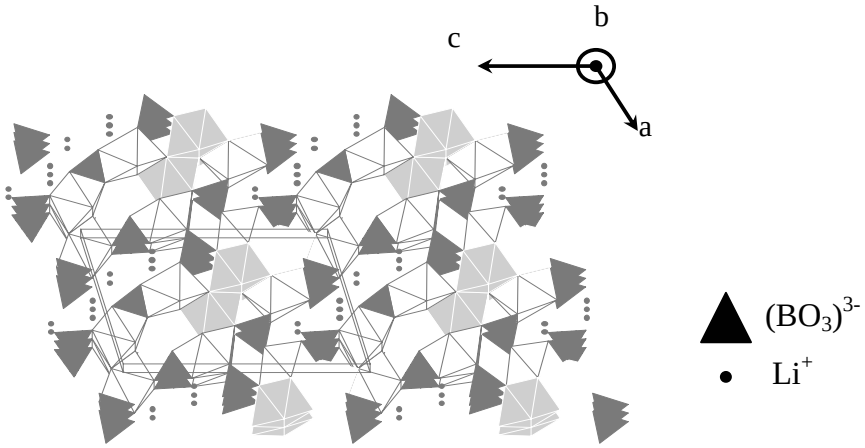

Fig. 3. Crystal structure of $Li_2Yb_5O_4(BO_3)_3$ – Projection on the (010) plane.

The gadolinium atoms occupy different coordination polyhedra in sevenfold coordination (monocapped octahedron) and eightfold coordination (highly distorted cube). The three-dimensional framework of Gd polyhedra, $(Gd_6O_{14})^{10-}$, presents a distorted fluorite-type array. 1/5 of the Gd cationic sites are vacant, forming cavities occupied by lithium and borate groups, $(Li_2B_6O_{18})^{16-}$. Some oxygen atoms share only Gd polyhedra justifying the oxyborate label.

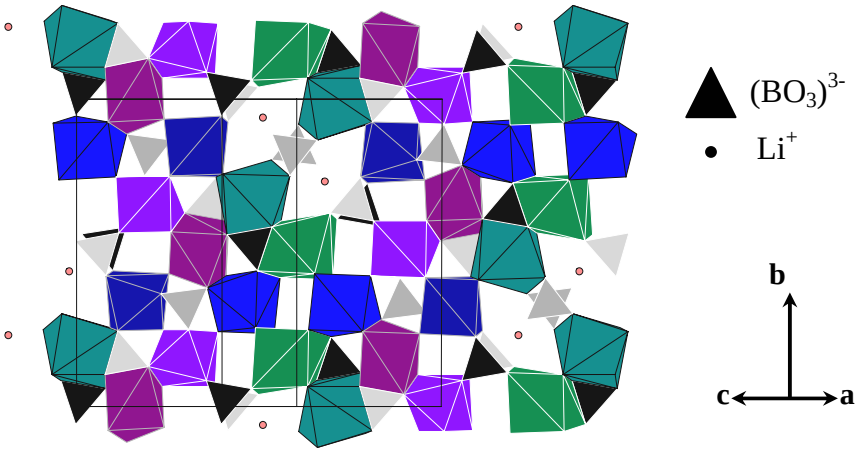

Fig. 4. Crystal structure of $LiGd_6O_5(BO_3)_3$ - Projection on the (102) plane.

Three types of lithium and rare earth borates can be encountered depending on the way of connection between the rare earth polyhedra.

-$Li_6Ln(BO_3)_3$ (*Ln*: from Nd to Yb) presents a mono-dimensional character; each *Ln* polyhedron is bounded by common edge in a single direction parallel to the c axis giving rise to a *Ln-Ln* chain with *Ln-Ln* distance of 3.84 Å. The shortest distance between two *Ln-Ln* chains is equal to 7.15 Å (case of *Ln*= Gd).

- a second arrangement appears in $Li_2Yb_5O_4(BO_3)_3$ with independent thick layers of ytterbium polyhedra with a quasi bi-dimensional character (Yb-Yb distances: from 3.42 Å to 3.73 Å in a layer and from 4.56 Å to 7.37 Å between consecutive layers).

-$LiLn_6O_5(BO_3)_3$ (*Ln*: from Pr to Tm) presents a tri-dimensional array of *Ln* polyhedra, which can be related to that of the fluorite CaF_2 (Gd-Gd distances range from 3.62 Å to 3.98 Å in the (ac) plane and from 3.56 Å to 4.27 Å in the (102) plane).

3.2 Optical properties

Here are summarized the principal optical properties of these borates activated by trivalent europium, thulium and cerium ions. The purpose of this work was twofold: search of new phosphors under U.V. and V.U.V. excitation and search of new efficient scintillators and especially neutron detectors as studied matrices contain both lithium and boron, elements which present the highest neutron capture reaction energies.

Eu^{3+}-activated oxides and borates are well known as efficient phosphors under U.V. and V.U.V. excitation. Eu^{3+} can be also used to confirm a local environment of the rare earth. The number of lines corresponding to the $^5D_0$-$^7F_0$ transition indicates the number of sites occupied by the rare earth.

Low temperature studies (10K) confirmed the existence of different crystallographic sites for each phase. For instance, six independent sites were identified by selective excitation for Eu^{3+}-$LiY_6O_5(BO_3)_3$ in agreement with the crystallographic data.

Emission spectra were recorded for excitation in the charge transfer band at 250 nm for Eu^{3+}-$Li_6Y(BO_3)_3$, Eu^{3+}-$LiY_6O_5(BO_3)_3$ and Eu^{3+}-$Li_2Lu_5O_4(BO_3)_3$ (Fig. 5a, 5b, 5c). This band corresponds to an electron transfer from the oxygen 2p orbital to the 4f empty orbital of the rare earth. The maximum of the emission comes from the $^5D_0$-$^7F_2$ electric dipole transitions, which confirms the low symmetry of the rare earth environments. The calculated color coordinates correspond to a deep red color. Decay times are shorter (respectively 2.15 ms, 1.38 ms and 2.88 ms) than that of Eu: (Y, Gd)BO_3 for which $^5D_0$-$^7F_1$ magnetic dipole transitions (~3.5 ms) are predominant.

Trivalent thulium activated compounds have been studied in order to find a blue phosphor showing good characteristics for use in P.D.P..

The position of the charge transfer band is at low enough energy to favor the energy transfer from the charge transfer state to the $^1D_2$ excited level of thulium in the Tm^{3+}-$Li_6Y(BO_3)_3$, Tm^{3+}-$LiY_6O_5(BO_3)_3$ phases (Fig. 5a´, 5b´). Consequently the most intense lines observed in emission spectra correspond to the $^1D_2$-$^3F_4$ transitions which are located at about 450 nm in the blue. Up to now, the experimental equipment did not permit to study the emission spectrum of Tm^{3+}-$Li_2Lu_5O_4(BO_3)_3$ in the same conditions. V.U.V. excitation is necessary.

Decay times of the blue emission are about tens of μs (8 μs for Tm^{3+}-$LiY_6O_5(BO_3)_3$). The color coordinates are close to characteristics required for use in P.D.P.

One of the requirements demanded for scintillator is a short decay time. Concerning the luminescent center, it is well known that spin-allowed and electric dipole allowed $4f^n - 5d^14f^{n-1}$ transitions of rare earths have a decay time of 10-70 ns depending on the emission. Trivalent cerium exhibits this fast luminescence and consequently the study of these borates as host lattice has been considered.

More than one absorption band are detected in the excitation and absorption spectra of the cerium activated $Li_6Y(BO_3)_3$ and $LiY_6O_5(BO_3)_3$. They are due to the crystal field splitting of the 5d (^2D) excited state of trivalent cerium (Fig. 6a).

The Ce^{3+}-$Li_6Y(BO_3)_3$ borate presents a band located at 390 nm for an excitation at 300 nm in an cerium absorption band (Fig. 6b). At low temperature two emission maxima can clearly be distinguished at 380 nm and 410 nm with a splitting of 2000 cm^{-1} corresponding to the transition from the lower 5d state to the spin-orbit components $^2F_{5/2}$ and $^2F_{7/2}$ of the ground state. The Stokes shift which corresponds to the energy difference between the maximum of the emission and its excitation band is equal to 3800 cm^{-1}.The decay time of the emission corresponds to a fully allowed transition (29 ns). The color coordinates indicate that the emission is violet.

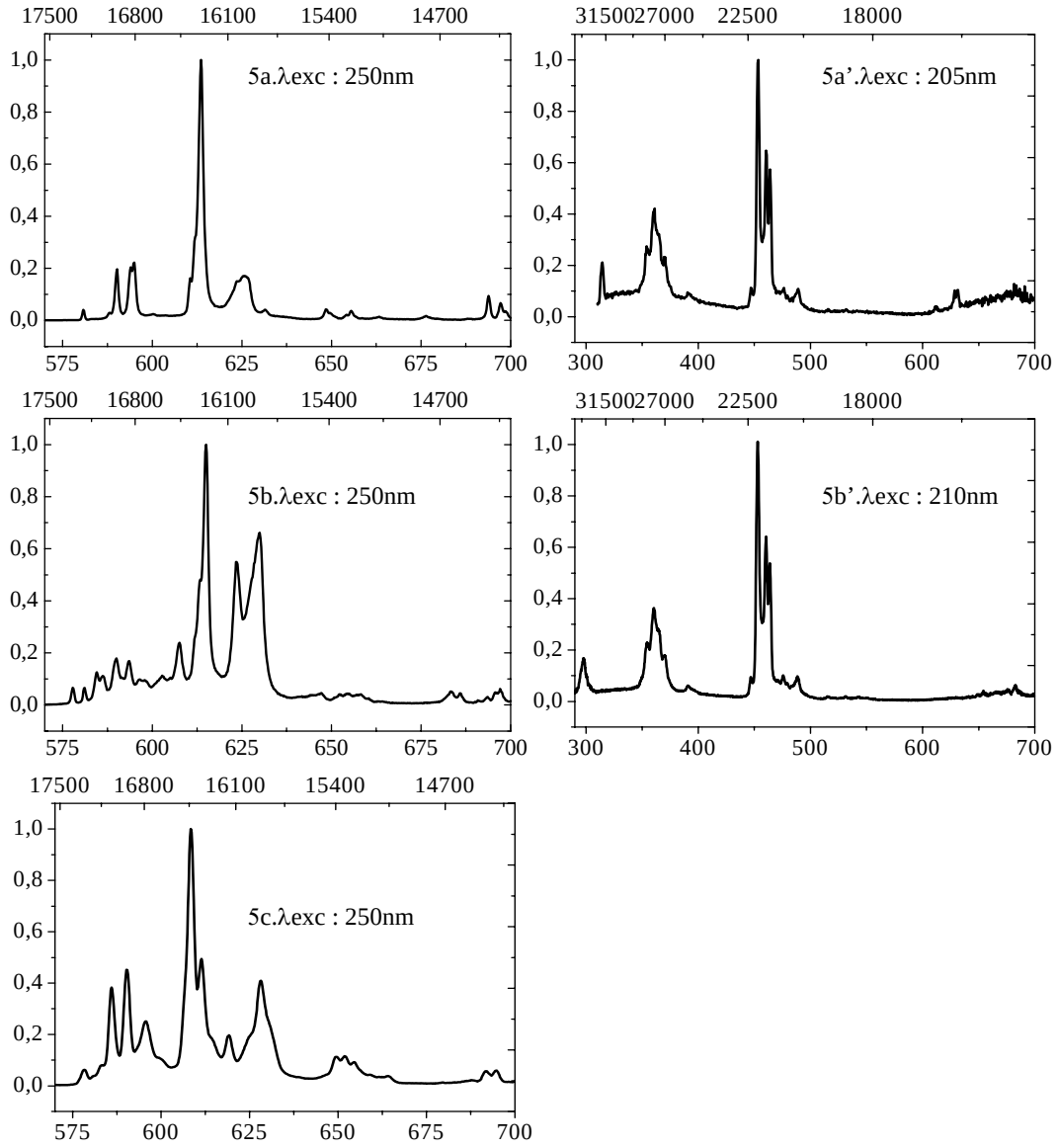

Fig. 5. Emission spectra. x axis in cm^{-1} top, x axis in nm bottom, y axis a.u. 5a.Eu^{3+}-$Li_6Y(BO_3)_3$, 5a'. Tm^{3+}-$Li_6Y(BO_3)_3$, 5b. Eu^{3+}-$LiY_6O_5(BO_3)_3$, 5b'. Tm^{3+}-$LiY_6O_5(BO_3)_3$, 5c. Eu^{3+}-$Li_2Y_5O_4(BO_3)_3$.

The Ce^{3+}-$Li_6Gd(BO_3)_3$ excitation and emission spectra look very similar. Nevertheless as the Gd^{3+} emission at 313nm lies near the maximun of a 4f-5d Ce^{3+} transition an excitation of the Gd^{3+} sublattice leads to an efficient energy transfer to Ce^{3+}, effect which is enhanced by the mono-dimensional character of the structure (linear zigzag chains of rare earth polyhedra).

Scintillation properties were performed by irradiation with a ^{241}Am source at MSI Photogenics [4-5]. The energy released in the lattice by particles resulting from the neutron capture is transferred to Ce^{3+} ions, which emit this energy radiatively at 390 nm. The Gd borate and the Y borate respectively exhibited scintillation efficiency 6 times and 1.3 times that of the Li –glass actually used as detector. As discussed before, the Gd borate enhances the energy transfer to Ce^{3+} ions.

The emission of Ce^{3+}: $LiY_6O_5(BO_3)_3$ at room temperature is totally quenched. But a decrease in temperature to 6K revealed a strong band centered at 610nm in the red for an excitation at 370nm (Fig. 6b). The Stokes Shift is about 10000 cm^{-1}. In view of this peculiar behavior, it may be wondered

whether this emission is really due to trivalent cerium centers. But several reasons seem to confirm this hypothesis.

The two components of the trivalent cerium can be distinguished by de-convolution at 650 nm (15380 cm^{-1}) and 565 nm (17665 cm^{-1}). They are separated by 2300 cm^{-1}. The decay time of this emission is equal to 32ns which corresponds to an allowed 5d→4f transition.

All the syntheses were performed under pure hydrogen atmosphere, which is required for the stabilization of cerium at the 3+ oxidation state. In order to control the Ce^{3+} state, syntheses have been done under nitrogen and oxygen atmospheres. Only a pure hydrogen atmosphere seems to be able to reduce cerium to the trivalent state: diffuse reflection spectra did not reveal the different absorption bands of trivalent cerium for synthesis under inert or oxidizing atmosphere.

The E.P.R. measurements confirmed these results; only the H_2 prepared compounds present several peaks corresponding to the fingerprint of trivalent cerium.

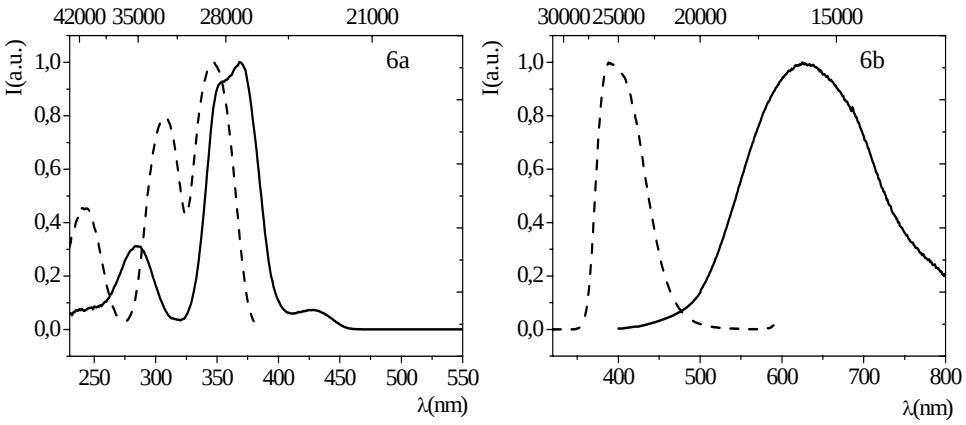

Fig. 6. Excitation spectra. x axis in cm^{-1} top, x axis in nm bottom, y axis a.u. 6a.Ce^{3+}-$Li_6Y(BO_3)_3$ (dot line) λem : 400nm, T : 300K ; Ce^{3+}-$LiY_6O_5(BO_3)_3$ (full line) λem : 630nm, T : 10K Emission spectra; 6b.Ce^{3+}-$Li_6Y(BO_3)_3$ (dot line) λexc : 300nm, T : 300K ; Ce^{3+}-$LiY_6O_5(BO_3)_3$ (full line) λexc : 385nm, T : 10K

4. Conclusions

We have performed the synthesis and crystal growth of borates belonging to the ternary phase diagrams Li_2O-B_2O_3-Ln_2O_3. The complete crystal structure of two new borates has been established: $Li_2Ln_5O_4(BO_3)_3$ for the ytterbium compound and $LiLn_6O_5(BO_3)_3$ for the gadolinium compound. These two new borates families can be labeled oxyborates as they contain oxygen atoms only bounded to the rare earth atom. The former is characterized by a bi-dimensional framework of edge and corner-sharing LnO_7 polyhedra, the second by a three dimensional array of seven and eight coordinated *Ln* atom. The third phase $Li_6Ln(BO_3)_3$, which is an orthoborate, exhibits chains of edge sharing LnO_8 polyhedra. In all structures boron triangles and lithium polyhedra insured the connection between the *Ln* array.

The crystal growth conditions of the $Li_6Ln(BO_3)_3$ material activated with Ce^{3+} for *Ln*= Gd and Y by the Czochralski method have been specified. Monocrystalline boules of dimensions up to 3 cm diameter, 6 cm long were prepared.

The first optical studies have been undertaken with the Eu^{3+}, Tm^{3+} and Ce^{3+} ions as activators in the three types of borates.

For Eu^{3+}-$Li_6Y(BO_3)_3$, Eu^{3+}-$LiY_6O_5(BO_3)_3$ and Eu^{3+}-$Li_2Lu_5O_4(BO_3)_3$, the maximum of the emission comes from the $^5D_0$-$^7F_2$ electric dipole transitions which confirmed the low symmetry of the rare earth environments. The calculated trichromatic coordinates indicate a deep red color. Decay times are respectively 2.15 ms, 1.38 ms and 2.88 ms.

For Tm^{3+}-$Li_6Y(BO_3)_3$ and Tm^{3+}-$LiY_6O_5(BO_3)_3$ phases the maximum observed in emission spectra corresponds to the $^1D_2$-$^3F_4$ transitions which are located at about 450 nm in the blue. Decays times of the blue emission are about tens of μs (8μs for Tm^{3+}-$LiY_6O_5(BO_3)_3$).

The color coordinates are close to characteristics required for use in P.D.P.'s.

The Ce^{3+}-$Li_6Y(BO_3)_3$ or Ce^{3+}-$Li_6Gd(BO_3)_3$ borates present a band located at 390 nm for an excitation at 300nm in a cerium absorption band. The decay times of the emission correspond to a fully allowed transition (about 28-30 ns). These borates present a high scintillation efficiency as much as six times that of Li-glass scintillators for the Gd material. Moreover interest of such scintillators is the ability to tailor their response to the neutron spectrum by varying the isotopic composition of the starting elements (Li, Gd (Y), B).

An unusual red luminescence at low temperature for Ce^{3+}: $LiY_6O_5(BO_3)_3$ is observed. Its origin was clearly demonstrated. It seems to be a particular behavior of Ce^{3+} in oxyborate compounds whereas in orthoborates Ce^{3+} exhibits a strong emission in the 350-420 nm domain.

References

[1] D. A. Keszler, Current Opinion in Solid State and Materials Science **1**, 204 (1996).
[2] P. Becker, Adv. Mater **10**, 979 (1998).
[3] M. Knitel, "New Inorganic Scintillators and Storage Phosphors for Detection of Thermal Neutrons", Delft University Press, Delft (1998).
[4] J. P. Chaminade, O. Viraphong, F. Guillen, C. Fouassier, B. Czirr, IEEE Transactions on Nuclear Science (submitted.).
[5] J. B.Czirr, G. M. MacGillivray, R. R. MacGillivray, P. J. Seddon, Nuclear Instruments and Methods in Physic Research **A424**, 15 (1999).
[6] J. P. Chaminade, P. Gravereau, V. Jubera, C. Fouassier, J. Solid State Chem. **146**, 189 (1999).
[7] V. Jubera, P. Gravereau, J. P. Chaminade, C. Fouassier, J. Solid State Chem. (submitted).
[8] G. K. Abdullaev, K. S. Mamedov, Sov. Phys. Crystallogr. **22**(2), 220 (1977).
[9] G. K. Abdullaev, K. S. Mamedov, P. F. Rza-Zade, S. A. Guseinova, G. G. Dzhafarov, Russian J. Inorg. Chem. **22**(12),1765 (1977).