Orthoborates processed by soft routes: correlation luminescence structure

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Abstract

YBO_3 and H–Ln BO_3 (Ln=La, Nd, Sm, and Eu) orthoborates have been prepared by an original sol–gel mineral process. This synthesis method over solid state reaction offers the possibility of obtaining high quality materials at low temperatures, without parasitic phases. Luminescent europium ions have been used as structural probes to investigate these orthoborate phases. Due to the purities of the different powders the symmetries of the europium ion in the different matrices have been determined unambiguously and a comparison between the luminescence results and the structural descriptions given in the literature has been realized. © 2001 Published by Elsevier Science B.V.

Keywords: Sol–gel; Borate; Luminescence; Structure; Rare-earth

1. Introduction

Over the last few years, intensive research has been devoted to the realisation of efficient luminescent materials due to the versatility of their applications in the field of the fluorescent lamps, display devices, detector system represented by X-ray screens and scintillators of phosphor marking. The borates have proved to be potential candidates for the aforementioned applications.

The present tendency of development of such materials is not oriented especially towards new phases but mostly towards a better knowledge and a better control of the microstructures and resulting optical properties of existing materials.

Among the parameters, which govern the luminescence efficiency, the method of preparation of these materials has been shown by experience, to be the most significant and important. It is well established that wet processes such as sol–gel mineral, offer the possibility in comparison with solid state reactions of obtaining high quality materials without parasitic phases [1,2].

YBO_3 and H–LnBO_3 (Ln=La, Nd, Sm and Eu) have been prepared by a mineral sol–gel technique and the thermal domain of stability of these orthoborates versus sintering temperature and the rare earth ionic radius, have been reinvestigated.

Luminescent europium ion has been used as a structural probe to investigate these orthoborate phases. Due to the

high quality of the samples prepared by the mineral sol–gel process, the site symmetries of the europium ions in the different matrices have been determined unambiguously and a comparison between luminescent results and the structural descriptions given in the literature have been made.

2. Synthesis

Orthoborate phases have been prepared by a mineral sol–gel method developed in our laboratory [2]. This synthesis route can be described briefly as follows: the first step reaction consists of the preparation of a gel from lanthanide nitrate, boric acid in addition to an ammonia solution. After heat treatment, the gel yields the desired borate as a powder. We have shown that parameters such as the Y/B ratio (not necessarily the stoichiometric one), pH and of course the temperature, all govern the purity of the final compounds. Table 1 gives the values of the Y/B ratio, pH and temperature determined for the different phases.

Table 1
Y/B ratio and pH to yield to pure YBO_3 and H–LnBO_3 phases

	pH	B/Ln
H–LaBO_3	8	1
H–NdBO_3	8	1
H–SmBO_3	8	1
H–EuBO_3	7	1
YBO_3	7	1.2

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3. Characterisation

X-ray diffraction (XRD), high temperature XRD, thermal characterisation and infra-red spectroscopy (IRS) have been used to confirm the purity and the high quality of the powdered orthoborates prepared by this mineral sol–gel route.

Analysis of the room temperature XRD powder patterns was carried out for the borate samples prepared by the sol–gel mineral process and classical solid state reaction. The stability of the $LnBO_3$ and $H-LnBO_3$ borates versus the temperature and synthesis method were established by recording the room temperature XRD spectra after heating the sample for 4 h at a given temperature [3]. The results obtained can be described briefly as follows:

- $H-NdBO_3$ borate prepared by solid state reaction has been obtained for a temperature higher than 1300°C.
- Similar observations have been made for europium and samarium orthoborates where only the vaterite phase appears above 750°C.
- In the case of the neodymium and lanthanum samples, the simultaneous presence of the phases $H-LnBO_3$, Ln_2O_3 and $LnBO_3$ is identified for a temperature lower than 750°C, while by the sol–gel mineral process, pure $H-LnBO_3$ orthoborates have been observed, below 650, 700, 800 and 900°C for Ln corresponding to La, Nd, Sm, and Eu, respectively. Concerning the YBO_3 orthoborate, both techniques yield to the vaterite form.

IR spectroscopy was carried out with the objective of specifying the coordination of boron in the YBO_3 and $H-LnBO_3$ orthoborates. It has been already established that the BO_3^{3-} anions are in the form of an equilateral triangle with boron in the center in the $H-EuBO_3$ phases [4]. In this description two types of BO_3 groups have been identified with B–O distances slightly different, while only one BO_3 group exists in the description of the $H-LaBO_3$ structure [5]. For the vaterite YBO_3, boron ions are in 4-fold coordination with two types of BO_4 groups [6].

4. Optical results

The global time resolved emission spectra (TRS) shown in Fig. 1 were recorded at 14 K for Eu^{3+} doped $H-LaBO_3$, $H-EuBO_3$ and YBO_3 samples under excitation in the $^5D_2$ level of Eu^{3+}. For all the samples, the emission from the $^5D_0$ level of Eu^{3+} is efficient, whereas emission from the higher excited ^5D_J levels is quenched via a multiphonon process associated with the borate groups. In $H-LaBO_3$ and $H-EuBO_3$, the electric dipole $^5D_0 \rightarrow ^7F_2$ electronic transition is more intense than the magnetic dipole $^5D_0 \rightarrow ^7F_1$ magnetic transition, while an opposite observation is made for the Eu doped YBO_3 borate. So, due to these spectral distributions, Eu doped $H-LaBO_3$ and $H-$

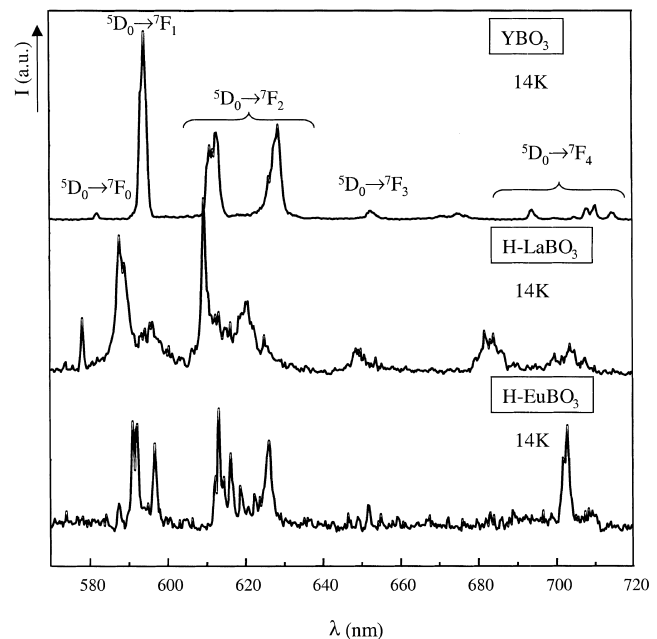Fig. 1. Global time resolved emission spectra recorded at 14 K for Eu^{3+} doped $H-LaBO_3$, $H-EuBO_3$ and YBO_3 orthoborates under excitation in the $^5D_2$ level of Eu^{3+}.

$EuBO_3$ exhibit a red fluorescence while Eu doped YBO_3 gives an orange emission. For the three matrices, the $^7F_0 \rightarrow ^5D_0$ excitation spectrum obtained by monitoring characteristic $^5D_0 \rightarrow ^7F_1$ transitions, is displayed in Fig. 2. The $H-LaBO_3$ (Fig. 2a) and $H-EuBO_3$ (Fig. 2b) spectra consist respectively of one and two peaks indicating the presence of a single site for Eu^{3+} in lanthanum orthoborate and of two local sites for europium ions in $H-EuBO_3$. Moreover, the numbering of the optical transitions $^5D_0 \rightarrow ^7F_J$ (J varying from 0 to 2) is in agreement with one site of C_3 symmetry for $H-LaBO_3$ and with two sites of C_1 symmetry for $H-EuBO_3$.

The revision of the crystal structure of $H-EuBO_3$ to the $P\bar{1}$ space group, proposed recently in the literature [4] indicates two types of europium polyhedra EuO_8 in $H-EuBO_3$. The general position of europium ions is in agreement with a C_1 symmetry in excellent correlation with optical results. For $H-LaBO_3$, the luminescence results indicate that the splittings for the J manifolds for Eu^{3+} ions in this matrix are 1, 2 and 3 for $J=0$, 1 and 2, respectively. According to Böhlhoff [5], $H-LaBO_3$ crystallizes in the monoclinic system with $P2_1/m$ as the space group, showing unique C_S point symmetry for the rare earth. The optical results show clearly the disagreement with the given structure description since 1, 3, and 5 transitions are expected in a C_S symmetry.

Recently, the vaterite form of orthoborate has been described in a rhombohedral subcell by analysis of electron diffraction patterns of the isostructural vaterite $GdBO_3$. The deviated results have been applied to the yttrium orthoborate. In this description, the yttrium ion occupies a

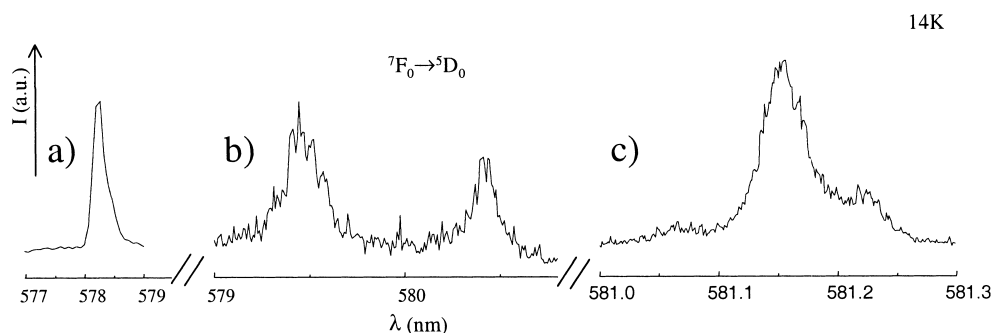Fig. 2. $^5F_0 \rightarrow ^5D_0$ excitation spectrum obtained by monitoring characteristic $^5D_0 \rightarrow ^7F_1$ transitions (a) for H–LaBO$_3$, (b) for H–EuBO$_3$ and (c) for YBO$_3$.

single site with C_1 symmetry. This structural description is clearly in disagreement with optical results where three sites have been identified. It appears unambiguously that this structural description cannot revise the hexagonal structural description [7] which is in excellent agreement with optical results, where three sites, all in C_3 symmetry, have been described for the yttrium ion in the hexagonal structural description (Fig. 2c).

5. Conclusion

YBO$_3$ and H–LnBO$_3$ (Ln=La, Nd, Sm, and Eu) activated by Eu^{3+} have been prepared by using a convenient alternative route, the sol–gel mineral method. The advantages of the sol–gel mineral process over the solid state reaction include lower temperature processing, higher sample homogeneity and purity. Thanks to these last properties, it has been possible to identify, unambiguously, the symmetry site of the trivalent rare-earth by using europium ion as a structural probe. For H–EuBO$_3$ and YBO$_3$ orthoborates, we have shown that there is a good correlation between the structural description and the

optical results. In the case of H–LaBO$_3$ the site symmetries determined by the study of the emission spectra show a disagreement with the structural description found in the literature [5]. For this reason, we have undertaken the structural redetermination on a single crystal grown by the flux method.

References

[1] D. Boyer, G. Bertrand-Chadeyron, R. Mahiou, C. Caperaa, J.C. Cousseins, J. Mater. Chem. 9 (1999) 211.
[2] G. Chadeyron, A. Arbus, M.T. Fournier, D. Zambon, J.C. Cousseins, C.R. Acad. Sci. Paris 320 (1995) 199.
[3] S. Lemanceau, G. Bertrand-Chadeyron, R. Mahiou, M. El-Ghozzi, J.C. Cousseins, P. Conflant, R.N. Vannier, J. Solid State Chem. 148 (1999) 229.
[4] C. Corbel, M. Leblanc, E. Antic Fidancev, M. Lemaître-Blaise, J.C. Krupa, J. Alloys Comp. 287 (1999) 71.
[5] R. Böhlhoof, H.U. Bambauer, W. Haffman, Z. Kristallogr. 133 (1971) 386.
[6] R. Ren, J.H. Lin, Y. Dong, L.Q. Yang, M.Z. Su, Chem. Mater. 11 (1999) 1576.
[7] C. Chadeyron, M. El-Ghozzi, R. Mahiou, A. Arbus, J.C. Cousseins, J. Solid State Chem. 128 (1997) 261.