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$SrB_4O_7:Sm^{2+}$: crystal chemistry, Czochralski growth and optical hole burning

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The crystal chemistry of the Sm^{3+} to Sm^{2+} reduction in tetraborate lattices was investigated. In crystalline SrB_4O_7 in air it is mainly Sm^{2+} that is incorporated from a melt or glass containing predominantly Sm^{3+}. For the process in air, a reduction and pick-up mechanism is assumed to take place at the crystal/nutrient interface. Stabilization of Sm^{2+} in SrB_4O_7 at high temperature and in an oxidizing atmosphere seems to be a particular property of the system, because no Sm^{2+} inclusion could be observed along the series MB_4O_7 (M = Ca, Ba, Cd, Pb), if similar reaction conditions were applied. So far, there is only one other oxide lattice (BaB_8O_{13}) known where at high temperatures significant amounts of Sm^{2+} are obtained for reactions in the air.

Single crystals of $SrB_4O_7:Sm^{2+}$ were grown by the Czochralski method (k_{eff} for Sm is 0.5). Optical hole burning experiments for the transition $^5D_1$–$^7F_0$ were performed at 80 K. A hole with a width of 0.21 cm^{-1} and a depth of 5.25% was formed for the first time for Sm^{2+} in a borate crystal excited by the beam of a single frequency dye laser. A rather small inhomogeneous linewidth of 0.28 cm^{-1} allowed the burning of a single hole only.

Introduction

In solids, some of the lanthanide (Ln) ions can be present in their divalent, trivalent or even tetravalent state. Luminescence from Ln^{2+} ions in crystals, ceramics and glasses has attracted much attention over the last fifteen years.[1] The most studied divalent lanthanide species are Eu^{2+}, Yb^{2+} and Sm^{2+}, with Sm being the most difficult for stabilizing the 2+ state in solids.[2] The most commonly used reducing atmospheres are H_2–N_2, or H_2–Ar gas mixtures. Strontium tetraborate is a suitable host lattice to accommodate divalent lanthanide ions, Eu^{2+},[3] Sm^{2+},[4] Yb^{2+},[5] including Tm^{2+},[6] Bi^{2+},[7] and Nd^{2+},[1] on the Sr^{2+} site. Recently, the preparation of ceramic $SrB_4O_7:Ln^{2+}$ ($Ln^{2+} = Eu^{2+}$, Yb^{2+}, Sm^{2+}) without any notable reducing agent was reported.[8] The solid state reaction was simply performed in *air*. So far, there is only one other example (ceramic $BaB_8O_{13}:Sm^{2+}$)[9] where a quantitative valence change from Sm^{3+} to Sm^{2+} could be achieved in air, in an *oxide lattice* and at *high temperature*.

In a more general context, borate materials represent an important class in nonlinear optics.[10] The acentric crystal structure of SrB_4O_7 shows a wide range of transparency from 130 nm to 3200 nm.[11] Single crystals of SrB_4O_7 have been investigated for their electro-optic properties by Bohatý *et al.*[12] SrB_4O_7 crystallizes in the orthorhombic space group $P2_1nm$, the structure consists of an unusual type of borate framework, which is assumed to be a prerequisite for stabilizing Sm^{2+} in an oxygen environment.[8] The compound was reported to be the first example of an anhydrous borate featuring only tedrahedrally coordinated boron in which all the boron and oxygen atoms are involved in the borate network. Although the tetrahedra form a three-dimensional network, by corner sharing, the borate network has the appearance of a layer-like structure because there are comparatively few links in the *c*-direction. The layers can be described in terms of chains (parallel to the *a*-axis) of six-membered rings having B–O edges in common. Furthermore, the network generates channels parallel to the *b*-axis. The Sr ions fit into these channels (Fig. 1a). Another unusual structural feature is the occurrence of an oxygen atom coordinated to *three* boron atoms. These triple-coordinated oxygen atoms are located in the second coordination sphere of the Sr atom at a distance of 3.04–3.2 Å. There are nine nearest-neighbor oxygen atoms surrounding the Sr^{2+}, at distances ranging from 2.52 to 2.82 Å, providing C_s site symmetry (Fig. 1b).[13] The size of the divalent lanthanide dopants is much more suitable than the size of these ions in the trivalent state for a substitution of Sr^{2+}. From what is known, it is thought that the lattice of SrB_4O_7 does not provide an evident charge compensation mechanism, which is necessary for a substantial substitution of Sr^{2+} by trivalent lanthanide ions.

Sm^{2+} is an interesting ion for the investigation of optical hole burning[14–18] and laser properties.[19,20] A known mechanism of spectral hole burning occurs in two steps: first, absorption of a photon at the wavelength of the spectral hole and second, photoionization.[21–24] SrB_4O_7 represents a new material for the investigation of optical hole burning of Sm^{2+} in an *oxide* lattice.

In this study we discuss solid-state reactions of Sm-doped SrB_4O_7 and other members of the tetraborate composition: MB_4O_7 (M = Ca, Ba, Cd, Pb). The $SrB_4O_7:Sm$ crystals were grown by the Czochralski method for both the spectroscopy and optical hole burning experiments. A hole with a maximum depth of 5.25% and a linewidth of 0.21 cm^{-1} could be burned in the $^5D_1$–$^7F_0$ transition at 80 K. We also have performed experiments to elucidate a possible mechanism for the reduction of Sm^{3+} to Sm^{2+} during the process of crystal growth of SrB_4O_7.

Experimental

Ceramic samples and glasses

Ceramic samples of $SrB_4O_7:Sm^{2+}$ were prepared by solid-state reactions in air. Stoichiometric amounts of $SrCO_3$ and H_3BO_3, including 1 mol% excess of H_3BO_3 to compensate for

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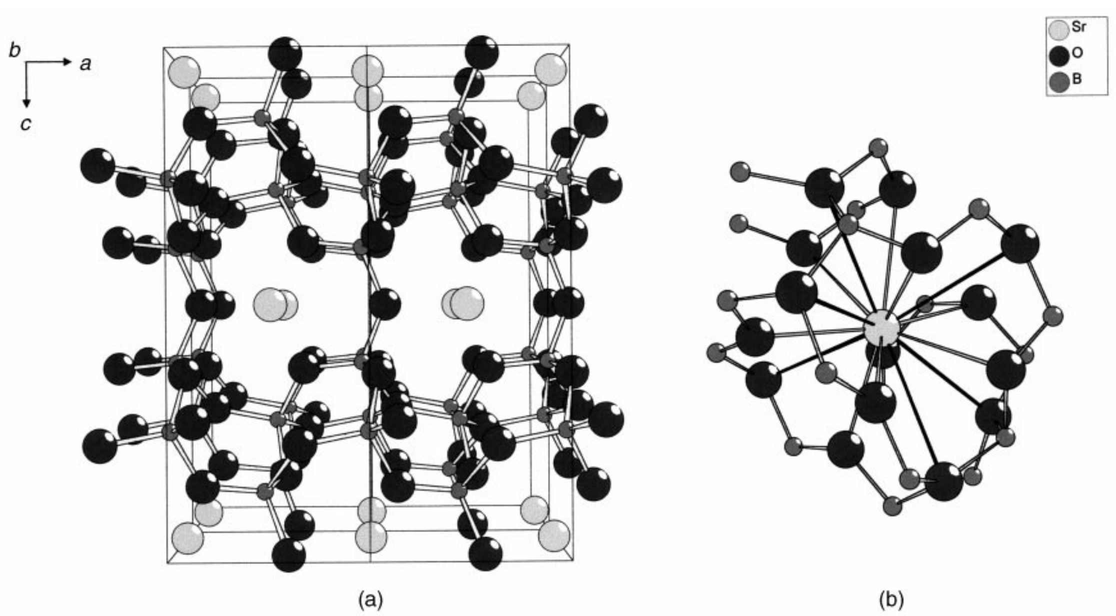

Fig. 1 (a) Structure of SrB_4O_7 showing the boron–oxygen network. (b) First and second coordination sphere of the Sr^{2+} site in SrB_4O_7. The black bonds are drawn from Sr to oxygen atoms of the second coordination sphere and the grey lines correspond to bonds to the oxygen within the first coordination sphere. Note that the oxygens of the second coordination sphere (dark) are coordinated to three boron atoms.

the B_2O_3 evaporation, were mixed and ground. The mixtures were heated at 700 °C in either a corundum, porcelain or platinum crucible for 5 h to effect the removal of CO_2. A second annealing step was necessary at 850 °C in order to accomplish the reactions (followed by powder X-ray measurements). To this 0.5 mol% Sm_2O_3 was added and the mixtures were heated a third time up to 850 °C for another 5 h.[8] All these steps were carried out in air. Following this procedure, the fluorescence spectrum of ceramic $SrB_4O_7:Sm$ (Fig. 2) showed the emission lines of Sm^{2+} (300 K), even with excitation at 403 nm, which is the best wavelength for the excitation of Sm^{3+} (Fig. 3); the luminescence intensity ratio between Sm^{2+} and Sm^{3+} can differ with respect to the excitation wavelength.

Glasses were prepared from ceramic $SrB_4O_7:Sm^{2+}$ by superheating the sample up to 1080 °C in air, Ar or H_2–Ar. The melt was kept at this temperature for 30 min, followed by cooling to room temperature in 15 min. All the glasses produced under different atmospheres showed the emission lines of the transitions $^4G_{5/2}$–$^6H_{5/2,7/2,9/2,11/2}$ attributed to *trivalent* samarium. The ^5D_J–^7F_J transitions of divalent samarium could be obtained at 80 K, however, at low intensity (Fig. 4). The linewidths of the transitions ^5D_J–^7F_J described in the literature for glasses[25–27] are much broader than in our case: the linewidth of Sm^{2+} in the glassy phase is in the same range as that obtained for crystals. The narrow fluorescence lines of Sm^{2+} may indicate that it is embedded in microcrystallites present in the glassy phase. The lack of sharp diffraction patterns in the X-ray powder diffraction analysis of the glass confirms that the crystals that are possibly incorporated are very small (< 1 μm). In contrast, the intense and broad bands of the $^4G_{5/2}$–^6H_J transitions support the idea that Sm^{3+} is surrounded by a glassy matrix.

Due to the intensity ratio of $Sm^{2+}:Sm^{3+}$, as found in crystals, we conclude that a valence change from divalent to trivalent samarium obviously took place *during the phase change into the liquid/glassy state*. In the liquid phase, the trivalent state seems to be more stable. Surprisingly, even a glass made by melting materials under a H_2 atmosphere featured mostly *trivalent* samarium, according to the absorption spectrum.[26] However, recrystallization of such a borate

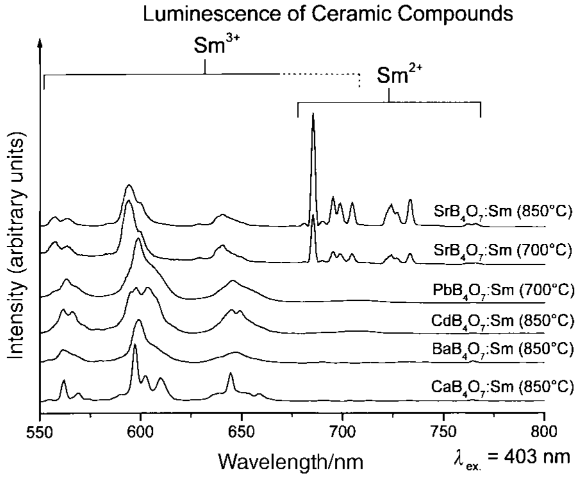

Fig. 2 Fluorescence spectra at 300 K of ceramic samples of $CaB_4O_7:Sm^{3+}$, $BaB_4O_7:Sm^{3+}$, $PbB_4O_7:Sm^{3+}$, $CdB_4O_7:Sm^{3+}$ and $SrB_4O_7:Sm^{3+/2+}$ (the annealing temperatures are given in brackets). $\lambda_{ex}=403$ nm is suitable for excitation of Sm^{3+} (*cf.* Fig. 3).

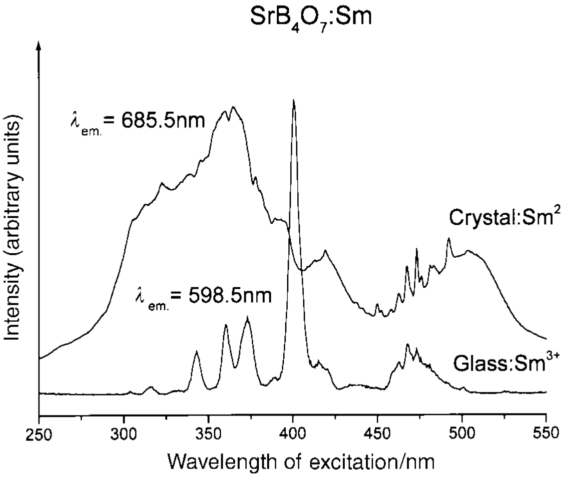

Fig. 3 Excitation spectra (300 K) of: (i) Sm^{3+} in a glassy state of SrB_4O_7, and (ii) Sm^{2+} in crystalline SrB_4O_7. $\lambda_{em}=598.5$ nm for Sm^{3+}, and $\lambda_{em}=685.5$ nm for Sm^{2+}.

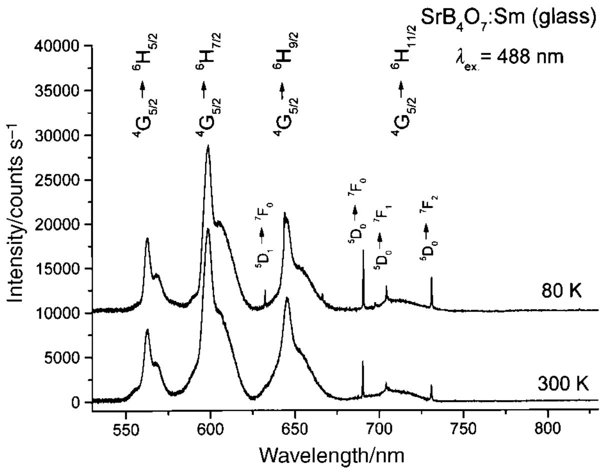

Fig. 4 Fluorescence spectra of Sm in a glassy state of SrB_4O_7 at 80 K and at 300 K. The broad band $^4G_{5/2}$–^6H_J transitions belong to trivalent samarium and the narrow lines can be attributed to the ^5D_J–^7F_J transitions of divalent samarium in microcrystals of SrB_4O_7.

glass in air at 850 °C induced a valence change mostly into the *divalent* state of Sm.

Due to the spectra (Figs. 4 and 5, traced at an excitation wavelength of 488 nm, which is a suitable excitation for Sm^{2+} and Sm^{3+}, see also Fig. 3), we assume that in the glassy phase of SrB_4O_7 (Fig. 4) Sm^{3+} exists predominantly and in the crystalline state mainly Sm^{2+} (Fig. 5). There is another report on spectroscopic properties, where we have elaborated a method to distinguish between Sm^{3+} and Sm^{2+}.[28]

Looking at the phenomena as reported, we have investigated other members of the tetraborate composition MB_4O_7 (M = Ca, Ba, Cd, Pb) in order to elucidate a possible redox mechanism. Fig. 2 shows the fluorescence spectra of the MB_4O_7 : Sm (M = Ca, Sr, Ba, Cd, Pb) series: in the case of the Ca-, Ba-, Cd-, Pb-tetraborate compounds, lines of Sm^{3+} are dominating the spectra at 300 K. Also there is no evidence for detectable *divalent* samarium by using another excitation wavelength, such as 367 nm, which preferentially excites Sm^{2+}.

Therefore, ceramic samples support a particular stabilization of Sm^{2+} *in the lattice of* SrB_4O_7. All other compounds providing the stoichiometry of MB_4O_7 (some of them featuring different crystalline structures) indicate no valence change of the trivalent samarium when conditions similar to those for the synthesis of SrB_4O_7 were applied. This is particularly unusual with respect to PbB_4O_7, because the lead compound shows the same crystal structure as strontium tetraborate. For substitution by Sm^{2+} (1.32 Å; CN: 9), the size of the Pb^{2+} site (1.35 Å; CN: 9) should almost be as suitable as the one given by Sr^{2+} (1.31 Å; CN: 9). However, there is the effect of the lone pair of Pb^{2+}. A valence change from trivalent to divalent samarium may not arise along the series MB_4O_7 (M = Ca, Ba, Cd), because of the size of the M^{2+} being different from Sr^{2+}. Other aspects may be related to the local coordination polyhedron and due to differences in the structural details.

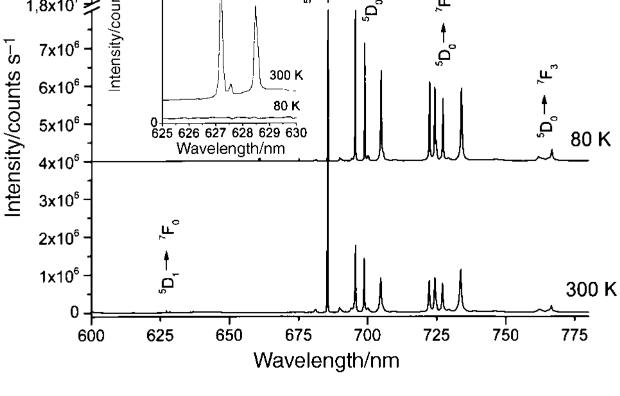

Fig. 5 Fluorescence spectra of Sm^{2+} in crystalline SrB_4O_7 at 80 K and 300 K. Inset: a zoom into the region of the $^5D_1$–$^7F_0$ transition.

Czochralski growth of SrB_4O_7 : Sm^{2+} and a possible reduction mechanism for Sm^{3+} to Sm^{2+}

Strontium tetraborate crystals can be grown from the melt by the Czochralski method due to congruent melting of $SrO{\cdot}2B_2O_3$ at a temperature of 970 °C.[29] The starting material resulted from ceramic synthesis, as described above. An excess of typically 2 mol% B_2O_3 was necessary to compensate for the vapor loss during growth experiments using a Pt crucible. Spontaneous nucleation was initiated on a tapered Ir-wire. Nucleation was not possible in cases of large deviation from the stoichiometric composition of the melt. In order to minimize the losses of B_2O_3, an insulation lid (mullite) was placed about 25 mm above the top of the crucible. A charge proved to be useful for one run of growth only. The high viscosity of the melt and a tendency to form a glass required a slow pulling rate of $0.2\ \mathrm{mm\ h^{-1}}$. The best results were achieved by using a [001] seed. A rotation rate of 20–25 rpm was applied. The concentration of Sm given in the melt as Sm_2O_3 was varied from 0.05 to 0.12 mol%, referring to the SrO concentration. Although it was known that in the glassy phase mainly Sm^{3+} (Figs. 3, 4) was present, surprisingly, crystals growing from the melt contained predominantly Sm^{2+} (Figs. 3, 5).

We suggest the following equilibrium reactions to be responsible for Sm^{2+} found in the crystal of SrB_4O_7:

$$2Sm^{3+}(m) + 3O^{2-}(m) \rightleftharpoons 2Sm^{2+}(m) + 2O^{2-}(m) + 0.5O_2(g) \quad (1)$$

$$Sm^{2+}(m) \rightleftharpoons Sm^{2+}(c) \quad (2)$$

where (c) means crystalline SrB_4O_7 and (m) stands for the melt or the glass of SrB_4O_7. Equilibrium eqn. (1) is hence influenced by the partial pressure of O_2. From the luminescence spectra (Fig. 4), we know that the concentration of Sm^{2+} is very small in the glassy phase (or in the melt), indicating that at temperatures around 1000 °C the equilibrium in eqn. (1) is in favor of Sm^{3+}. For the equilibrium eqn. (2) we assume a reaction at the crystal/liquid interface. It is probable that the strong preference for Sm^{2+} to enter the Sr^{2+} site of SrB_4O_7 is the driving force for the reduction process described above. In the case of other lattices, a H_2 atmosphere was necessary to promote incorporation of Sm^{2+} (eqn. (1)).

Another reduction mechanism, including the formation of peroxide or superoxide, may be possible as well. In the literature, the formation of a $Nd_2O_2(O)_2$(III) oxide peroxide is reported.[30] In the lattice of B_2O_3 a significant change in the coordination of boron from trigonal to tetrahedral coordination is known from the literature for the incorporation of hydroxy groups.[31] However, experiments to find which would support peroxide or superoxide formation resulted with no success. EPR experiments were performed on single crystals, and the glass and ceramic samples between RT and 4.2 K. One crystal was examined after X-ray irradiation (40 kV, 30 mA, 1.5 h). No signal pertaining to O_2^- was observed within the detection limit of 0.5 ppm (with respect to Sr^{2+}). Thermogravimetry (TG) provided no evidence for a significant solid state/gas equilibrium; the TG data did not indicate a mass change that would accord with superoxide or peroxide entering or leaving the lattice during heating up to 950 °C, at $5\ ^\circ\mathrm{C\ min^{-1}}$, followed by cooling to room temperature at the same rate. FT-IR showed no signals which unambiguously could be attributed to peroxide or superoxide bonds. Therefore, we assume that a possible reduction of Sm^{3+} to Sm^{2+} follows eqns. (1) and (2) without substantial contribution of a peroxide or superoxide formation.

Characterization and optical properties

Distribution coefficients, k_{eff}

The total samarium concentration was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis. For the ICP analyses, small pieces of crystals were dissolved in HNO_3 (0.7 mol). Solutions of Sm_2O_3 in HNO_3 (0.7 mol) were used for calibration. The Sm-doping concentration and the distribution coefficients $k_{eff} = c_{crystal}/c_{melt}$ measured for different Sm amounts added to the melt are shown in Table 1. An average for k_{eff} of 0.5 was calculated.

Optical properties and hole burning experiments

For excitation, an Ar-laser with an output of 6 W at 488 nm (20492 cm^{-1}) was used. Relatively sharp fluorescence lines were observed around 685 nm (14600 cm^{-1}), 699 nm (14300 cm^{-1}), 727 nm (13750 cm^{-1}), and 766 nm (13050 cm^{-1}), which can be attributed to the $^5D_0$–$^7F_{0,1,2,3}$ transitions of the Sm^{2+} ion. The $^5D_0$–$^7F_1$ transition is split into three distinct lines; being in agreement with the splitting of the $^7F_1$ level into a maximum of three levels for C_s symmetry.[26] The emission from the $^5D_1$ level is almost completely suppressed at 80 K (Fig. 5) as described in the literature.[32] The emission spectra at 80 K and 300 K are shown in Fig. 5.

An excitation spectrum obtained at 80 K of the $^5D_1$–$^7F_0$ transition is shown in Fig. 6. Optical hole burning was performed at 80 K into the $^5D_1$–$^7F_0$ band at 628.677 nm (Fig. 7). A 100 mW laser beam focused to a diameter of about 300 µm and a typical exposure time of 60 s were used. Hole formation was detected in the excitation spectrum by monitoring the fluorescence of the $^5D_0$–$^7F_2$ line around 727 nm. A single hole with a maximum depth of 5.25% could be burned. The hole was fitted to a Lorentzian curve yielding a full-width at half maximum (FWHM) of 6.2 GHz (0.21 cm^{-1}).

For a comparison of different hole burning materials, the ratio of the inhomogeneous width (Γ_{ih}) over the homogeneous width (Γ_h) is an important figure of merit. The inhomogeneous linewidth (8.5 GHz corresponds to 0.28 cm^{-1}) of the $^5D_1$–$^7F_0$ transition used for hole burning in SrB_4O_7 was much smaller than those of borate (96 cm^{-1})[27]or silicate glasses (100 cm^{-1}).[33] The inhomogeneous width was almost independent of temperature in the range 80–300 K.[33] Mixed crystals of the PbFCl-type family (composition: $Sr_yBa_{1-y}FCl_xBr_{1-x}$) showed an inhomogeneous linewidth of 39 cm^{-1}.[24] In lattices providing less disorder, such as SrFCl, a smaller Γ_{ih} of 2.07 cm^{-1} was reported for room temperature.[34] The small inhomogeneous linewidth of strontium tetraborate may be due to the well formed three-dimensional network of SrB_4O_7, providing a small distribution of ligand field variation for Sm^{2+} ions. The width of the hole at 80 K for the $^5D_1$–$^7F_0$ transition in SrB_4O_7 crystals was of a smaller value, as found at 80 K in borate and silicate glasses (≈ 3 cm^{-1})[33,35] or for crystals of $SrFCl_{1/2}Br_{1/2}$ at room temperature (3.5 cm^{-1}).[23] The narrow width of the inhomogeneous line of the $^5D_1$–$^7F_0$ transition of Sm^{2+} in SrB_4O_7 is assumed to be responsible for the fact that only one hole could be burned.

Table 1 Concentration of Sm in mol% and k_{eff} for different SrB_4O_7 crystals measured by the ICP method (the mol% correspond to the Sr^{2+} ions in the melt or in the crystal)

Melt (mol%)	Crystal (mol%)	Effective distribution coefficient k_{eff}
0.115	0.055	0.48
0.095	0.045	0.47
0.046	0.023	0.5

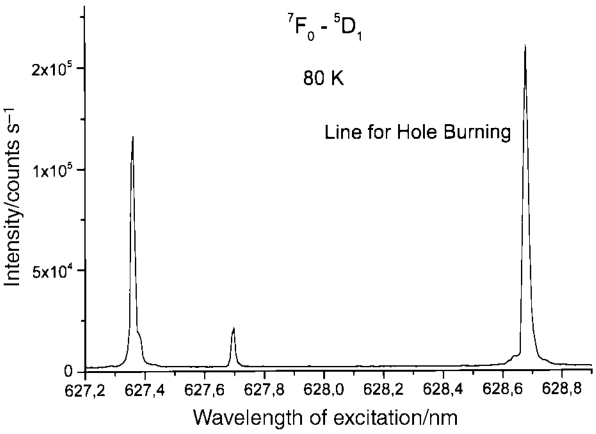

Fig. 6 Excitation spectrum of the $^7F_0$–$^5D_1$ transition at 80 K.

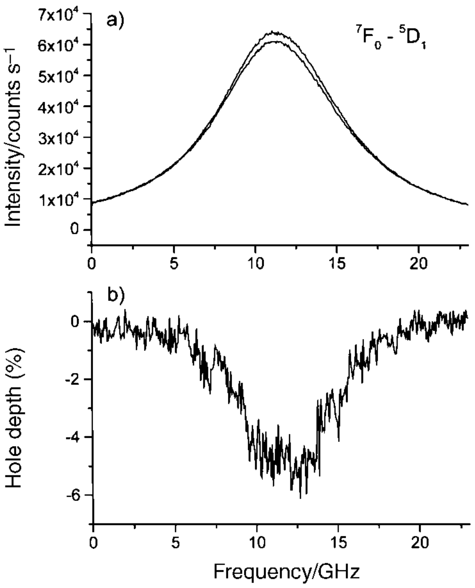

Fig. 7 (a) Excitation spectra of the $^7F_0$–$^5D_1$ transition at 628.677 nm at 80 K before and after 1 min of hole burning with a laser power of 100 mW. (b) Difference signal of the two curves in (a) resulting in a hole depth of 5.25% and a FWHM of 6.2 GHz (0.21 cm^{-1}).

Summary and conclusions

In this work we report on the preparation and crystal growth of $SrB_4O_7:Sm^{2+}$ in air. In the melt, predominantly Sm^{3+} could be traced, meaning that during the process of crystallization a valence change from the trivalent to the divalent state of samarium takes place. The lattice of SrB_4O_7 provides so far a rare example of a system where a valence change of Sm^{3+} to Sm^{2+} can occur without any notable reducing agent. A distribution coefficient k_{eff} of 0.5 for Sm makes it evident that Sm^{2+} is entering SrB_4O_7 quite easily. Hole burning experiments were performed for the $^5D_1$–$^7F_0$ transition (80 K), showing an inhomogeneous linewidth of 0.28 cm^{-1}. A hole width of 0.21 cm^{-1} was obtained. The ratio (Γ_{ih}) : (Γ_h) may be increased by disordering the structure. Disorder seems possible by the formation of mixed crystals, *e.g.*, $Sr_{1-x}Ca_xB_4O_7$.[36] Due to the broad absorption bands of the 4f–5d transition and the intense narrow luminescence lines of the $^5D_0$–^7F_J transitions, investigations of the laser properties of $SrB_4O_7:Sm^{2+}$ are similarly of interest.

Recently, optical hole burning was performed for another oxide crystal, namely, $Sr_2MgSi_2O_7:Sm$. However, only traces of Sm^{2+} could be included into this lattice.[37]

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References

1 W. Xu and J. R. Peterson, *J. Alloys Compd.*, 1997, **249**, 213.
2 P. Mikhail and J. Hulliger, *Comments Inorg. Chem.*, 1999, **21**, 263.
3 A. Meijerink, J. Nuyten and G. Blasse, *J. Lumin.*, 1989, **44**, 19.
4 A. Lacam and G. Chateau, *J. Appl. Phys.*, 1989, **66**, 366.
5 G. Blasse, G. J. Dirksen and A. Meijerink, *Chem. Phys. Lett.*, 1990, **167**, 41.
6 W. J. Schipper, A. Meijerink and G. Blasse, *J. Lumin.*, 1994, **62**, 55.
7 G. Blasse, A. Meijerink, M. Nomes and J. Zuidema, *J. Phys. Chem. Solids*, 1994, **55**, 171.
8 Z. Pei, Q. Su and J. Zhang, *J. Alloys Compd.*, 1993, **198**, 51.
9 Q. Zeng, Z. Pei, Q. Su and S. Lu, *J. Lumin.*, 1999, **82**, 241.
10 P. Becker, *Adv. Mater.*, 1998, **10**, 979.
11 Y. S. Oseledchik, A. L. Prosvirnin, A. I. Pisarevskiy, V. V. Starshenko, V. V. Osadchuk, S. P. Belokrys, N. V. Svitanko, A. S. Korol, S. A. Krikunov and A. F. Selevich, *Opt. Mater.*, 1995, **4**, 669.
12 L. Bohatý, J. Liebertz and S. Stähr, *Z. Kristallogr.*, 1985, **172**, 135.
13 A. Perloff and S. Block, *Acta Crystallogr.*, 1966, **20**, 274.
14 K. Holliday and U. P. Wild, in *Molecular Luminescence Spectroscopy, Chem. Anal. Ser.*, ed. S. G. Schulman, Wiley, New York, 1993, Vol. 77, p. 149.
15 K. K. Rebane and L. A. Rebane, in *Persistent Spectral Hole-Burning: Science and Applications*, ed. W. E. Moerner, Springer-Verlag, Berlin, 1988, Sect. 2.8.
16 R. M. Macfarlane and R. M. Shelby, in *Spectroscopy of Solids Containing Rare Earth Ions*, eds. A. A. Kaplyanskii and R. M. Macfarlane, Elsevier Science Publishers B.V., Amsterdam, 1987, p. 51.
17 O. Sild, in *Zero-Phonon Lines and Spectral Hole Burning in Spectroscopy and Photochemistry*, eds. O. Sild and K. Haller, Springer-Verlag, Berlin, 1988.
18 A. Renn and U. P. Wild, *Appl. Opt.*, 1987, **26**, 4040.
19 P. P. Sorokin and M. J. Stevenson, *IBM J. Res. Develop.*, 1961, **5**, 56.
20 P. P. Sorokin, M. J. Stevenson, J. R. Lankard and G. D. Pettit, *Phys. Rev.*, 1962, **127**, 503.
21 A. Winnacker, R. M. Shelby and R. M. Macfarlane, *Opt. Lett.*, 1985, **10**, 350.
22 C. Wei, K. Holliday, A. J. Meixner, M. Croci and U. P. Wild, *J. Lumin.*, 1991, **50**, 89.
23 R. Jaaniso and H. Bill, *Europhys. Lett.*, 1991, **16**, 569.
24 H. Bill, R. Jaaniso, H. Hagemann, D. Lovy, A. Monnier and M. Schnieper, *Opt. Eng.*, 1995, **34**, 2333.
25 D. H. Cho, K. Hirao, K. Tanaka and N. Soga, *J. Lumin.*, 1996, **68**, 171.
26 J. W. M. Verwey, G. J. Dirksen and G. Blasse, *J. Phys. Chem. Solids*, 1992, **53**, 367.
27 K. Hirao, S. Todoroki, D. H. Cho and N. Soga, *Opt. Lett.*, 1993, **18**, 1586.
28 P. Mikhail, J. Hulliger and K. Ramseyer, *Solid State Commun.*, 1999, **112**, 483.
29 Y. S. Oseledchik, A. L. Prosvirnin, V. V. Starshenko, V. V. Osadchuk, A. I. Pisarevsky, S. P. Belokrys, A. S. Korol, N. V. Svitanko, A. F. Selevich and S. A. Krikunov, *J. Cryst. Growth*, 1994, **135**, 373.
30 K. J. Range, M. Stadler, F. Rau and U. Klement, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 1174.
31 D. B. Dingwell, M. Pichavant and F. Holtz, in *Boron: Mineralogy, Petrology and Geochemistry*, ed. E. S. Grew and L. M. Anovitz, The Mineralogical Society of America, Washington D.C., 1996, Vol. 33, p. 331.
32 G. H. Dieke, in *Spectra and Energy Levels of Rare Earth Ions in Crystals*, ed. H. M. Crosswhite and H. Crosswhite, Interscience Publishers, New York, 1968, p. 182.
33 M. Nogami and Y. Abe, *SPIE - Int. Soc. Opt. Eng.*, 1997, **3136**, 239.
34 R. Jaaniso, H. Hagemann, F. Kubel and H. Bill, *Chimia*, 1992, **46**, 133.
35 K. Hirao, *J. Non-Cryst. Solids*, 1996, **196**, 16.
36 R. Jaaniso, H. Hagemann and H. Bill, *J. Chem. Phys.*, 1994, **101**, 10323.
37 P. Mikhail, M. Schnieper, H. Bill and J. Hulliger, *Phys. Status Solidi B*, 1999, **215**(2), R17.

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