Different incorporation of Cu$^+$ and Cu$^{2+}$ in lithium tetraborate single crystals

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Abstract. The incorporation site of Cu in the scintillator and thermoluminescent dosimeter material lithium tetraborate Li$_2$B$_4$O$_7$:Cu has been shown to depend on the charge state of the dopant. As confirmed by a refined analysis, the EPR spectra of an unpaired hole can be ascribed to Cu$^{2+}$ situated near the Li lattice site with C$_1$ symmetry, in contrast to the higher (C$_2$) overall symmetry reported earlier for Cu$^+$ in its relaxed excited state, the latter suggesting interstitial incorporation for the monovalent dopant. Consequences for charge transfer processes involving copper ions are discussed.

1. Introduction

The acousto- and optoelectronic material lithium tetraborate (Li$_2$B$_4$O$_7$) owes its remarkable properties to its low-symmetry crystal structure (space group I$_4$1cd belonging to the point group C$_{4v}$) and the related large polarizability of its lattice. The Li$^+$ ions are accommodated at general positions with no symmetry (C$_1$) and stabilize the =B-O-B= covalent network consisting of a frame of alternating oxygen bonded BO$_4$ and BO$_3$ oxyanions [1] (see figure 1). The basic structural unit of the network is a cradle-like B$_4$O$_7$ group. Similarly to other borates Li$_2$B$_4$O$_7$ is transparent also in the ultraviolet (UV) up to 160 nm, which is useful for non-linear optical applications based on higher harmonics. Appropriately doped Li$_2$B$_4$O$_7$ is also a scintillator suited for neutron detection; stable intrinsic defects introduced by neutron irradiation have been characterised by EPR [2, 3].

If activated by small amounts of Cu, Li$_2$B$_4$O$_7$ can be used as a tissue-equivalent thermoluminescent (TL) dosimeter; outstanding sensitivities exceeding that of the well-known LiF:Mg,Ti phosphor (TLD-100) can be achieved if Cu is used together with co-dopants like Ag and P [4, 5]. Recent studies on Li$_2$B$_4$O$_7$:Cu single crystals indicate that Cu is present in two charge states. Cu$^{2+}$, traceable by EPR, is incorporated at a site with C$_1$ symmetry which may be a strongly relaxed Li site [6], while the non-paramagnetic Cu$^+$ charge state, detectable due to its UV-induced luminescence, displays higher, apparently C$_2$ overall symmetry, in its dynamic excited state [7]. As further EPR studies, showing also regular saturation behaviour, exclude a similar dynamic configuration for Cu$^{2+}$, further attempts to understand the relation between both charge states and their incorporation in the lattice have been undertaken. The results have recently been summarized in Ref. [8]. Here the main points stressing the difference between the sites in question will be discussed concerning also the consequences for charge trapping at copper ions, which in turn may lead to a better understanding of the TL mechanisms.
2. Ground state properties of Cu$^{2+}$ derived from EPR measurements

Our earlier EPR investigations on copper doped lithium tetrahaborate [6, 8] showed that the principal directions of the $g$-tensor (see table 1) and the Cu$^{63}$ hyperfine tensor practically coincide as expected for a well-localized 3$d^9$ single-hole type state of Cu$^{2+}$ ions. All principal axes (shown in figure 2) form large angles with the single $C_2$ symmetry axis of the lattice. The main (third) principal axis corresponding to the smallest $g$-value ($g_3$) and the largest HF splitting is nearly parallel to a [110] type direction of the lattice. As the minimal $g$-value tends to discern a direction where a pair of nearest oxygen neighbours with Cu-O distances near 2 Å are located (compare Cu$^{2+}$ and isoelectronic Ni$^{2+}$ ions in other oxides like LiNbO$_3$ [9] or PbWO$_4$ [10]), the only straightforward choice for the dopant’s location in its divalent state is a more or less displaced Li site. As shown by a calculation assuming a displacement of only the dopant ion, a relaxation (indicated in figure 2) of the Cu$^{2+}$ ion from the Li site roughly towards the midpoint of the nearest oxygen neighbours 1 and 2 in fact may result in a configuration explaining all main features of the spin Hamiltonian tensors [8] (for more detail see table 2). It should be noted that such a relaxation qualitatively improves the agreement: while the $g_3$ direction is essentially given by the line connecting oxygen neighbours 1 and 2, the principal direction corresponding to the second $g$-eigenvalue ($g_2$) tends to be defined by the next nearest oxygen neighbour which is no more oxygen No. 3 but No. 6 (see figure 2). The directions in question show an agreement (compare tables 1 and 2) which can be considered as remarkable taking into account that no local adjustment of the covalently bound $\equiv\text{B-O-B}\equiv$ frame has been assumed. No other site for the
Figure 2. Projection along a [110] type axis, showing Cu\(^+\) at an interstitial position and Cu\(^{2+}\) substituted at a Li site with possible relaxation indicated by an arrow. The nearest oxygen neighbours of the chosen Li site are numbered 1-6; the principal directions of the Cu\(^{2+}\) g tensor given in Table 1 are also indicated. Note that the main principal axis is nearly perpendicular to the plane of the projection.

Cu\(^{2+}\) ion, and in particular no other pair of potential first-neighbour oxygens, with the properties required for reproducing the EPR results even approximately, can be found in the Li\(_2\)B\(_4\)O\(_7\) lattice.

It should be pointed out that on the basis of the EPR data presently no conclusion about the presence and location of local charge compensator(s) can be made, the simplest assumption being a Li vacancy at one of the two nearest neighbour Li sites (appearing as the closest Li neighbours also on the projection shown in figure 2). However, the EPR spectra belong to a well-defined species, either locally charge-compensated, or not.
Table 1. Principal values and eigenvector coordinates of the $g$ tensor [8].

| $g$ tensor | 2.515 ± 0.013 | 2.220 ± 0.010 | 2.0265 ± 0.0010 |
|------------|----------------|----------------|------------------|
|            | 0.423          | 0.551          | -0.720           |
|            | 0.389          | 0.606          | 0.693            |
|            | 0.818          | -0.573         | 0.042            |

Table 2. Distances and position vectors of the six nearest oxygen neighbours with respect to a Li$^+$ site [1]. The chosen Li$^+$ site is shown in figures 1 and 2 having the cell coordinates $x/a=y/a=0.342$ and $z/c=0.36$, where $a=9.47$ Å and $c=10.26$ Å are the lattice constants. Also included are a possible relaxation vector $S$ of the Cu$^{2+}$ ion substituted at this Li$^+$ site and the changed position vectors of its oxygen neighbours.

| Position vectors | $O^1$ | $O^2$ | $O^3$ | $O^4$ | $O^5$ | $O^6$ |
|------------------|-------|-------|-------|-------|-------|-------|
| $r$ (Å)          | 1.815 | 2.08  | 2.15  | 2.28  | 2.55  | 2.76  |
| $x/r$            | 0.475 | -0.842| 0.432 | -0.859| 0.585 | -0.429|
| $y/r$            | -0.851| 0.446 | 0.004 | -0.245| 0.585 | -0.710|
| $z/r$            | 0.226 | 0.301 | -0.902| -0.450| 0.562 | 0.558 |

$S = \frac{1}{2}(O^1 + O^2)$

| $r$ (Å) | $S$ (Å) | $O^1 - S$ (Å) | $O^2 - S$ (Å) | $O^3 - S$ (Å) | $O^4 - S$ (Å) | $O^5 - S$ (Å) | $O^6 - S$ (Å) |
|---------|---------|---------------|---------------|---------------|---------------|---------------|---------------|
| 0.75    | 1.81    | 2.83          | 2.18          | 2.80          | 2.08          |
| -0.594  | -0.722  | 0.485         | -0.696        | 0.692         | -0.355        |
| -0.411  | 0.683   | 0.112         | -0.115        | 0.643         | -0.795        |
| 0.692   | 0.113   | -0.867        | -0.709        | 0.327         | 0.491         |

3. Discussion of the excited state properties of Cu$^+$

As reported in refs. [7, 8], the optical absorption and luminescence properties of Li$_2$B$_4$O$_7$:Cu single crystals, observed for excitations up to 20 eV, also reflect the low-symmetry properties of the host. The only Cu-related emission band at 3.35 eV is due to the Cu$^+$ charge state and can be ascribed to the transition from the lowest excited triplet state of its 3$d^94$s term to the 3$d^{10}$ ground state [8,11,12], a transition which is normally parity- and spin-forbidden. This band corresponds to the spectral properties of the first prominent TL peak observed near 350 K in Li$_2$B$_4$O$_7$ powders co-doped by Cu, Ag, and P [5]. The corresponding 3$d^{10} \rightarrow 3d^94s$ transitions in the excitation and absorption spectra near 5 eV have substantial relative intensities compared to the allowed 3$d^{10} \rightarrow 3d^94p$ transitions near 7 eV. Along with the observed polarisation anisotropy of all spectra this indicates some low-symmetry position for the Cu$^+$ charge state [7, 8].

More stringent requirements on the local symmetry of Cu$^+$ in its relaxed excited 3$d^94s$ type state are imposed by the anomalous decay kinetics of the emission [7, 8]. In the temperature region 6-295 K the decay kinetics is represented by a single exponential decay component. As shown by the two-plateau type temperature dependence of its time constant, for temperatures near 6 K only the lowest metastable singlet level of the excited triplet is populated. However, below this temperature a second, faster exponential decay component shows up, that can only be explained by assuming a tunnel
splitting of the singlet level. This can occur only for a site with at least twofold symmetry having at the same time a vibronic instability, leading to a double or multi-well potential at low temperatures [13]. Similar phenomena have been observed for the Cu⁺ ground state in KCl and most other alkali halides with a cation-anion distance exceeding ~3 Å (for a summary see [14]). Positions like the relaxed Li site derived above for Cu²⁺ in Li₂B₄O₇, may have some approximate local symmetry due to a nearly linear O-Cu-O configuration, but as all further neighbours occupy strongly asymmetric positions (see table 2), tunnelling phenomena in such a configuration are rather improbable. For the excited Cu⁺ ion therefore an alternative interstitial site on the C₂ symmetry axis has to be considered (which is the only nontrivial local symmetry element of the lattice space group I4₁cd). Accordingly the Cu⁺ ion has to be assumed at some medium position between two B₂O₅ groups having the same C₂ axis (see figure 2). A Cu⁺ ion at ~1.7 Å ‘below’ the on-axis oxygen (5), while clearly restricted to move towards these B₂O₅ groups, would have no oxygen neighbours within ~3.1 Å in near-‘horizontal’ directions. Such a site is clearly characterized by a double-well potential: in fact, the exact on-centre position may be less advantageous for Cu⁺ mainly because of the presence of the on-axis oxygen and two boron neighbours at 2.3 Å, but there would be enough space for off-centre displacements. The site in question is an interstitial site where the Cu⁺ ion may require some charge compensation. However, any local charge compensators, if present, also have to comply with C₂ symmetry, leaving as the only reasonable local possibility a pair of nearest neighbour Li vacancies (see the Li sites at both sides of the interstitial site shown in figure 2). These, being actually an overcompensation of the surplus charge, would provide additional freedom of motion. It should be pointed out that the luminescence spectra observed originate from a well-defined Cu⁺ species, either locally charge-(over)compensated, or not, similarly to the statement made for Cu²⁺ in the previous section.

4. Discussion of Cu sites and charge transfer processes

The above-described results on the copper ions in Li₂B₄O₇ clearly indicate the difference between the incorporation sites of both charge states. While for the Cu²⁺ ion a stable low-symmetry position more than 2 Å away from the C₂ axis has been found, the Cu⁺ ion should be located in a double-well potential preferably centred on the C₂ axis. Though this configuration for Cu⁺ has been derived for its relaxed excited state, it can be assumed that the 3d¹⁰-type ground state also possesses tunnelling characteristics at low temperatures, given the smaller radius of the Cu⁺ ion in the ground state and the similar properties observed for this state in the alkali halides with sufficiently large lattice constant [14].

The difference between Cu²⁺ and Cu⁺ incorporation shows how sensitively the Li₂B₄O₇ lattice reacts to an additional charge of the dopant. This is clearly facilitated by the properties of the Li sublattice, where the non-covalently bound Li⁺ ions occupy weakly defined positions with relatively large distances to most of their oxygen neighbours (see table 2), which should be compared to the tetrahedrally coordinated Li⁺ ion in Li₂O with a Li-O distance of 1.963 Å [15]. Accordingly, in addition to possible Li vacancies, local relaxation of the Li sublattice has to be a major ingredient of charge compensation for both copper ions.

Given the substantially different sites, anomalies may be expected for charge trapping at a copper site leading to Cu⁺ ↔ Cu²⁺ transfer in either direction, as such a process may involve major displacements of the Cu ion, possibly with a symmetry change of the Cu defect site between C₁ and C₂, and/or the appearance of other, less stable Cu species. This would tend to reduce the effective trapping cross sections. The difference between the sites may be further stressed if the charge states found stable have different nearby charge-compensating defects. In the latter case charge trapping probably would lead to the appearance of some further, differently compensated Cu species. Preliminary luminescence measurements made on X-irradiated Li₂B₄O₇:Cu crystals, however, failed to demonstrate the presence of a new Cu⁺ species. This finding does not contradict the predictions about the differently incorporated and possibly differently charge-compensated Cu⁺ and Cu²⁺ ions. In addition to further experimental work the described properties and open alternatives for both Cu defects should be verified by detailed calculations of the electronic structure.
5. Summary

As shown by the analysis of the experimental results obtained recently by the complementary methods of EPR and time resolved luminescence, the markedly different but well-defined substitution sites of the Cu charge states are a puzzling property of the Li$_2$B$_4$O$_7$:Cu system. While Cu$^{2+}$ has a frozen-in substitutional position near to a Li site with strong additional distortion of its surroundings, Cu$^+$ has a dynamic excited state with an overall C$_2$ symmetry suggesting interstitial incorporation of the monovalent dopant ion. The different character and the large distance between these states should result in large relaxational movements during charge trapping processes. Evidently, the properties of the different Cu sites are related to the low symmetry of the matrix and the soft character of its Li sublattice being also at the origin of the large ionic polarizability of the Li$_2$B$_4$O$_7$ lattice.

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References

[1] Krogh-Moe J 1962 Acta Cryst. 15 190-3
[2] Malovichko G I, Grachev V G and Matkovskii A O 1991 Fiz. Tverd. Tela 33 1966-72; Engl. transl. Sov. Phys. Solid State 33 1107-11
[3] Malovichko G I, Vitruk L E, Yurchenko N Yu, Burak Ya V, Grachev V G, Matkovskii A O and Sugak D Yu 1992 Fiz. Tverd. Tela 34 509-12; Engl. transl. Sov. Phys. Solid State 34 272-4
[4] Prokic M 2002 Radiat. Prot. Dosim. 100 265-8
[5] Can N, Karali T, Townsend P D and Yildiz F 2006 J. Phys. D: Appl Phys 39 2038-43
[6] Corradi G, Watterich A, Polgár K, Nagirnyi V, Hofstaetter A, Rakitina LG and Meyer M 2007 phys. stat. sol. (c) 4 1276-9
[7] Nagirnyi V, Kotlov A, Corradi G, Watterich A and Kirm M 2007 phys. stat. sol. (c) 4 885-8
[8] Corradi G, Nagirnyi V, Kotlov A, Watterich A, Kirm M, Polgár K, Hofstaetter A and Meyer M 2008 J. Phys.: Cond. Matter 20 025216/1-9
[9] Corradi G, Polgár K, Bugai A A., Zaritskii I M, Rakitina L G, Grachev V G and Derjugina N I 1986 Fiz. Tverd. Tela 28 739-48 Engl. transl. Sov. Phys. Solid State 28 412-7
[10] Hofstaetter A, Laguta V V, Meyer B K, Nikl M, Rosa J and Zhu R Y 2004 Radiat. Meas. 38 703-6
[11] Ignatovich M, Holovey V, Watterich A, Vidóczky T, Baranyai P, Kelemen A, Ogenko V and Chuiko O 2003 Radiat. Phys. Chem. 67 587-91
[12] Ignatovich M, Holovey V, Watterich A, Vidóczky T, Baranyai P, Kelemen A and Chuiko O 2004 Radiat. Meas. 39 567-70
[13] Liidja G, Nagirnyi V, Soovik T and Zazubovich S 1989 Phys. Stat. Sol. (c) 152 563-75
[14] Payne S A 1987 Phys. Rev. B 36 6125-31
[15] Rodeja J G, Meyer M, Hayoun M 2001 Model. Simulat. Mater. Sci. Eng. 9 81; http://www.cond-mat.physik.uni-mainz.de/~horbach/cecam2005/cecam_hayoun.ppt#1

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