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Evolution of the optical properties of chromium doped calcium tetraborate glass under high pressure



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ABSTRACT

In this contribution, we present luminescence properties of calcium tetraborate glass (CaB₄O₇) activated with Cr³⁺ ions. Excitation spectra, steady state and time resolved luminescence spectra at temperatures between 10 K and 300 K and at high hydrostatic pressure up to 120 kbar were measured. The excitation spectrum consists of two broad bands peaking at 420 nm and 580 nm related to transitions from the ⁴A_{2g} ground state to ⁴T_{1g} and ⁴T_{2g} excited states, respectively. Ambient pressure luminescence spectrum consists of two bands peaking at 690 nm and 850 nm. First band is related to the spin forbidden ²E_g → ⁴A_{2g} transition, whereas the second broad band is related to the spin allowed ⁴T_{2g} → ⁴A_{2g} transition. Widths of both bands are significantly greater than natural due to inhomogeneous broadening. The ratio between intensities of these bands is strongly temperature and pressure dependent. At pressure below 50 kbar relative contribution of the ²E_g → ⁴A_{2g} luminescence decreases with increasing temperature and increases when pressure is applied. For pressure higher than 50 kbar only the emission related to the ²E_g → ⁴A_{2g} transition is observed. Analysis of luminescence lineshape and kinetics allowed to estimate the width of the crystal field distribution and show that even at ambient pressure most of the Cr³⁺ ions occupy high field sites with energy of the ⁴T_{2g} higher than the energy of the ²E_g state.

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1. Introduction

Energetic structure of the Cr³⁺ ion in crystal field is determined by distribution of three electrons that occupy unfilled 3d orbitals of the ion. In octahedral coordination the fivefold degenerated 3d state splits into the triply degenerated t_{2g} (lower) and the doubly degenerated e_g (higher) state. The ground state of the Cr³⁺ is the ⁴A_{2g}, in which all three electrons occupy the lower electronic manifold t_{2g}, with parallel spins. The Cr³⁺ ion can be excited either by excitation of one electron to the e_g electronic manifold without change of spin, resulting in the excited state ⁴T_{2g} or by inversion of the spin of one electron without changing the electronic manifold. The latter case corresponds to the excitation of the system into the ²E_g and ²T_{1g} excited states. The next excited state is the ⁴T_{1g}, which belongs to the same electronic configuration as the ⁴T_{2g}. As the result absorption spectrum of the Cr³⁺ ions

in octahedral coordination consists of two bands related to the spin-allowed ⁴A_{2g} → ⁴T_{2g} and ⁴A_{2g} → ⁴T_{1g} transitions.

The energies of the electronic states of Cr³⁺ centre depend on values of Racah parameters *B* and *C*, which describe the Coulomb and exchange interaction between the 3d electrons and the crystal field strength 10*Dq*, which depends the interaction of the 3d electrons with ligands. 10*Dq* is equal to the e_g-t_{2g} splitting energy and is proportional to the Cr³⁺-ligand distance, *R* as *R*⁻⁵. As the results energy of the ⁴T_{2g} state with respect to the ground state is equal to the crystal field strength 10*Dq*, whereas the energy of the lowest doublet ²E_g with respect to the ground state weakly depends on the crystal field and for the reasonable values of *Dq/B* between 1.5 and 3.5 is equal to [1].

$$E(^2E_g) \cong 7.90B + 3.05C - 1.80 \left(\frac{B^2}{Dq} \right) \quad (1)$$

Depending on the crystal field strength, represented by the ratio *Dq/B*, the first excited state is either ⁴T_{2g} (the low field case for *Dq/B* < 2.4) or ²E_g (the high field case for *Dq/B* > 2.4). In the low field materials the Cr³⁺ emission is characterised by broad band luminescence related to the spin allowed, parity forbidden

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${}^4T_{2g} \rightarrow {}^4A_{2g}$ transition [1], that decays with tenths or hundreds μ s, whereas in high field system the luminescence consists of the sharp lines (called R lines) related to parity and spin forbidden ${}^2E_g \rightarrow {}^4A_{2g}$ transition decaying in ms time scale.

In the glass host, where the long distance order is not conserved the Cr^{3+} sites differ from each other by distribution of ligands, average central ion – ligand distance and even by coordination number. As the result the emission spectrum and luminescence lifetime of the Cr^{3+} ion in the particular site depends on the local environment, which can be either high field or low field one, whereas the luminescence in macroscopic scale is a superposition of the emission from different sites and usually is manifested as a broad band.

The specific electronic structure, which yields strong dependence of the Cr^{3+} luminescence on temperature, as well as inhomogeneous effects introduced by glass and glass ceramic hosts caused intensive investigations of glass and glass – ceramic materials doped with Cr^{3+} for potential application in optical thermometry [2,3].

There have been several approaches that relate the inhomogeneous broadening of the Cr^{3+} emission in the disordered materials to crystal field strength distribution, or distribution of the energy of the 4T_2 state [4–11]. The inhomogeneous broadening has been quantitatively analysed for Cr^{3+} in gallogermanates [12,13] and in aluminosilicate glass [14]. In the framework of this approach the Cr^{3+} site distribution has been parameterised by the distribution of the crystal field strength (equivalently by energy of the 4T_2 state) and the distribution of the electron–lattice coupling. The distributions of both these quantities have been recovered by analysing the dependence of the emission peak position on the excitation energy [12–14] and temperature [15].

Lattice disorder alters not only the energy of the 4T_2 state but also the emission lifetime [16]. The latter effect is related partly to breaking the Laporte rule for the radiative transitions by odd parity crystal field and partly to the nonradiative processes that additionally depopulate the excited systems. In disordered materials both the odd parity crystal field and the nonradiative internal conversion rate usually varies from site to site and this results in non-exponential luminescence decays. Since the ${}^2E_g \rightarrow {}^4A_{2g}$ transition is spin forbidden, the R lines luminescence takes place mainly due to the spin-orbit coupling between the 2E_g and ${}^4T_{2g}$ states. As the result the R line luminescence lifetime is dependent on the difference between the energies of the 2E_g and ${}^4T_{2g}$ states, and the non-exponential decay of the R line luminescence is the result of different energy of the ${}^4T_{2g}$ state in different sites [17,18].

Since the excited ${}^4T_{2g}$ and the ground ${}^4A_{2g}$ states are splitted by the energy of the crystal field strength which depends on the ion–ligand distance as R^{-5} , the energy of the ${}^4T_{2g}$ state should increase with high hydrostatic pressure. Actually a blue pressure shift of the ${}^4T_{2g} \rightarrow {}^4A_{2g}$ emission band, of the order of tenths $\text{cm}^{-1}/\text{kbar}$, has been observed in the low field materials [19]. A small red shift of the R lines emission, related to the ${}^2E_g \rightarrow {}^4A_{2g}$ transition, in the Cr^{3+} ions in the high field systems [17,20–22] is also well known.

The combined effect of a large increase in the energy of the ${}^4T_{2g}$ state and essentially no change in the energy of the 2E_g state with pressure is responsible for the observed electronic cross-over. The change from a spin-allowed ${}^4T_{2g} \rightarrow {}^4A_{2g}$ emission to a spin-forbidden ${}^2E_g \rightarrow {}^4A_{2g}$ emission leads to the observed transformation from a smooth, broadband emission spectrum to a sharp, structured emission spectrum. The ${}^4T_{2g} \rightarrow {}^2E_g$ crossover has been observed in many materials. The latest reviews on high pressure spectroscopy of the Cr^{3+} doped materials one can be found in Refs. [19] and [23].

The focus of this paper is the luminescence and luminescence kinetics of a Cr-doped calcium tetraborate glass $\text{CaB}_4\text{O}_7:\text{Cr}^{3+}$ (CBO: Cr^{3+}), measured at different temperature and pressure. Presented

results demonstrate the local disorder of glass host, and pressure induced transformation of low field Cr^{3+} to the high field ones.

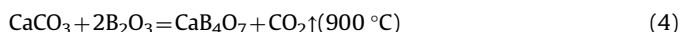
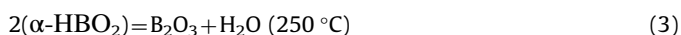
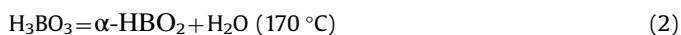
2. Samples preparation, experimental methods and lifetime distribution calculations

2.1. Synthesis of the glass

The Cr-doped calcium tetraborate glasses with CaB_4O_7 ($\text{CaO}-2\text{B}_2\text{O}_3$) basic composition were obtained in the air atmosphere from the corresponding polycrystalline compounds according to standard glass synthesis and technological conditions, which were described in [24,25]. Quantitative composition of the CaB_4O_7 glass can be also presented as 33.33% $\text{CaO}-66.66\% \text{B}_2\text{O}_3$.

For solid-state synthesis of the CaB_4O_7 polycrystalline compound; the calcium carbonate (CaCO_3) and boric acid (H_3BO_3) of high chemical purity (99.999%, Aldrich) were used. The chromium impurity was added to the raw materials as Cr_2O_3 of chemical purity (99.99%) in amount of 1.0 mol%.

Solid-state synthesis of the polycrystalline calcium tetraborate compound was performed using multi-step heating reactions [24,26], which can be described for CaB_4O_7 compound by the following chemical equations:



Large samples of the Cr-doped CaB_4O_7 glasses were obtained by fast cooling of the corresponding melt, heated more than 100 K above the melting point (for CaB_4O_7 compound $T_{\text{melt}} = 980 \text{ }^\circ\text{C}$ (1253 K) [25]) to make the crystallisation process impossible. The X-ray diffraction and electron paramagnetic resonance (EPR) spectroscopy show glassy structure of the obtained samples [24,26].

2.2. Spectroscopy: methods and equipment

Photoluminescence excitation (PLE) spectra were measured using a Fluoromax-4P (Horiba) spectrofluorometer with a Hamamatsu R928P photomultiplier. The excitation light source was a 150 W ozone-free xenon lamp which enables excitation in the range of 250–850 nm. The spectra were corrected for spectral response of the apparatus.

Photoluminescence (PL) spectra were acquired using a Shamrock SR750 D1 grating spectrometer with an iDus 420 CCD detector (Andor Technology). The spectral range of the spectrometer was 220–1000 nm. The excitation source was a IK5352R-D He–Cd continuous wave laser (Kimmon Koha) operating at 442 nm. Low temperature was obtained by placing the sample in a DE-2045L closed cycle helium cryostat (APD Cryogenics).

The excitation part of the apparatus for time resolved spectroscopy consists of a PG 401/SH optical parametric generator pumped by a PL2134A/SS pulse YAG:Nd laser (Ekspla). The optical parametric generator converts the 355 nm pulses produced by the laser into pulses of selected wavelength ranging from 210 to 2300 nm. Pulse duration is 30 ps. Time-resolved PL spectra and PL decay profiles were acquired using a 2501S grating spectrometer (Bruker Optics) combined with a C4334-01 streak camera (Hamamatsu). Luminescent response of the sample (spectrally and temporally resolved by the acquisition apparatus) is recorded in the form of a streak image on a 640 by 480 pixel CCD array. Software based photon counting algorithm transforms the result into a 2D matrix of photon counts vs. wavelength and time.

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