Cathodoluminescence of CdZnSSe crystals synthesized in 19th century bead glass

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(Dated: 31 January 2019)

The letter presents an experimental study of band edge cathodoluminescence spectra of CdZnSSe crystals that nucleated and grew in glass melt during red glass manufacturing. The crystallites exhibit bright band edge cathodoluminescence both at room temperature and at liquid nitrogen temperature. Band edge cathodoluminescence of these crystals has been found to peak in the range from 2.00 to 2.03 eV at 300 K and from 2.02 to 2.06 eV at 80 K. We have estimated the band gap width temperature coefficient ($dE_g/dT$) in the interval from 80 to 300 K and found it to range from 0 to $-2.5 \times 10^{-4}$ eV/K.

PACS numbers: 71.55.Gs, 71.35.-y, 78.60.Hk

Keywords: Cathodoluminescence, CdZnSSe, crystals in glass

Cd$_x$Zn$_{1-x}$S$_y$Se$_{1-y}$ thin films are known from the literature to be promising for usage in quantum well lasers and solar cells. However, band edge luminescence of CdZnSSe is insufficiently studied at present; this especially relates to the bulk crystals and the compounds with high content of sulfur.

In this letter, we present band edge cathodoluminescence (CL) spectra of CdZnSSe ($x = y = 0.5$) crystallites that nucleated and grew in glass melt during red bead glass manufacturing in the 19th century.

The following equipment was used in the study. Elemental compositions of glass was analyzed using a M4 TORNADO X-ray fluorescence (XRF) microspectrometer (Bruker). Mira 3 XMU (Tescan Orsay Holding) scanning electron microscope (SEM) was employed for imaging of glass structure and elemental analysis. Mira 3 LMH (Tescan Orsay Holding) equipped with Nordlys Nano electron backscatter diffraction (EBSD) unit and AZtecHKL Advanced software (Oxford Instruments Nanoanalysis) was used for the structural analysis of crystallites in glass. EDS X-MAX 50 (Oxford Instruments Nanoanalysis) energy dispersive X-ray spectrometers were used for microanalysis and mapping of elemental composition. Finally, micro cathodoluminescence (CL) was investigated both at room temperature and at liquid nitrogen temperature using MonoCL3 system (Gatan) mounted at JSM-7001F SEM (Jeol).

Investigating glass corrosion in historical seed beads of the 19th century that often originates from crystalline inclusions synthesized in glass melt in the process of the glass production, we have found that turbid Zn-rich glass of red beads (Table I) contains numerous submicron hexagonal crystallites (Fig. 1), which have been identified using EDS and EBSD as CdZnSSe (ICSD Entry 43368: hexagonal crystal system, P6$_3$mc (186) space group).

We mapped panchromatic CL of various samples of analogous glass, as well as CL at different wavelengths, and found the CdZnSSe crystallites to exhibit intense CL peaked around the wavelength of 600 nm, both at 300 and
FIG. 2. Micro CL images of CdZnSSe crystallites in glass: (a) a panchromatic map (300 K); (b, c) another sample (80 K), (b) a panchromatic map and (c) a map obtained at $\lambda = 602$ nm.

TABLE I. Mean relative content of some chemical elements in the glass samples measured using XRF analysis (at.%).

| Chemical element | Al  | Si  | Se  | Ca  | Fe  | Zn  | As  | Pb  | S   | Cd  |
|------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Mean content     | 1.50| 78.24| 0.39| 1.95| 0.04| 16.78| 0.45| 0.05| 0.14| 0.47|
| Standard deviation | 0.34| 0.48| 0.01| 0.05| 0.01| 0.27| 0.02| 0.01| 0.07| 0.28|

80 K (Fig. 2).

Examples of CL spectra obtained from individual CdZnSSe crystallites at 300 and 80 K are plotted in Fig. 3. We assign the intense bands peaked around 2.0 eV to CdZnSSe crystals; the weak bands peaked in the range from 3.1 to 3.2 eV may be tentatively assigned to amorphous ZnO dissolved in Zn-rich glass. The latter bands are related to CL of glass surrounding the crystals. Fig. 4 presents the CL bands of CdZnSSe in the vicinity of 2 eV obtained from different crystallites. Maxima of the CL bands are seen to shift for particular crystals: they usually move within the range from about 2.00 (curve 1) to nearly 2.03 eV (curve 2) at room temperature sometimes coming down to 1.95 eV for some crystallites (curve 3-1). (The band peaked at 1.85 eV (curve 3-2) is likely due to admixture of the surrounding glass CL.)

No pronounced temperature dependence of peak maxima was observed for crystals of CdZnSSe. At liquid nitrogen temperature, the CL bands top out in the range from about 2.02 to nearly 2.06 eV (the spectral line shown by curve 4 peak at 2.03 eV and the line depicted by curve 5 reaches its maximum at 2.055 eV).

Previously, optical band gap of polycrystalline CdZnSSe films prepared using chemical bath deposition on glass substrates, estimated from light absorption spectra, was shown to decrease due to annealing from 2.21 to 2.01 eV with the increase of annealing temperature (the annealing temperatures were 100, 300 and 500°C). The authors of that article explained such a behavior of the band gap by the decrease in originally increased interatomic spacing in the crystal grains or by particle size enlargement and enhancement in crystallinity with increasing annealing temperature. However, we believe...
that shifts in the CL band maxima cannot be explained by those factors in the case of CdZnSSe micro crystals in glass. Notice that no one made any efforts to achieve high uniformity of their properties, crystalline perfection or strict adherence to stoichiometry at that time. Moreover, no one knew their chemical composition or had an idea about the structure of the crystals. They grew just like “wild” natural crystals in minerals. Nevertheless, all the crystallites were synthesized in glass melt at very close conditions at the temperature higher than 1000°C and their dimensions vary in the range from several hundreds of nanometers to about one micrometer, thus neither the difference in their sizes nor difference crystal perfection may explain the observations. We explain this observation by minor changes in elemental composition of crystallites, which cannot be registered by EBSD within the accuracy of experiments yet can slightly change the band gap. So, e.g., the stoichiometry shift towards CdSe would decrease the band gap, whereas composition changes towards CdS, ZnSe or ZnS would increase it. Hence, minor deviation of the CdZnSSe elemental composition from the strict \( \text{Cd}_{0.25} \text{Zn}_{0.25} \text{S}_{0.25} \text{Se}_{0.25} \) one would result in red or blue shift of its band edge (excitonic) CL.

We can estimate the value of the band gap width temperature coefficient in the vicinity of 300 K \( \frac{dE_g}{dT} \) form the maximum temperature shift of the band edge CL peak position. The obtained estimate is \( 0 > \frac{dE_g}{dT}_{300 K} \gtrsim -2.5 \times 10^{-4} \text{ eV/K} \).

In summary, we would like to emphasize the main statements of the letter.

First, we have observed hexagonal crystallites of sub-micron sizes in 19th century Zn-rich seed bead glass and identified them as CdZnSSe crystals \( ([\text{Cd}] = [\text{Zn}] = [\text{S}] = [\text{Se}] = 0.25) \). The crystallites exhibit intense band edge cathodoluminescence both at room temperature and at liquid nitrogen temperature.

Second, band edge CL of these crystals tops out in the range from 2.00 to 2.03 eV at room temperature and from 2.02 to 2.06 eV at liquid nitrogen temperature. Shifts of the band edge CL peak position in different crystallites are supposedly due to minor variations of stoichiometry of individual crystallites that lead to changes in the band gap width.

Finally, the temperature dependence of the band edge CL peak position is weak or even negligible in CdZnSSe crystals. We have estimated the band gap width temperature coefficient \( (dE_g/dT) \) in the interval from 60 to 300 K; the obtained value ranges from 0 to \(-2.5 \times 10^{-4} \text{ eV/K}\).

It should be noted in conclusion that luminescent glass-cystal composites or ceramics based on Zn or Cd-rich silicate glasses, similar to that made in the mid-19th century and presented in this letter, might find numerous applications both in photonics and arts and crafts. Varying glass melt elemental composition and crystal growth conditions to obtain crystallites of the required II–VI compound in the required concentration, it is possible to produce luminescent glasses with the required optical properties, which are easy to shape either using standard technologies of glassware making or using 3D printing technology.

\[ \text{Cd}_{0.25} \text{Zn}_{0.25} \text{S}_{0.25} \text{Se}_{0.25} \times 5 \times 10^{-4} \text{ eV/K} \]

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