Mechanical and optical properties of hybrid materials based on inorganic glass matrix and organic metal complex phosphors

I Ch Avetissov¹, O B Petrova¹, M O Anurova¹, A V Khomyakov¹, A A Akkuzina¹, I V Taidakov²

¹Department of Chemistry and Technology of Crystals, Dmitry Mendeleev University of Chemical Technology of Russia, 125047 Moscow, Russia
²P.N. Lebedev Physical Institute of the Russian Academy of Sciences, 119991, Moscow, Russia

E-mail: igor_avetisov@mail.ru

Abstract. Hybrid materials (HM) consisting nanoparticles of an organic functional agent dispersed in an insulating matrix, are widely used in photonics as active and passive elements as well as integral optics components. Highly efficiently phosphors used in OLED technology are promising organic agent. One of the problems which can be solved by the creation of HM is protection of organic phosphors from environmental conditions (oxygen, water vapor, UV light, etc.) which lead to the destruction of metal-organic complexes and their loss of luminescence properties.

1. Introduction

Organo-inorganic hybrid materials (HM) are widely used in photonics as active and passive elements as well as integral optics components [1]. One of the problems which can be solved by the creation of HM is a creation of a material stable to environmental conditions and (oxygen, water vapor, UV light, etc.) which lead to the destruction of metal-organic complexes and their loss of luminescence properties [2]. The possibility of synthesis of photoluminescent HM based on 8-hydroxyquinoline [3] and phenantroline [4] metal organic phosphors and inorganic low melting glasses as a matrix using a non-aqueous technique has been demonstrated.

For the synthesis of HM by the melt technology, a glass matrix should fulfill a number of requirements on temperature, mechanical and optical characteristics. Glasses from lead borate and borosilicate systems meet the conditions mentioned above. These systems were previously studied for fabrication of low melting solvents for the growth of crystals from melt solution [5-6] and sealing glasses [7]. The substitution of lead oxide by lead fluoride in glass composition resulted to a decrease in melting point and viscosity [8-9], as well as the optical properties changing. In the 600–700 °C temperature range the above mentioned melts have viscosity in 3 orders of magnitude lower than the for B₂O₃ melt, which facilitates the process of mass transfer during synthesis with stirring. The glasses of these compositions have sufficiently high values of mechanical and chemical resistances.

One of the problems in the production of fluoro-borate glasses is pyrohydrolysis of lead fluoride, leading to significant losses of fluorine during the synthesis of glasses. This process is associated with
the interaction of fluorides with water vapor at temperatures above 400°C [10]. The use of dried boron oxide and synthesis under dry atmosphere can significantly reduce fluoride losses.

The high content of OH-groups in the glass leads to quenching of the luminescence of many both inorganic activators [11-12] and organic metal complexes. Thus, the producing of HM based on glasses with a reduced content of OH-groups should lead to an increase in the luminescence intensity.

2. Experimental

2.1. Pyrification and drying of B2O3
To keep the fluorine vaporization resulting from pyrohydrolysis which was controlled by residual water content in boric acid and commercial boron oxide preparations we prepared specially dried boron oxide (100 ppm residual water content) and used it for HM fabrication. Boric acid purchased from KOMPONENTREZKIV (Russia) (99.999 wt%) had been recrystallized several times from acidified hot solution. Impurity content of recrystallized boric acid was determined by the inductively coupled plasma technique (NexION 300D, Perkin Elmer Inc.). The final probe of boric acid was as pure as 99.9998wt% (metal based). Extra pure B2O3 was made by slow decomposition of the boric acid in a platinum crucible using the multy-step heating with one hour exposition at 130, 170, 300°C. This regime allowed preserving intense water vaporization. The heating of a preparation to 700°C and further exposition during 6 hours resulted to the B2O3 melting followed by the formation of homogeneous transparent mass. The final removal of the residual water was made by annealing of the amorphous B2O3 at 500°C during 3 hours under dynamic vacuum (10−1 Pa) in a home-made reactor in a platinum crucible. The residual water content was measured by a humidity analyzer AGS50 (AXIS, Poland) and it was less than 500 ppm.

2.2. Synthesis of glasses and HM
As raw materials we used boric acid (99.999 wt% from KOMPONENTREZKIV, Russia), additionally purified and dried B2O3 (see above), commercial boron oxide (99.999 wt% from IREA2000 Ltd., Russia) and specially prepared dried boron oxide (99.9995 wt%). The glasses of nominal compositions of 70PbO-30B2O3 and 70PbF2-30B2O3 were synthesized using PbO and PbF2 of at least high purity grade (LANHIT Ltd.). All glasses were obtained in closed corundum crucibles (30 ml) under the same conditions: 50 g batch charge, 950°C temperature, 15 minutes exposure. The melt was poured into heated steel molds. In the present research we have synthesized and studied hybrid materials based on 8-hydroxyquinoline metal complexes with metals of I, II, and III groups of the Periodic Table having general formula Mq6 (Liq, Kq, Rbq, Mgq2, Znq2, Alq3). Purity of 8-oxiquinolin metal complexes measured by the ICP-MS technique was not less 99.99wt% (metal based). Besides, HM's were synthesized in alumina crucibles. A pre-synthesized glass (5 g) was melted at 700°C then cooled up to 550°C and a powdered organometallic phosphor (0.1 wt%) was poured into the melt. Then a mixture was stirring during 10-15 s. The HM samples were obtained by rapid casting into steel molds.

2.3. Measurement techniques
Elemental analysis Scanning Electron microscopy (VEGA-3-LMU, Tescan) equipped with an energy-dispersive spectrometer (EDS Inca Energy X-MAX-50, Oxford Instruments) supported by AZTec software was used for data gathering and processing. The glass composition was determined by SEM-EDX analysis after carbonization, the beam energy was 30 keV for glasses. The micro-hardness was determined by the Vickers method using a PMT-3 micro-hardness tester, in the range of loads 50 - 200 g. The absorption spectra of glasses and HM were recorded using a Varian Cary 5000 (UV/VIS/IR) spectrophotometer in 400–3000 nm wavelength range with 1 nm step and a Tensor 27 (Bruker) IR-Fourier spectrometer (2750-6250 nm). A QE65000 (Ocean Optics, USA) spectrometer with a 785 nm excitation for Raman spectra recording was used.
A Fluorolog FL3-22 spectrofluorimeter (Horiba JobinYvon, USA) with double grating excitation and emission monochromators was used for luminescent measurements in a wavelength range of 400–700 nm with a 0.1 nm step.

All measurements were carried out at room temperature.

### 3. Results and discussion

As a result of the synthesis, transparent optically high-quality glass-matrices were obtained. Glasses obtained in the 70PbO - 30B₂O₃ system were yellowish while the 70PbF₂-30B₂O₃ system made it possible to get colorless preparations.

Analysis of the elemental composition of the glasses (Table 1) showed that the dried boron oxide reduces two times the losses of fluorine compared to the commercial boron oxide, and three times compared to the boric acid. We associate this result with the suppression of pyrohydrolysis in a drained system. The fluoro-borate melt is more aggressive than the borate melt, as a result of its interaction with the crucible, about 4 mol.% aluminum oxide is transferred to the glass, compared to 1.5 mol.% for the borate melt. However, the use of dried boron oxide reduces the proportion of dissolved aluminum oxide by half, both for borate and fluoro-borate systems. Thus, the use of dried boron oxide reduces the aggressiveness of borate melts, which can be used in the production of crystals and glasses based on high-purity borate.

| Batch composition (mol%) | Volatilization of fluorine, C³⁶₅ / C³⁶₅ \(\times 100\%\) | Al content (at%) ±0.5 | Micro-hardness (kg/mm²)±10 | Cutoff wavelength (nm) ±1 |
|--------------------------|------------------------------------------------|-----------------------|-----------------------------|--------------------------|
| 70PbF₂-30(H₂BO₃)₂        | 41                                              | 8.7                   | 144                         | 398                      |
| 70PbF₂-30B₂O₃            | 26                                              | 9.6                   | 139                         | 397                      |
| 70PbF-30B₂O₃ (dried)     | 13                                              | 4.0                   | 144                         | 365                      |
| 70PbO-30(H₂BO₃)₂         | -                                               | 2.7                   | 143                         | 461                      |
| 70PbO-30B₂O₃             | -                                               | 3.2                   | 147                         | 482                      |
| 70PbO-30B₂O₃ (dried)     | -                                               | 1.5                   | 157                         | 449                      |

This comparatively small transmission (less than 75%) of pure, transparent glasses could be explained by the large losses in the reflection (Fresnel losses) arising from the large refractive index, inherent in all high-lead glasses (Figure 1).

The cutoff of the transmission of glasses depends on the fluorine content: in glasses of nominal composition 70PbF₂-30B₂O₃, obtained from non-dried components, it lies about 400 nm, in a glass of the same nominal composition, obtained from dried boron oxide - 365 nm. For glasses in the 70PbO-30B₂O₃ system, the transmission edge is in the region of 450–480 nm. Photoluminescence (PL) of the used organic phosphors is achieved by the excitation of ligands with the energy more than 3 eV [13]. Thus the glasses with the cutoff wave length longer that 400 nm will absorb the excitation energy and we will fail to get the luminescence in hybrid materials.

The long-wavelength edge of the transparency window lies at around 3500 nm. A broad band in the 2950 nm (3400 cm⁻¹) region is associated with the absorption of OH-groups. As the water content in the initial reagents decreases, this band naturally decreases. Moreover, in the fluoro-borate glasses, the band is initially smaller, which may be due to a decrease in the hydroxyl group content as a result of volatilization upon interaction with fluorides, and also with a lower viscosity of fluoro-borate melts, which contributes to the volatilization of water vapor.
Several broad bands are visible on the Raman spectra (Figure 2). The spectra of borate and fluoro-borate glasses differ evidently. The band intensity corresponding to the vibrations of tetrahedral units of PbO$_4$ (306 cm$^{-1}$) is noticeably lower in fluoro-borate systems than in borate systems, which is due to the fluoride surroundings of lead in fluoro-borate glasses and the predominance of Pb-F bonds, whose vibrational energy is much lower.

As it was demonstrated in Ref. [14], the replacement of PbO by PbF$_2$ led to an increase in the intensities of the combinational lines associated with the oscillation of the BO$_4$ units (Table 2). This was explained by the fact that the bonds with PbO$_4$ stabilized the triple coordination of boron in the glass. The energy of the phonons of the BO$_4$ units is lower than that of BO$_3$, which is favorable for the production of luminescent materials. The reduced energy of the phonon matrix reduces the probability of non-radiative relaxation in the activator ions and promotes an increase in the luminescence intensity.
IOP Conf. Series: Journal of Physics: Conf. Series 1045 (2018) 012006  doi:10.1088/1742-6596/1045/1/012006

| Peaks (cm⁻¹) | Oscillations [14-15] |
|-------------|----------------------|
| 306         | Deformation oscillations of tetrahedral units PbO₄          |
| 580         | Deformation oscillations of B-O-B in various borate groups with a predominance of BO₃- units |
| 710         | Symmetric stretching vibrations of a six-membered borate ring with one units BO₄, |
| 905         | Valence oscillations of B-O in BO₄ with the participation of bridging oxygen |
| 1250        | Deformation oscillations of B-O in BO₃-triangles and boroxsol rings with non-bridging oxygen |
| 1350        | Deformation oscillations of B-O in BO₄ with one or two non-bridging oxygen |
| 1500        | Deformation oscillations of B-O in BO₃ with three non-bridging oxygen |
| 1560        | Valente oscillations of B-O-B in triangles BO₃ |
| 1660        | Valente oscillations of B-O-B in triangles BO₃ |

Table 2. Raman peaks in glass-matrices

The micro-hardness of all the glasses obtained was similar (Figure 3, Table 1). The values of the hardness of the glass are affected by a number of factors. In this case, some factors are oppositely directed: so changing the oxide to fluoride usually reduces hardness, but at the same time the melt aggressiveness and concentration of aluminum oxide increase, which contributes to the hardness increase [16]. The micro-hardness of the synthesized glasses varied from 140 to 150 kg/mm² (Figure 3), while for HM’s we obtained the values up to 210 kg/mm² due to the fluoride loss and alumina content increase (from crucible interaction) of the melt during HM’ synthesis. The micro-hardness both glasses and HM’s fabricated using dried B₂O₃ was higher comparing to the synthesis with boric acid and commercial B₂O₃.

![Figure 3](image-url)

**Figure 3.** Micro-hardness a) glass-matrices in system 70PbO-30B₂O₃; b) glass-matrices in system 70PbF₂-30B₂O₃; c) glass-matrices in system 70PbF₂-30B₂O₃ and HM based its

All HM showed a wide PL band in the range 400-700 nm (Figure 4).

The use of dried B₂O₃ led to an increase in the PL intensity (Figure 5). We assumed that the PL intensity growth for matrix made with the dried B₂O₃ could be resulted for reducing of hydroxyl groups’ content in the HM. The latter could result either to the reduction of luminescence quenching at a non-radiative transitions on OH-groups’ oscillations or to the increasing of an organic ligands content in the case of the less aggressive glass melt.

4. Conclusions
The use of dried boron oxide in the synthesis of fluoro-borate glasses and organo-inorganic hybrid materials on their basis resulted to the reducing the pyrohydrolysis of the fluoride components, to the reducing of glass melt aggressiveness, and to the increasing of the glass transparency and the PL intensity in the case of the hybrid materials.
Figure 4. The PL spectra of HM’s based glass-matrices in system 70PbF₂-30B₂O₃

Figure 5. The PL spectra of HM (Liq) based glass-matrices 70PbF₂-30B₂O₃

Acknowledgments

The research was financially supported by the Ministry of Education and Science of the Russian Federation RFMEFI57716X0218.

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