



# Article New Glasses in the PbCl<sub>2</sub>–PbO–B<sub>2</sub>O<sub>3</sub> System: Structure and Optical Properties

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**Abstract:** New oxychloride lead borate glasses in the  $xPbCl_2-(50-0.5x)PbO-(50-0.5x)B_2O_3$  system were synthesized with a maximum lead chloride content of 40 mol%. The characteristic temperatures and mechanical and optical properties were studied. The incorporation of lead chloride led to a significant expansion of the transparency range in the UV (up to 355 nm) and IR regions (up to 4710 nm). Decreases in the Vickers hardness, density, and glass transition temperature were the consequences of a change in the structure. The studied glasses are promising materials for photonics and IR optics. The structure of the PbCl<sub>2</sub>–PbO–B<sub>2</sub>O<sub>3</sub> system was analyzed in detail using vibrational spectroscopy and X-ray diffraction.

Keywords: oxychloride glasses; lead chloride; optical absorption; glass network structure



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# 1. Introduction

The variety of compositions and extremely interesting properties of glasses based on boron oxide have attracted the attention of many researchers. In the last few decades, the importance of borate glasses has increased because they exhibit an exceptional combination of properties, such as transparency in a wide spectral range, mechanical strength, chemical resistance, as well as thermal shock and crystallization resistance [1].

Borate glasses containing lead compounds have unique characteristics. The inclusion of PbO and PbX<sub>2</sub> (X = F, Cl, and Br) in glass compositions leads to a significant increase in electrical conductivity [2], transparency in the IR and UV ranges [3,4], high refractive indices [5], and optical nonlinearity [6].

Oxyhalide glasses are very promising as matrix materials for applications such as modern laser systems and fiber communication lines [7]. The incorporation of lead halides (PbX<sub>2</sub>) into glasses leads to low phonon energies, which makes them promising materials due to a decrease in nonradiative losses because of multiphonon relaxations [8]. The optical properties of glasses of the PbX<sub>2</sub>–PbO–B<sub>2</sub>O<sub>3</sub> system doped with *d*-elements [5,9] and *f*-elements [4,10,11] have been studied. The positive effect of lead halides on their spectral and luminescent properties has been proven. However, the preparation and usage of many oxyhalide glasses are often limited due to their high tendency to crystallize, the toxicity of reagents, and the rather high content of OH<sup>-</sup> groups [4,10]. There is no information on the preparation of borate glasses with a PbCl<sub>2</sub> content of more than 25 mol% and there are limited data on their optical properties in the IR region and their structures.

This work aimed to develop a synthesis technique for new oxychloride lead borate glasses with a large amount of lead chloride (up to 40 mol%) and to investigate their optical, mechanical, and thermal properties.

# 2. Materials and Methods

The glasses were synthesized with the general formula  $xPbCl_2$ -(50-0.5x)PbO-(50- $(0.5x)B_2O_3$ , where x varied from 0 to 40 mol% with a 5 mol% step. PbCl<sub>2</sub>, PbO powder preparations (99.9, Himkraft, Kaliningrad, Russia) and B<sub>2</sub>O<sub>3</sub> glassy strips (99.9, Reachim, Moscow, Russia) were used as initial components for synthesis. The necessary amounts of components were weighed using an Explorer Ohaus PA64 electronic balance (Ohaus, Shanghai, China). The mixture was homogenized by repeated grinding in an agate mortar. The sample weight for one experiment was ~15 g. The charge was placed in a corundum crucible with a cover and melted for 30 min at 900 °C in a PM-12M1 muffle furnace (EVS, St. Petersburg, Russia) under ambient atmosphere. The melt was then cast into a glassy carbon mold and quickly pressed by another glassy carbon mold. To reduce quenching stresses, the glasses were annealed in a SNOL 7.2/1100 furnace (Umega Group, Ukmerge, Lithuania) at 240 °C for samples with PbCl<sub>2</sub> content  $\geq$ 20 mol% and at 300 °C for samples with PbCl<sub>2</sub> content  $\leq$  15 mol%. The residual stress was controlled by using the optical polarization method with a PKS-250M polariscope-polarimeter (Zagorsk Optical and Mechanical Plant, Sergiev Posad, Russia). Plane-parallel samples of 2 mm thickness were polished using a T-080.00.00 stone-cutting machine (Togran, Moscow, Russia).

The amorphous nature of the glasses was confirmed by X-ray diffraction analysis using an Equinox 2000 X-ray diffractometer (Thermo Fisher Scientific, Saint-Herblain, France) with CuK<sub> $\alpha$ </sub> radiation ( $\lambda = 1.54060$  Å) in the 2 $\Theta$  angle range from 10° to 100°, with a 0.01° scanning step and 2 s/step exposure. The diffraction patterns were analyzed using Match! software (2003–2015 CRYSTAL IMPAC T, Bonn, Germany).

We used X-ray fluorescent spectroscopy (XFS) to estimate the element composition of the synthesized glasses. The measurements were carried out using a TESCAN VEGA3-LMU scanning electron microscope (TESCAN ORSAY HOLDING, Brmo, Czech Republic) equipped with an X-MAX-50 EDS detector (Oxford Instruments, Abingdon, UK) at 30 kV voltage.

The absorption spectra were recorded using a JASCO V-770 spectrophotometer (JASCO Corporation, Tokyo, Japan) in the range of 190–2700 nm. The absorption spectra were obtained using a Bruker Tensor 27 FT-IR spectrometer (Bruker, Berlin, Germany) in the 1.25–27.00  $\mu$ m range.

The refractive index of glass samples was measured on a Metricon 2010 refractometer (Metricon, Pennington, NJ, USA). The measurement method was based on determining the critical angle of incidence at which light began to penetrate the sample volume through the surface of the measuring prism, similar to the Abbe refractometer. The refractive index was measured at three wavelengths: 633, 969, and 1539 nm.

Glass transition ( $T_g$ ), crystallization ( $T_c$ ), and melting ( $T_m$ ) temperatures were determined by differential scanning calorimetry (DSC) using an SDT Q-600 thermal analyzer (TA Instruments, New Castle, DE, USA) at 10 °C/min rate from RT to 800 °C. Aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) was used as a reference. For analysis, glass samples were preliminarily ground into powder. At the same time, thermogravimetric analysis was performed to assess the volatilization of glass components.

The structure of the glasses was studied using Fourier transform IR spectra and Raman spectra (RS). FT-IR spectroscopy was performed on a Bruker Tensor 27 spectrometer (Bruker, Berlin, Germany). For FT-IR measurements, the glass samples were ground into a fine powder and then mixed with KBr powder in a weight ratio of 0.01:0.19. The prepared mixture was pressed into pellets, which were immediately measured (in the range of 400–8000 cm<sup>-1</sup>) to avoid exposure to atmospheric moisture. Raman spectra were recorded in the 80–3500 cm<sup>-1</sup> range using standard laser excitation on a Vertex 70 FT-IR spectrometer with the Raman module RAM II (Bruker, Berlin, Germany) equipped with a 1064 nm neodymium laser. The laser power was 350 mW. Powder preparations were used for Raman measurements.

The glass density was determined using the hydrostatic weighing method with a MERTECH M-ER 123 ACF JR balance and special equipment (MERTECH, Moscow, Russia).

Vickers hardness of glasses was measured by indenting a diamond pyramid with a square base and an angle between the faces equal to 136°. To increase the statistical reliability, the measurements were carried out 5 times for each of the four weight loads (50, 100, 150, and 200 g), and the measurement results were averaged. For each point, the average deviation was calculated, and these were then averaged. Samples were measured using a PMT-3 tester (LOMO, St. Petersburg, Russia).

### 3. Results and Discussion

### 3.1. Glass Composition and Structure Characterization

The compositions of the obtained glasses are shown in Figure 1.



**Figure 1.** The compositions of glasses in the PbCl<sub>2</sub>–PbO–B<sub>2</sub>O<sub>3</sub> system: 1—our work; 2—[2]; 3—[12]; 4—[13,14]; 5—[5]; 6—[15]; 7—[16]; 8—[4,10,11].

The diffraction patterns of the synthesized glasses confirmed the amorphous nature of the samples (Figure 2).



Figure 2. XRD patterns of glasses in the *x*PbCl<sub>2</sub>–(50-0.5*x*)PbO–(50-0.5*x*)B<sub>2</sub>O<sub>3</sub> system.

Figure 2 shows that the glass halo underwent significant changes upon the addition of PbCl<sub>2</sub>, which indicated a change in the short-range order structure. We assumed that at high PbCl<sub>2</sub> concentrations, the local glass structure tended toward the structure of crystalline PbCl<sub>2</sub> but with a greater degree of disorder, which was specific for the glassy state (Figure S1) [17,18]. Heavily doped glasses (>20%) were possibly partly crystallized (nanocrystals formation), but the limited resolution of the patterns did not allow a clear conclusion. When glasses with a PbCl<sub>2</sub> content of more than 40% were synthesized, partial

crystallization of the melt occurred with the formation of the PbCl<sub>2</sub> phase (Figure S1). The PbCl<sub>2</sub> phase was rhombic (space group *Pnma*, *a* = 7.623 Å, *b* = 9.048 Å, *c* = 4.535 Å, *Z* = 4). Card ID 01-084-1177 (MATCH) or pdf 26-1159 PCPDFWIN.

The synthesis of oxychloride glasses is complicated due to the high hygroscopicity of Cl-containing components. In the process of glass melting, in addition to direct volatilization, pyrohydrolysis occurs [4]:

$$PbCl_2 + H_2O \rightarrow PbO + 2HCl\uparrow$$
(1)

An exchange reaction is also possible [19]:

$$3PbCl_2 + B_2O_3 \rightarrow 3PbO + 2BCl_3\uparrow$$
(2)

The results of the elemental analysis (Table S1) showed that the Cl/Pb ratio in the synthesized glasses remained almost the same as in the initial batch (Figure 3).



**Figure 3.** Comparison of Cl/Pb ratio in the batch and glasses synthesized in the *x*PbCl<sub>2</sub>–(50-0.5*x*)PbO–(50-0.5*x*)B<sub>2</sub>O<sub>3</sub> system.

To evaluate the volatilization of the glass components during synthesis, we applied a direct weighing technique. It was shown that volatilization remained almost constant for all compositions with PbCl<sub>2</sub> below 35 mol% (Figure 4). Thus, we assumed that  $B_2O_3$  and water volatilized simultaneously with PbCl<sub>2</sub>. However, there was no way to confirm this assumption, since the XFS technique is limited in detecting light elements such as boron ( $Z_B = 5$ ). This is the reason that the data in Table S1 are presented in the form of ratios of elements.



**Figure 4.** Volatilization of glass components from the melt during synthesis depending on PbCl<sub>2</sub> content for glasses in the xPbCl<sub>2</sub>–(50-0.5x)PbO–(50-0.5x)B<sub>2</sub>O<sub>3</sub> system. The line provides a guide for the eyes.

The synthesized glasses contained a small amount of aluminum (Table S1) because of the dissolution of the corundum crucible by the aggressive PbO-based melt. However,  $Al_2O_3$  has a positive effect on the spectral and mechanical properties of glasses due to it being a network former [20]. We did not observe significant losses of PbCl<sub>2</sub> during synthesis, which made it possible to correctly describe the physicochemical properties of the glasses based on their batch composition.

The glass structure was studied by Raman spectroscopy in the 80–3500 cm<sup>-1</sup> range, which was divided into 3 parts for detailed analysis: 80–250 cm<sup>-1</sup> (Figures 5, S2 and S3), 250–1750 cm<sup>-1</sup> (Figure 6), and 1750–3500 cm<sup>-1</sup> (Figure S4). In Raman spectroscopy, vibrations with wavenumbers less than 400 cm<sup>-1</sup> are usually attributed to vibrational modes associated with heavy metal atoms. In addition, the frequencies of halide compounds with predominantly ionic bonds are generated in this range [21,22].



**Figure 5.** Raman spectra of *x*PbCl<sub>2</sub>–(50-0.5*x*)PbO–(50-0.5*x*)B<sub>2</sub>O<sub>3</sub> glasses (80–250 cm<sup>-1</sup> range).



Figure 6. Raman spectra of *x*PbCl<sub>2</sub>-(50-0.5*x*)PbO-(50-0.5*x*)B<sub>2</sub>O<sub>3</sub> glasses (250-1750 cm<sup>-1</sup> range).

We observed a broadened peak in the 80–250 cm<sup>-1</sup> range (Figure 5), which was a superposition of several fundamental modes and a bosonic peak [4,23]. The assignment of vibrational modes to the corresponding structural groupings is presented in Table 1. The observed broadened peak underwent significant changes depending on the glass composition. For the 50PbO–50B<sub>2</sub>O<sub>3</sub> glass composition, we observed 4 main modes at 80, 90, 105, and 135 cm<sup>-1</sup> (Figure S2). These were the result of bending vibrations in PbO<sub>4</sub> structural units [23], stretching of the ionic component of the Pb–O bond [24], Pb<sup>2+</sup> cations in the glass network [25], and covalent symmetric stretching of the Pb–O bond in PbO<sub>4</sub> tetrahedra [26], respectively. In lead borate glasses with a high PbO content,  $[PbO_4]^{2-}$  pyramids are glass network-forming units and most of the lead went into building these pyramids. The rest of the lead acted as a charge compensator in the form of free Pb<sup>2+</sup> ions. [PbO<sub>4</sub>]<sup>2-</sup> units preferentially bridge bonds with BO<sub>3</sub> groups rather than BO<sub>4</sub> groups [25]. The dominant units in these glasses are BO<sub>3</sub> and [PbO<sub>4</sub>]<sup>2-</sup> with Pb–O–B bridges between

them. The introduction of lead chloride caused a sharp decrease in mode intensity around 135 cm<sup>-1</sup>, indicating the destruction of these bridges [25].

In addition, local peaks with maxima at 80 and 90  $\text{cm}^{-1}$  were strongly smoothed and had reduced intensities, which also indicated the disappearance of  $PbO_n$  units in the glass network. On the other hand, we observed a generation of new bands at 91, 105, and 120 cm<sup>-1</sup>. They belonged to vibrations of Cl<sup>-</sup> [27] ions, Pb<sup>2+</sup> [28] cations, and stretching vibrations of the Pb-Cl bond [29]. The further growth of PbCl<sub>2</sub> concertation up to 40 mol% resulted in the generation of new modes at  $150-180 \text{ cm}^{-1}$  [27], while the modes related to the structural units of PbOn practically disappeared. Cl<sup>-</sup> acts as a non-bridging anion and two halogen anions replace one  $O^{2-}$ . This leads to the destruction of  $[PbO_4]^{2-}$  units and the formation of Pb<sup>2+</sup> cations. The appearance of Raman bands related to vibrations of chlorine anions and the Pb-Cl bond directly indicated the formation of new chlorine- and lead-containing structural units. It was suggested that such units could be presented as  $Cl^{-}Pb^{2+}[BO_{4/2}]^{-}$  complexes [2]. This composition of structural units could be explained by the fact that chlorine entered the glass network only in interstitial positions and acted as a non-bridging anion in the glass network [2,25]. Because the strength of an ionic bond is inversely proportional to the square of the ionic radius, substitution of O<sup>2-</sup> with  $r_{O^{2-}} = 1.40$  Å by Cl<sup>-</sup> with  $r_{Cl^-} = 1.81$  Å further weakened the bonds in the glass network. Thus, depolymerization and weakening of the glass network occurred with the formation of isolated ion-containing structural units.

Table 1. Interpretation of Raman bands in glasses.

	Range of 80−250 cm <sup>−1</sup>		Range of 250–1750 cm <sup>-1</sup>				
Wavenumber, $\mathrm{cm}^{-1}$	Interpretation	Reference	Wavenumber, cm <sup>-1</sup>	Interpretation	Reference		
80	Bending vibrations in structural units of PbO <sub>4</sub>	[23,30]	310	Vibrations of $[PbO_4]^{2-}$ units	[23,31]		
90	Stretching of predominantly	[23 24]	476	Pb-O bond vibrations	[32,33]		
20	ionic Pb–O bonds in polyhedral PbO <sub>n</sub> units		570	Oscillations of borate tetrahedrons BØ <sub>4</sub> <sup>-</sup>	[23,25]		
91	Vibrations associated with	[21,22,27,34,35]	620	Deformation modes of BO <sub>3</sub> metaborate chains	[23,26]		
	PbCl <sub>2</sub> , presumably Cl		710	BO <sub>3</sub> deformation modes in ring metaborate groups	[23,26]		
105	Cations Pb <sup>2+</sup>	[25,28,36]	870	Oscillations $BØ_4^-$ in pentaborate groups	[26,37]		
120	Pb-Cl stretching vibration	[22,29],	910	Oscillations $BØ_4^-$ in ortho- and pentaborate groups	[26,37]		
135	Symmetric Pb–O stretching in the [PbO <sub>4</sub> ] <sup>2–</sup> pyramid configuration	[25,26,32,38]	980	Oscillations $BØ_4^-$ of diborate groups	[26,39,40]		
150–180	Valence vibrations of Pb–Cl, bending vibrations of the Pb–Cl bond	[22,27,32,34,35,41]	1050 1075	Oscillations $BØ_4^-$ of diborate groups Oscillations $BØ_4^-$ of diborate groups	[23,39,40] [23,39]		
	i berbola		1285	(BØ <sub>2</sub> O <sup>-</sup> ), mostly forming chain structures. A minor fraction: BØ <sub>3</sub> extensions	[23,25,33]		

We observed several characteristic bands related to different groups in the glass structure in the 250–1750 cm<sup>-1</sup> range (Figure 6). An increase in PbCl<sub>2</sub> content resulted in a decrease in band intensities.

The band around  $310 \text{ cm}^{-1}$  indicated the existence of PbO<sub>4</sub> polyhedral units in the network [23]. This was caused by the superposition of two bands centered at 280 and 330 cm<sup>-1</sup>, which were attributed to vibrations of these units in PbO crystals with orthorhombic and tetragonal symmetry, respectively [18]. The decrease in the band intensity indicated the destruction of PbO<sub>4</sub> tetrahedra in the network with PbCl<sub>2</sub> content growth. The band at 476 cm<sup>-1</sup> was also assigned to Pb–O bond vibrations and it underwent similar changes [33].

The 570 cm<sup>-1</sup> band was associated with the borate tetrahedron ( $BO_4^-$ ) and it decreased with PbCl<sub>2</sub> content growth. The BO<sub>3</sub>—PbO<sub>4</sub> bridge bond formed a fourfold coordination of boron with oxygen [23].

Bands at 620 and 710 cm<sup>-1</sup> were assigned to the deformation modes of metaborate chains and rings, respectively [23,26,37]. They also lost their intensity with PbCl<sub>2</sub> content

growth. However, the band at 710 cm<sup>-1</sup> conserved its shape even for systems with 40 mol% of lead chloride, which indicated greater stability of the ring metaborate groups.

The 870 and 910 cm<sup>-1</sup> bands decreased while the PbCl<sub>2</sub> content grew to 20 mol% and then remained constant with further PbCl<sub>2</sub> content growth. The 980, 1050, and 1075 cm<sup>-1</sup> bands referred to the presence of  $BØ_4^-$  in diborate groups and showed a similar evolution with PbCl<sub>2</sub> content growth.

The 1285 cm<sup>-1</sup> band referred to B-O<sup>-</sup> extensions in metaborate triangles (B $\emptyset_2$ O<sup>-</sup>), mostly forming chain structures, and to B $\emptyset_3$  stretching. The band intensity strongly decreased with PbCl<sub>2</sub> content growth.

For the 50-50 glass composition, the intensity of the bands related to the  $BO_4^-$  vibrations was noticeably lower than for the bands related to the  $BO_3$  vibrations, primarily at 710 and 1285 cm<sup>-1</sup>. We observed a reduction in the  $I_{710}/I_{1285}$  ratio with PbCl<sub>2</sub> content growth resulting from destruction of the Pb-O bond. The glass network was rearranged to a more ionic and depolymerized one, with the gradual replacement of  $BO_3$  groups by  $BO_4$ groups [25].

In the range up to  $3500 \text{ cm}^{-1}$  (Figure S4), only water oscillations were observed.

The FT-IR spectra showed several bands (Figures 7 and S5), interpreted in Table 2.



Figure 7. FT-IR spectra of synthesized glasses.

The 470 cm<sup>-1</sup> band referred to the vibrations of Pb<sup>2+</sup> cations and its intensity increased with PbCl<sub>2</sub> content growth. The 660 cm<sup>-1</sup> band referred to vibrations of free BO<sub>4</sub> groups. It was practically absent in the 50-50 glass but it manifested itself and increased with PbCl<sub>2</sub> content growth.

The 691 cm<sup>-1</sup> band was associated with B-O vibrations in the PbO—BO<sub>3</sub> bridge and the band intensity rapidly decreased with PbCl<sub>2</sub> content growth, which directly indicated the destruction of PbO<sub>4</sub> tetrahedra.

Peaks in the 800–1200 cm<sup>-1</sup> range referred to vibrations of the B–O bond in units of BO<sub>4</sub>. The bands were retained and even slightly increased with PbCl<sub>2</sub> content growth, which indicated the retention of BO<sub>4</sub> units in the grid.

Peaks in the 1300–1700 cm<sup>-1</sup> range were attributed to bond fluctuations in the BO<sub>3</sub> groups. Their intensities decreased with PbCl<sub>2</sub> content growth, which indicated the destruction of the corresponding structural units.

We should note that the FT-IR data were in full agreement with the Raman spectroscopy data.  $PbCl_2$  content growth resulted in the generation of new lead-chloride structural-chemical units, accompanied by a significant decrease in concentrations of BO<sub>3</sub> groups and PbO<sub>4</sub> tetrahedra.

Wavenumber, ${ m cm}^{-1}$	Corresponding Vibrational Mode	Reference
~466	Lead cation oscillations Pb <sup>2+</sup>	[42,43]
~560	Oscillations of free BO <sub>4</sub> groups	[44]
~610	bending vibrations of the $B-O-B$ bonds in the $BO_3$ group	[45]
~691	B-O oscillations associated with the PbO—BO <sub>3</sub> bridge in the lead borate network	[45,46]
~760	Bending vibrations of the O <sub>3</sub> B–O–BO <sub>4</sub> bond	[5]
~800–1200	Tensile vibrations of the B–O bonds of the tetrahedral block $BO_4$ in ortho-, pyro-, and metaborate groups	[5,45,46]
970	Tensile vibrations of $B-O$ bonds in $BO_4$ groups	[45,46]
~1050–1150	Tensile B-O oscillations in $BO_4$ units from tri-, tetra-, and pentaborate groups	[4,5]
1300-1700	Bond fluctuations in BO <sub>3</sub> groups	[4,5,45,46]
~1505, 1559, 1611	Asymmetric relaxations of B–O bond stretching of BO <sub>3</sub> trigonal blocks	[44]
~2350	Asymmetric modes of $CO_2$ stretching	[47]
~3445	Stretching vibrations of OH <sup>-</sup> groups	[4,44,47]

Table 2. Interpretation of FT-IR bands in glasses.

# 3.2. DSC Characterization and Physical Properties

The presented DSC data (Figures 7, S6–S10, Table 3) led us conclude that for the glasses of this system, the glass transition temperature ( $T_g$ ) decreased with PbCl<sub>2</sub> content growth. For the boundaries of PbCl<sub>2</sub> composition, the difference was 80 °C. Such a significant change in the glass transition temperature ( $T_g$ ) has been observed by other researchers and was attributed to structural changes in the glass network [16,48,49].

Table 3. Glass characteristic temperatures \*.

Glass Composition, mol%	$T_{g\prime} ^{\circ} \mathbf{C}$	$T_{x1}$ , °C	$T_{c1}$ , °C	$T_{x2}$ , °C	$T_{c2}$ , °C	$T_{m1}$ , °C	$T_{m2}$ , °C	$\Delta T = (T_{x1} - T_g), ^{\circ}\mathbf{C}$
50PbO-50B <sub>2</sub> O <sub>3</sub>	331	-	-	-	-	-	-	-
10PbCl <sub>2</sub> —5PbO-45B <sub>2</sub> O <sub>3</sub>	327	405	427	485	540	522	601	78
20PbCl <sub>2</sub> -40PbO-40B <sub>2</sub> O <sub>3</sub>	303	402	447	-	-	383	604	99
30PbCl <sub>2</sub> -35PbO-35B <sub>2</sub> O <sub>3</sub>	279	408	436	-	-	390	470	129
40PbCl <sub>2</sub> -30PbO-30B <sub>2</sub> O <sub>3</sub>	251	381	397	428	-	381	467	130

\*—the determination error for all characteristic temperatures was  $\pm 1$  °C.

The incorporation of halogen ions (Cl, Br, I) into the gaps of the borate network led to a violation of the order of the BO<sub>3</sub> groups. The overall disorder in halogen-doped glass occurred mainly due to the expansion of the boron–oxygen network [50,51]. Glasses with PbCl<sub>2</sub> concentrations < 20 mol% consisted mainly of BO<sub>3</sub> units, which had a relatively open structure. The large Cl<sup>-</sup> ions could be easily incorporated in the network only in interstitial positions. With the further addition of PbCl<sub>2</sub> (>20 mol%), the B–O network began to expand due to PbCl<sub>2</sub>. The network retained its connectivity, but it contained large voids that allowed the placement of Cl<sup>-</sup> ions. The expansion of the B–O network, and hence the progressive weakening of the structure, manifested itself in a significant decrease in the glass transition temperature ( $T_g$ ) [16]. This mechanism was confirmed by our structural studies.

At the same time, the DSC curves showed that the characteristics of crystallization in the studied glasses changed. The 50PbO–50B<sub>2</sub>O<sub>3</sub> sample did not exhibit an exothermic peak corresponding to crystallization. However, we observed a broadened exothermic peak of crystallization with PbCl<sub>2</sub> content growth. A further increase in PbCl<sub>2</sub> content resulted in the splitting of the peak into two components. At 40 mol% PbCl<sub>2</sub>, we observed only the crystallization peak with a lower  $T_c$ .

The lead borate oxychloride glasses demonstrated two endothermic peaks at continuous heating, marked as  $T_{m1}$  and  $T_{m2}$  (Figure 8). This indicated the stepwise nature of the glass softening. We observed the final melting temperature of the studied glasses at  $\leq 600 \,^{\circ}$ C, which made it possible to classify these glasses as low-melting glasses (Figures S6–S10).



Figure 8. DSC curves of synthesized glasses.

One of the most important criteria for glasses is the thermal stability coefficient ( $\Delta T$ ), defined as the difference between the onset of crystallization ( $T_x$ ) and glass transition ( $T_g$ ) [52] temperatures (Table 3). For all glass compositions,  $\Delta T$  was higher than 70 °C. This meant that the studied glasses were resistant to crystallization. An increase in  $\Delta T$  indicated an increase in glass stability with PbCl<sub>2</sub> content growth [53–55].

According to the TGA data, volatilization of the studied glasses began in the temperature region of 540–630 °C, and PbCl<sub>2</sub> content growth intensified the volatilization (Figure 9). In contrast, the 50PbO–50B<sub>2</sub>O<sub>3</sub> glass did not volatilize up to 800 °C. Since the crystallization of the corresponding compositions occurred before active volatilization had begun, one could conclude that it was possible to create glass-crystalline materials based on glasses without changing the chemical composition.



Figure 9. Results of thermogravimetric analysis of synthesized glasses.

Based on the data from measuring the density ( $\rho$ ) of the glass samples, the molar volume V<sub>m</sub> was calculated using formula (3):

$$V_{\rm m} = M/\rho, \tag{3}$$

where M is the average molecular weight of the glass [9].

The glass density gradually decreased with increasing  $PbCl_2$  content in glass (Figure 10). In similar oxychloride glass systems [5,16,49], the same dependencies were observed.



**Figure 10.** Dependence of density (black) and molar volume (blue) on the content of  $PbCl_2$  in  $xPbCl_2-(50-0.5x)PbO-(50-0.5x)B_2O_3$  glass.

An increase in PbCl<sub>2</sub> concentration caused the density decrease and molar volume growth that were associated with a change in the structure of the glass network [5]. The big Cl<sup>-</sup> ion occupies more space than the smaller  $O^{2-}$  and expands the glass network, thereby increasing the molar volume [9,12], which was consistent with the data on the glass structure.

Glass samples containing a larger amount of PbCl<sub>2</sub> had lower Vickers hardness (Figures 11 and S11). Similar results for the same glass systems were presented in [14,48]. The transition from triangular BO<sub>3</sub> groups to tetrahedral BO<sub>4</sub> groups reduced the hardness and increased the non-bridging oxygens in binary [56] and ternary [57] borate glass systems. The trend towards a decrease in Vickers hardness with increased PbCl<sub>2</sub> composition was associated with the formation of a larger number of depolymerizable boron structural units and a decrease in the rigidity of covalent bonds within them [58]. According to [20], the Vickers hardness of lead borate glasses mainly depends on the nature of the types of lead and boron structural units present in the glasses.



**Figure 11.** Dependence of Vickers hardness on the content of  $PbCl_2$  in  $xPbCl_2-(50-0.5x)PbO-(50-0.5x)B_2O_3$  glass. The line is guide for the eyes.

# 3.3. Optical Properties

The optical absorption spectra obtained in the UV, visible, and near-IR regions of the glasses under study are shown in Figure 12. The optical absorption coefficient,  $\alpha(\lambda)$ , was calculated from the absorption,  $A(\lambda)$ , based on the following relation [9]:

$$\alpha(\lambda) = 2.303 \frac{A(\lambda)}{d},\tag{4}$$

50 40 Absorption coefficient, cm<sup>-1</sup> 50PbO-50B,O, 10PbCl<sub>2</sub>-45PbO-45B<sub>2</sub>O<sub>3</sub> 40 30 20PbCl<sub>2</sub>-40PbO-40B<sub>2</sub>O<sub>2</sub> 30PbCl<sub>2</sub>-35PbO-35B<sub>2</sub>O<sub>2</sub> 30 20 40PbCl\_-30PbO-30B\_O 20 10 500 400 450 10 350 0 500 1000 1500 2000 2500 Wavelength, nm

where *d* is the thickness of the glass sample.

Figure 12. Optical absorption spectra of synthesized glasses. Enlarged fragment in the inset.

On the other hand, the optical absorption coefficient,  $\alpha(\nu)$ , for amorphous materials is given by the Tauc equation [13]:

$$\alpha(\nu) = const \left[ \frac{\left( h\nu - E_g \right)^2}{h\nu} \right],\tag{5}$$

where hv is the photon energy and  $E_g$  is the optical energy gap. Thus, based on the Tauc plots (Figure 13), the optical gap ( $E_g$ ) of the studied glasses was estimated.



Figure 13. Tauc plots of optical absorption spectra of synthesized glasses.

The Tauc energy (optical band gap) increased linearly with an increase in the PbCl<sub>2</sub> content (Figure 14). This was the reason for the shift of the short-wavelength absorption edge of the glasses to the UV region (inset in Figure 12, Table 4).

The absorption edge in oxide glasses corresponds to the transition of an oxygen electron to the excited state [59]. The more weakly these oxygen electrons are bound, the more easily absorption occurs. In glasses, non-bridging oxygen is more negative than bridging oxygen. Increasing the proportion of ionized oxygen by converting it from bridging to non-bridging oxygen raises the valence band top, which leads to a decrease in the band gap ( $E_g$ ) [60].



**Figure 14.** Dependence of the optical band gap on the PbCl<sub>2</sub> content in glasses. The line provides a guide for the eyes.

Table 4. Optical properties of glasses.

Glass Composition, mol%	Short- Wavelength Absorption Edge λ, nm	Tauc Energy E <sub>g</sub> , eV *	Urbach Energy E <sub>e</sub> , eV *	Average Absorption Coefficient, cm <sup>-1</sup>	Long- Wavelength Absorption Edge λ, nm	Absorption of the OH <sup>–</sup> Group Band, cm <sup>–1</sup>
50PbO-50B <sub>2</sub> O <sub>3</sub>	365	3.307	0.468	5.7	3611	15.5
5PbCl2-47.5PbO-47.5B2O3	365	3.320	0.393	3.6	3626	22.0
10PbCl <sub>2</sub> -45PbO-45B <sub>2</sub> O <sub>3</sub>	363	3.327	0.504	4.7	3664	22.4
15PbCl <sub>2</sub> -42.5PbO-42.5B <sub>2</sub> O <sub>3</sub>	360	3.378	0.432	4.4	3690	20.3
20PbCl <sub>2</sub> -40PbO-40B <sub>2</sub> O <sub>3</sub>	360	3.376	0.435	5.0	3739	12.4
25PbCl <sub>2</sub> -37.5PbO-37.5B <sub>2</sub> O <sub>3</sub>	359	3.389	0.505	5.2	3788	11.9
30PbCl <sub>2</sub> -35PbO-35B <sub>2</sub> O <sub>3</sub>	357	3.406	0.377	2.4	4349	14.6
33PbCl <sub>2</sub> -33PbO-34B <sub>2</sub> O <sub>3</sub>	356	3.414	0.453	4.6	4370	10.9
35PbCl <sub>2</sub> -32.5PbO-32.5B <sub>2</sub> O <sub>3</sub>	356	3.423	0.434	4.4	4462	9.5
40PbCl <sub>2</sub> -30PbO-30B <sub>2</sub> O <sub>3</sub>	355	3.440	0.427	3.8	4710	9.4

\*—the determination errors for  $E_g$  and  $E_e$  were  $\pm 0.005$  eV.

In our case, the increase in the optical energy gap ( $E_g$ ) with PbCl<sub>2</sub> content growth could be explained by a decrease in the content of non-bridging oxygen together with BO<sub>3</sub> groups. On the other hand, the expansion of the band gap can be explained in terms of the  $E_g$  values of the initial glass components:  $E_g^{PbO} = 2.8 \text{ eV}$ ;  $E_g^{B_2O_3} = 5.4 \text{ eV}$ ; and  $E_g^{PbCl_2} = 4.9 - 5.0 \text{ eV}$  [61].

The absorption coefficient,  $\alpha(\nu)$ , in amorphous materials in the optical region near the absorption edge at a certain temperature obeys an empirical relation known as the Urbach rule [62]:

$$\alpha(\nu) = \alpha_0 exp(h\nu/E_e), \tag{6}$$

where hv is the photon energy,  $\alpha_0$  is a constant, and  $E_e$  is the energy, which is interpreted as the width of the localized state in the normal bandgap known as the Urbach energy. The Urbach energy values were obtained by finding the reciprocal of the tangent of the slope of the graph plotted in the  $ln(\alpha(v)) - hv$  coordinates and are presented in Table 4.

The origin of exponential absorption is still a matter of debate, but it is generally believed that random potential fluctuations are associated with any lattice distortions, which can affect the Urbach energy by the generation of energy states within the band gap [13]. The nonlinear change in the Urbach energy depending on the PbCl<sub>2</sub> concentration may have been due to the uneven distribution of defects in the studied glasses. Similar results for the Urbach energy were presented in [5,9].

For the mid-IR spectrum range, we found that an increase in PbCl<sub>2</sub> concentration shifted the long-wavelength absorption edge to the IR region (Figure 15, Table 4) due to the replacement of atoms with a low atomic number (B,  $Z_B = 5$ ) by atoms with a high atomic number (Pb,  $Z_{Pb} = 82$ ). The glass matrix became heavier when we increased the

total concentration of lead compounds (PbCl<sub>2</sub> and PbO). This resulted in the shift of the long-wavelength absorption edge in the IR region and the expansion of the transparency range of the glasses [63]. The addition of a low-energy phonon component (PbCl<sub>2</sub> is  $230 \text{ cm}^{-1}$  compared to borate glass ~1500 cm<sup>-1</sup>) also increased the transparency range in the IR region.



Figure 15. Optical absorption spectra of synthesized glasses in the range from 1500 to 5000 nm.

We observed a decrease in the intensity of the absorption band of hydroxyl groups with PbCl<sub>2</sub> content growth (Figure 15, Table 4). According to the FT-IR spectroscopy results of the starting reagents,  $B_2O_3$  had the largest content of OH<sup>-</sup> groups (Figure S12). To reduce the content of OH<sup>-</sup> groups, it is possible to use dry boron oxide [64] and bubble the melt with dry oxygen [65].

The theoretical refractive index of the studied glasses, (*n*), was calculated using Equation (7) [38]:

$$n = \chi(PbCl_2) \cdot n(PbCl_2) + \chi(PbO) \cdot n(PbO) + \chi(B_2O_3) \cdot n(B_2O_3), \tag{7}$$

where  $\chi(PbCl_2)$ ,  $\chi(PbO)$ , and  $\chi(B_2O_3)$  are the molar fractions of the corresponding glass components;  $n(PbCl_2)$ , n(PbO), and  $n(B_2O_3)$  are the refractive indices of pure lead chloride, lead oxide, and boron oxide, respectively.

The refractive index was determined experimentally at three wavelengths: 633, 969, and 1539 nm (Table 5). The dispersions of the refractive index depending on the wavelength are presented in Figure S13.

Table 5.	The values	of the	calculated	and	experimental	refractive	indices	( <i>n</i> )	of	glasses	in	the
xPbCl <sub>2</sub> -(5	50-0.5x)PbO-	-(50-0.5	x) system.									

		<b>Refractive Ind</b>	ices (n)	
Glass Composition, mol%	Estimated,			
	±0.01	633 nm	969 nm	1539 nm
50PbO-50B <sub>2</sub> O <sub>3</sub>	2.04	1.914	1.895	1.890
5PbCl <sub>2</sub> -47.5PbO-47.5B <sub>2</sub> O <sub>3</sub>	2.05	1.969	1.930	1.903
10PbCl <sub>2</sub> -45PbO-45B <sub>2</sub> O <sub>3</sub>	2.06	1.989	1.949	1.932
15PbCl <sub>2</sub> -42.5PbO-42.5B <sub>2</sub> O <sub>3</sub>	2.06	1.991	1.963	1.940
20PbCl <sub>2</sub> -40PbO-40B <sub>2</sub> O <sub>3</sub>	2.07	2.009	1.969	1.954
25PbCl <sub>2</sub> -37.5PbO-37.5B <sub>2</sub> O <sub>3</sub>	2,08	2.017	1.978	1.960
30PbCl <sub>2</sub> -35PbO-35B <sub>2</sub> O <sub>3</sub>	2.09	2.040	2.000	1.981
33PbCl <sub>2</sub> -33PbO-34B <sub>2</sub> O <sub>3</sub>	2.09	2.051	2.010	1.991
35PbCl <sub>2</sub> -32.5PbO-32.5B <sub>2</sub> O <sub>3</sub>	2.10	2.058	2.016	1.997
40PbCl <sub>2</sub> -30PbO-30B <sub>2</sub> O <sub>3</sub>	2.10	2.076	2.032	2.013

The values of the calculated refractive index were slightly overestimated relative to the experimental ones. We assumed that this was due to some difference in the nominal and actual compositions of the glasses, primarily due to the incorporation of  $Al_2O_3$  (n = 1.70-0.76) into the glasses, as determined by XPS [66].

#### 4. Conclusions

For the first time we investigated the properties of glasses in the  $xPbCl_2-(50-0.5x)PbO-(50-0.5x)B_2O_3$  system with a wide range of PbCl<sub>2</sub> concentrations from 0 to 40 mol%. This allowed us to fill gaps in the fundamental data for the system under study, which has applications for the production of optical fibers with extended transmission ranges for use in medical lasers and telecommunication systems.

The introduction of PbCl<sub>2</sub> modified the structural network and led to drastic changes in the glassy network, resulting in a significant decrease in the numbers of BO<sub>3</sub> groups and PbO<sub>4</sub> tetrahedra,  $T_g$  reduction by 80 °C with a simultaneous increase in resistance to crystallization by 52 °C, glass molar volume growth of 30%, Vickers hardness reduction by 2 times, and refractive index growth from 1.9 to 2.1.

The decrease in bridge oxygen content with  $PbCl_2$  content growth resulted in the expansion of transparency in the UV region by 10 nm. The increase in heavy metal content in the glass matrix resulted in a decrease in the phonon energy, which resulted in the expansion of the IR range to 4700 nm.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www. mdpi.com/article/10.3390/ceramics6030083/s1, Figure S1. Comparison of XRD patterns of glasses in the *x*PbCl<sub>2</sub>–(50-0.5*x*)PbO–(50-0.5*x*)B<sub>2</sub>O<sub>3</sub> system with crystalline PbCl<sub>2</sub>; Table S1. The composition of glasses according to the XFS data; Figure S2. Decomposition of the 50PbO–50B<sub>2</sub>O<sub>3</sub> glass Raman spectrum into Gaussian; Figure S3. Decomposition of the 40PbCl<sub>2</sub>–30PbO–30B<sub>2</sub>O<sub>3</sub> glass Raman spectrum into Gaussian; Figure S4. Raman spectra of *x*PbCl<sub>2</sub>–(50-0.5*x*)PbO–(50-0.5*x*)B<sub>2</sub>O<sub>3</sub> glasses (1750–3500 cm<sup>-1</sup> range); Figure S5. FT-IR spectra of synthesized glasses; Figure S6. DSC curve for glass composition 50PbO–50B<sub>2</sub>O<sub>3</sub> and characteristic temperatures; Figure S7. DSC curve for glass composition 10PbCl<sub>2</sub>–45PbO–45B<sub>2</sub>O<sub>3</sub> and characteristic temperatures; Figure S9. DSC curve for glass composition 30PbCl<sub>2</sub>–35PbO–35B<sub>2</sub>O<sub>3</sub> and characteristic temperatures; Figure S10. DSC curve for glass composition 40PbCl<sub>2</sub>–30PbO–30B<sub>2</sub>O<sub>3</sub> and characteristic temperatures; Figure S11. Dependence of Vickers hardness on the applied load in *x*PbCl<sub>2</sub>–(50-0.5*x*)PbO–(50-0.5*x*)B<sub>2</sub>O<sub>3</sub> glasses; Figure S12. FT-IR spectra of the initial reagents, with the indicated band of the OH<sup>-</sup> group; Figure S13. The dispersion of the refractive index of *x*PbCl<sub>2</sub>–(50-0.5*x*)PbO–(50-0.5*x*)B<sub>2</sub>O<sub>3</sub> glasses.

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