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Electrical and optical properties of glasses and glass-ceramics

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ABSTRACT

In this work, the electrical and optical properties of glasses and glass-ceramics are presented and discussed in details. Several electrical and optical parameters for glasses and glass-ceramics were determined. The conduction activation energy and DC conductivity depend on temperature, glass composition and concentration of glass modifiers. The optical properties of glasses and glass-ceramics containing Er^{3+} (or Er^{3+}/Yb^{3+}) ions have been analyzed for near-infrared luminescence centered at about 1.5 μm and up-conversion applications. In particular, luminescence bandwidths and lifetimes for the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} were determined as a function of host-matrices and then examined for near-infrared solid-state lasers and broadband optical amplifiers. The green up-conversion luminescence spectra for Er^{3+} and Er^{3+}/Yb^{3+} doped systems are temperature-dependent and can be used to optical sensors.

1. Introduction

Glasses and glass-ceramics belong to advanced functional materials. The processing, properties and applications of these materials have been presented and discussed in the excellent book published recently by Karmakar [1]. Their electrical and optical properties depend significantly on the local structure of the glass-host [2–6]. The structure and properties can be changed drastically during transformation from glasses to glass-ceramics under heat treatment process or laser irradiation [7]. Thus, transparent glass-ceramics can be applied to some optical devices. Electrically-insulating glass-ceramic materials can be used in magnetic media disks for hard disk drives, whereas some electrically-conducting glass-ceramics are promising solid electrolytes for batteries. Presence of semiconducting, ferroelectrical and nonlinear optical crystalline phases (preferred in nanometric scale) in glass-host, can fabricate quite interesting materials for different industrial applications. Furthermore, glass-ceramics due to their unique and wide range of potential electrical and optical properties possess many favorable features to successful commercial products, which was suggested by Zanotto [8].

Here, we present report on current state of the art in glasses and glass-ceramics. The work is divided into two parts. The first part deals with electrical properties of glasses and glass-ceramics. The conduction activation energy and DC conductivity in glass-hosts are compared in relation to temperature, glass composition and concentration of glass modifiers. The results for glass-ceramics are also presented and discussed. The second part is associated to optical properties of glasses and transparent glass-ceramics. The optically active ions are limited to the most popular and important Er^{3+} (or Er^{3+}/Yb^{3+}) ions [9,10] which were introduced to numerous glasses and glass-ceramics in relation to their potential applications as near-infrared solid-state lasers, broadband amplifiers and up-conversion luminescent systems used in the optical thermometry. The properties are compared to the results for different glasses and glass-ceramics reported in the literature.

2. Experimental details

2.1. Preparation of samples

Germanate glasses were synthesized with the following chemical composition (in mol%): (I) $45GeO_2$-$45PbO$-$9Ga_2O_3$-$1Er_2O_3$ and $45GeO_2$-$45PbO$-$4Ga_2O_3$-$1Er_2O_3$-$5Yb_2O_3$ (lead-based) and (II) $60GeO_2$-$30BaO$-$9Ga_2O_3$-$1Er_2O_3$ and $60GeO_2$-$30BaO$-$4Ga_2O_3$-$1Er_2O_3$-$5Yb_2O_3$ (lead-free). They were prepared by mixing and melting appropriate amounts of metal oxides of high purity (99.99%, Aldrich Chemical Co.). In order to prepare the glass samples, appropriate amounts of all components were mixed homogeneously together. Batches were weighted and stored in glove box, in a protective atmosphere of dried argon. Then, both lead-based and lead-free systems were melted at 1200 °C for 0.4 h. Pink glassy plates of 10 × 10 mm dimension were obtained. Each sample of 2 mm in thickness was polished for optical measurements. Glasses for electrical measurements were prepared using procedure given in [11–40].

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2.2. Characterization

The luminescence spectra and their decays were performed on a PTI QuantaMaster QM40 coupled with tunable pulsed optical parametric oscillator (OPO), pumped by a third harmonic of a Nd:YAG laser (Opotek Opolette 355 LD). The excitation and luminescence spectra were recorded using double 200 mm monochromators and multimode UVVIS PMT (R928) and Hamamatsu H10330B-75 detectors controlled by a computer. Resolution for luminescence spectra measurements was 0.5 nm. Luminescence decay curves were recorded and stored by a PTI ASOC-10 [USB-2500] oscilloscope with an accuracy of ± 1 μs. The up-conversion luminescence has been excited with cw laser-diode at 980 nm.

For electrical measurements, the polished glass samples were usually silver painted on both sides for good contacts with an appropriate electrodes (gold, platinum or copper). Electrical properties were measured using an appropriate electrometers and impedance analyzers. The experimental details are given in [11–40].

3. Results and discussion

3.1. Electrical properties

The electrical properties of different systems like glasses and glass-ceramics have been extensively studied [11–14]. Particular attention has been paid to the researches of materials for important application such as semiconductors, laser, solar energy converters and in number of electronic devices. The purpose of many studies is to examine the effect of the various factors on the electrical properties like DC conductivity and AC conductivity, dielectric constant, dielectric loss and electrical modulus. The main parameter DC conductivity could be evaluate by the following Arrhenius equation $\sigma_{dc} = \sigma_0 \exp(-E/kT)$, $\sigma_{dc} = \sigma_0 \exp\left(^{-E}/_{kT}\right)$ where σ_0 is a pre-exponential factor, E is a conduction activation energy, k is Boltzmann constant and T is thermodynamic temperature [15].

It is generally observed that the values of σ_{dc} strongly depend on temperature (Table 1). Furthermore, the influence of glass host on electrical properties was observed for different systems such as phosphate, borate and silicate. Table 2 presents the comparison of DC conductivity and conduction activation energy in relation to glass composition. Moreover, the kind of modifiers incorporated to host matrices and concentration of modifier ions are important factors that have been considered and well documented [16–18]. The study of sodium sulfo-phosphate glasses indicated the relationship between structural modifications in the glass network and electrical properties. It is known that the presence of modifier oxides like MgO, CaO and BaO in glass matrix leads to a disruption of the glass network and promotes the formation of non-bridging oxygens groups.

Furthermore, these network modifying ions influence the various electrical factors. The values of σ_{dc} for phosphate glasses containing CaO are slightly lower than for glass systems with MgO and BaO. However, the conduction activation energy changes in different direction. The highest value of E was determined for glasses containing calcium oxide and the lowest value of conduction activation energy was evaluated for glass systems doped with barium oxide. The obtained results for glasses with BaO modifier is related to the significant increase of ionic contribution due to an increase in the concentration of dangling bonds that have led to the substantial decrement in jump distance for sodium ions [19]. The dependence of structural and electrical properties of glasses was also observed for borate glass systems. The DC conductivity increases with an increase content of $BaCl_2$ whereas conduction activation energy decreases when BaO is replaced by $BaCl_2$ in glass composition. It was stated that $BaCl_2$ is acting as the network former so that Cl^- ions are participating in network formation and consequently the DC conductivity is increasing with the increase in Cl^- content [20]. Gedam and Ramteke [21] investigated the influence of CeO_2 addition on the electrical properties of lithium borate glasses. They stated that when B_2O_3 is replaced by CeO_2 in glass host the conductivity decreases.

Table 1
The comparison of DC conductivity in relation to temperature.

Glass composition	T [K]	σ_{dc} [Ω^{-1} cm^{-1}]	References
Alkalihalide borate	473	3.42E−12	[20]
	573	9.9E−12	[20]
Sodium borate	298	3.59E−09	[23]
	473	1.57E−05	[23]
	573	2.20E−04	[23]
	673	1.21E−03	[23]
Vanadate	303	4.7E−05	[29]
	473	2.17E−04	[29]

Table 2
The comparison of DC conductivity and conduction activation energy in relation to glass composition.

Glass composition	σ_{dc} [Ω^{-1} cm^{-1}]	E [eV]	References
Sodium sulfo-phosphate	1.40E−11	1.100	[19]
Alkali halide borate	1.38E−11	0.255	[20]
Lithium nickel borate	1.62E−08	0.730	[22]
Barium tellurite borate	9.33E−12	0.887	[28]
Vanadate	9.17E−05	0.200	[29]

On the other hand, the activation energy increases in relation to glass composition. The dependence of the conductivity on the activation energy suggests that the decrease in conductivity is directly related to the decrease in mobility of the monovalent lithium ions. The absence of polaronic conduction in these glasses can mainly be correlated with the contribution of Li^+ ions in the conduction process. Moreover, the effect of the alkaline earth modifiers ions (MO = BaO, CaO, MgO) in lithium nickel borate glass systems were evaluated by investigation of the electrical properties such as AC conductivity, dielectric constant and electrical modulus [22]. It was observed that the kind of modifier oxides influences the electrical parameters. For nickel-doped glasses studied the decrease of the AC conductivity from glass systems with BaO to glass with MgO was determined. The dependence of activation energy and kind of modifier oxides for borate glasses was opposite. The value of E was the highest for glass systems with MgO, while the lowest activation energy was obtained for glass with BaO. The decrease of the conductivity suggests that as the ionic radius of the modifying ion becomes smaller $Ba^{2+} \rightarrow Sr^{2+} \rightarrow Ca^{2+} \rightarrow Mg^{2+}$. Therefore, the variation of conductivity with the size of the modifier depends on the structural modifications of the glass system [22]. Moreover, it was indicated that electrical conductivities very slightly decreased with increasing the ionic radius of rare earth ions in sodium borate glasses [23].

It is worth noting that the influence of concentration modifiers and optical dopants on electrical properties of glass and glass-ceramics was also observed (Table 3). Ramesh Babu et al. [24] studied the effect of iron oxide Fe_2O_3 in lithium yttrium silicate glasses on electrical properties. The obtained results indicate that the AC and DC conductivities increase with increasing concentration of Fe_2O_3 in glass host. On the other hand, the values of activation energy decrease with the increase of iron oxide content. It is interesting to see that the value of electrical parameters strongly depend on structural properties in silicate glass systems. From this point of view, the decrease in activation energy and increase in the conductivity with increasing content of Fe_2O_3 is obviously caused by decreasing degree of augmented cross-links in the glass network. When the concentration of iron oxide increases from 0 to 0.5 mol%, the tetrahedral Fe^{3+} ions which form linkages with silicate units seem to be dominating. Furthermore, the decrease of conductivity and increase of activation energy in this concentration range are reason of a decrease of the mobility of the lithium ions.