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REVIEW

Advances in borate- and phosphate-based TL materials for in vivo dosimetry

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Abstract
Thermoluminescence (TL) materials are well known for a very large number of applications in various fields such as medical research, in vivo dosimetry, environmental dosimetry, personal dosimetry, etc. There are several TL materials available in the market such as fluoride, borate, phosphate, silicate, borosilicate glasses, etc. The TL properties of materials change with the doping of rare-earth and transition impurities in different hosts which are useful for different applications. These doped TL materials can be prepared by different techniques such as, the melt-quenching technique, combustion method, sol–gel method, and others. Radiations such as γ-rays, X-rays, β-rays, photon beam, electron beam, neutron beam, etc., can be used to irradiate these TL materials. In the present state of research, interest is being raised to develop new thermoluminescent materials for various applications in the field of material science and radiation therapy for in vivo dosimetry in view of the rise in the number of cancer patients across the globe. In the last few years, borate and phosphate-based TL dosimeters got more attention in radiation dosimetry. So, this review deals with the recent developments and advancements in borate- and phosphate-based TL materials for in vivo dosimetry.

Keywords Thermoluminescence · Dosimetry · Radiation · In vivo · Borate and phosphate glasses

1 Introduction

1.1 History of glasses

Glasses can be from ordinary jewelry beads to expensive artifacts to decorative window panes. There are several applications of different glasses depending on the requirements, and hence can be tailor made materials. The archeological evidence suggests that the first glass was made in coastal north Syria, Mesopotamia, or ancient Egypt [1]. There was a rapid growth in glass-making technology during the late bronze age in Egypt and western Asia. The development of glasses in India has begun in 1730BC [2]; the first site in India to manufacture the glasses was in Kopia, Uttar Pradesh between 700BC and 200AD [3]. The Indian glasses in this period differed significantly in chemical composition when compared to Roman and Chinese glasses [4].

In South Asia, glasses are being used as ornaments and casings since 100AD [5]. Although glass-making developed in China later than in Egypt and India, it played a very important role in arts and crafts making [6, 7]. In this period, the production of the glasses involved barium oxide (BaO) and lead (Pb), but the traditional use of BaO and Pb disappeared at the end of the Han Dynasty (220AD). The glass industry went through rapid technological growth in 100AD by Romans in Alexandria [8]. Colored glass production started in the Islamic world in 800AD and by the end of the eleventh century, clear glass mirrors were being manufactured in Islamic Spain. After the collapse of the western Roman empire, glass-making technologies emerged in northern Europe. Around 1000AD, the glass is made by potash obtained from wood ashes which is a breakthrough in north Europe. In the eleventh century, there was the emergence of new ways of making glass sheets in Germany.

1.2 Borate glass properties and applications

The borate glasses have more complex action and major differences in their optical properties than the Silicate glasses [9, 10]. The most important application of the borate glass

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over silicate is its low melting temperature (T_m) and low glass transition temperatures (T_g) [11]. Pure borate glasses have a glass transition temperature of approximately 260 ℃ [12] and a melting temperature of approximately 450 ℃ [13], which are very low as compared to silicate glasses. The pure form of borate glasses is not useful in most applications since they have very low chemical durability which can be increased by the addition of other oxides such as SiO_2, Al_2O_3, and alkali oxides. The addition of silica to the borate glasses leads to another type of glass which is known as borosilicate glass with a broad range of applications. These glasses have high chemical durability and electrical resistivity compared to the individual silicate and borate glasses. Borate glasses are preferred over silicate glasses in certain optical and photonic devices [14] due to their unique properties such as low melting temperatures, compatibility with rare-earth elements and transition metals, wide glass-forming range, and the second- and third-order nonlinearity [15–22]. Adding rare-earth oxides, such as La_2O_3, Pr_6O_{11}, Nd_2O_3, and Sm_2O_3 to the borate glasses, these glasses will show the Faraday effect [23] and this effect is a magneto-optical effect that involves the application of magnetic field; there is a rotation in the plane polarization plane of linearly polarized light.

The recent research on glasses is based on the advanced glasses for the use in insulation purposes, falcon for cosmetics and pharmaceuticals, renewable energy such as solar energy glasses, medical technology, optical glasses, biotechnology, and radiation protection such as X-ray and Gamma-ray protectors.

1.3 Radiation dosimetry

Radiation can be naturally occurring or man-made. The response of human being to radiation from different sources is subjected to the great scientific and promising field of study that can be understood. Radiation can be used in the medicinal field in the treatment of diseases such as cancer, in which even a small dose of radiation can cause damage to the living tissue or cell. Many factors affect the response of the human body to radiation such as the amount of radiation deposited in the tissue and the ability of the radiation to generate harm to the tissue. The value for the equivalent dose for a person by the international regulation is 1mSv/year [24, 25]. Therefore, it is very important to measure the absorbed dose for the treatment of cancer cells.

Thermoluminescence dosimetry (TLD) is one of the most useful techniques to measure the absorbed dose [26]. The TLD devices are used to monitor the radiation in different applications such as radiation therapy and the measurement of radiation leakage from isolated laboratories [27, 28]. There are many glass-based TLD devices are developed during the last few decades out of which borate-based TLDs are the most promising and useful thermoluminescence dosimeters. There is a continuous effort being made by the researchers to develop new materials for the advanced dosimetric properties to be used as efficient TLD materials over a wide range of radiation doses [29–31]. The borate-based glasses are also efficient in the field of radiation detection and thermoluminescence studies because of their near-human tissue absorption coefficient.

1.4 Developments in TLD materials

Thermoluminescence (TL) was first used in radiation dosimetry by Farrington Daniels in 1953 when introducing LiF as TL material [32] and that was patented as TLD-100 by Harshaw Chemical Company. Many new dosimetric glass materials have been reported over the last few decades that have different efficiencies for different dose ranges of radiation. Presently, there are many commercial dosimeters are available such as LiF: Mg, Cu, P (TLD-700H), Al_2O_3 (TLD-500), $CaSO_4$:Dy (TLD-900), and CaF_2:Dy(TLD-200) [33, 34]. Each of these dosimeters is not suitable for all ranges of doses as they depend on different factors such as linearity, reproducibility, dose rate, etc. Therefore, there is a need to develop a material that shows a TL response linearly over a wide range of doses and should satisfy all the requirements.

Over the last few decades, many new and dosimetrically useful TLD materials have been reported such as $Li_2B_4O_7$:Mn in 1965 [35], CaF_2:Dy in 1969 [36], Al_2O_3:Si,Ti in 1976 [37], CaF_2:Tm in 1977 [38], LiF:Mg,Cu,P in 1978 [39], $Li_2B_4O_7$:Cu in 1980 [40] and Al_2O_3:Cu in 1990 [41]. Recently, many research groups are involved in exploring new materials for advanced TLD applications. El-Adawy et al. studied the thermoluminescence characteristics of Ag-doped and undoped $Li_2B_2O_4$ (LB) glasses exposed to γ-radiation and observed a good fading response and linearity for 105 ppm Ag-doped LB glasses over the studied dose range [42]. Santiago and his colleagues studied the thermoluminescence and radio-luminescence properties of Dy-doped SrB_2O_4 glasses prepared by the sol–gel technique irradiated with the β-radiation source and it has been found that the TL and RL efficiency is high in Dy-doped metaborate and mixed borate and poor in tetraborates [43]. Ekdal et al. have reported Mn-doped $Li_2B_4O_7$ single crystal phosphor for TLD characteristics and found that the activation energy is about 1.21eV and the frequency factor of $3.71\times10^{11}S^{-1}$ [44]. Saidu et al. studied the thermoluminescence characteristics of Cu-doped $ZnLi_2B_2O_4$ glasses with the radiation dose varying from 0.5 to 4Gy and they have reported that the time-based thermal fading of the dosimeter is stable and it is having high potential ability to use in radiation processing dosimetry [45]. The dosimetric properties of Dy-doped $Li_2B_2O_4$ glasses irradiated by γ-radiation have been studied by different researchers, Ab Rashid et.al. [46], Bhaskar

Sanyal et.al. [47], and they found that Dy-doped LB glasses are having good linearity of regression coefficient which was useful for finding the quantitative estimation of absorbed dose, high reproducibility and high sensitivity compared to undoped glasses.

The neutron and gamma response of undoped and Dy-doped MgB_4O_7 thermoluminescent dosimeter has been studied by Iflazoglu et al., using computer glow curve deconvolution (CGCD) method [48] and they reported that MgB_4O_7:Dy (1 Mol%) has high sensitivity which is approximately 1.90 and 1.47 times than TLD-600 and TLD-700, respectively, which could be a promising material for the thermoluminescent neutron and gamma dosimeter. In similar material, Salama et al., using repeated initial rise (RIR) method [49], found that the dosimeter has high thermal fading and light sensitivity. The realization of Dy-doped $Li_2MgB_2O_4$ glasses as thermoluminescent solid detector and subjected to high dose dosimetry in the range 1–100Gy by irradiating to radio-active cobalt (Co-60) source was done by Hasim et al. [50, 51]. They reported that the dosimeter has minimal fading, high sensitivity, good linearity and reproducibility which indicates that the material is a good candidate for accurate radiation detection in photon beam. The neutron dosimetry of $LiMgBO_3:Dy^{3+}$ has been studied by Meghnath Sen et al., [52] and found that the TL sensitivity for neutron and gamma radiation is 0.6 and 0.3 times, respectively, than commercially available dosimeter TLD-100.

Further developed material for TLD applications is $NaBaBO_3:Ce^{3+}$ which was synthesized by the Combustion method by Mehmet Oglakci et al., [53] they concluded that the sample is a favorable material for the application in environmental dosimetry as one depicts good TL dose response with adequate linearity and sensitivity. Daisuke Nakauchi et al., have studied the optical and radio-induced luminescence properties of Ce^{3+}- and Sn^{+3}-doped $MgAl_2B_2O_7$ glasses, in the X-ray dose irradiated over 1–10Gy [54, 55] and reported that the TL intensity increases monotonically after the irradiation of X-rays with a dose of 1–10000mGy. Saidu et al., studied the thermoluminescence characteristics of Cu-doped $ZnLi_2B_2O_5$ and reported that the TL intensity had increased with the addition of Na within the dose range of 0.5–1000Gy [45, 56]. Ahmad et al., have reported the thermoluminescence dosimetric characteristics of Cu-doped $MgLi_2B_2O_5$ glasses which showed good linearity with a linear regression coefficient of 0.9980 and 0.9949, with the dose range of 1–10Gy and 10–100Gy, respectively [57]. Ismail Rammadhan and his colleagues have studied the thermoluminescence characteristics of Cu_2O-doped $CaLi_2B_2O_4$ glasses which were irradiated with ^{6} ℃o gamma rays having a range of 0.5–4Gy, 5–10Gy, and 20–100Gy and found the effective atomic number (Z_{eff}) as 8.84 which is nearer to the atomic number of soft tissues [58]. Salleh et al., have reported the effect of Strontium(Sr) concentration on the thermoluminescence glow curve of Cu-doped $MgLi_2B_2O_5$ glasses [59] and found that 0.003 Mol% of Sr has shown optimum TL intensity of 3.6×10^5 nCg^{-1}. Chopra et al., studied the TL properties of $Li_2B_4O_7$: Cu material prepared by combustion method and irradiated with a 3MeV proton beam [60] and according to their study, the sample has simple glow curve structure, good linearity and low fading makes it a good candidate for effective proton beam TL dosimeter for the treatment of cancer. Hossain et al., addressed the characteristics of Cu-doped and undoped $K_2B_4O_7$ glass for use as ionizing radiation dosimeters by studying the thermoluminescence response [61] and mentioned that the Cu-doped KB glasses have superiority in terms of linearity and sensitivity which is 6.75 times greater than undoped glasses. Prabhu et al., have investigated the structural and radiation shielding properties of Er^{+3}-doped zinc bismuth borate glasses by irradiating them with 1.25MeV gamma rays [62, 63] and reported that the glass shown the linearity in the dose range of 5–50kGy which proved their suitability for dosimetric applications in the food irradiation zones and in red LEDs.

Vijeta Bhatia et al., have developed Sm^{+3} and Er^{+3}-doped $MnK_2B_2O_5$ glasses and studied the structural, optical, and thermoluminescence properties [64, 65] and reported the high TL intensity recorded for 0.8Mol% Sm^{+3} under all irradiation sources with a good linear correlation factor of 0.997 which proves it is a suitable material for dosimetric applications. Anjaiah et al., have reported the preparation of Sm^{+3} and Eu^{+3}-doped $MLi_2B_2O_5$ (where M: Zn, Ca and Cd) glasses to study their absorption and luminescence properties to understand their lasing potentialities [66, 67]; they concluded that CdBSm glasses can be used as radiation dosimeters effectives as they exhibit high TL light output at high temperatures. Vinod Hegde et al., have studied the effects of high dose gamma irradiation on optical properties of Eu^{+3}-doped $ZnNa_2Bi_2B_2O_8$ glasses which shows TL linearity in the dose range 0.25–3kGy which proved their suitability for dosimetric application in the food irradiation zones in addition to the red LEDs (<1kGy) [68]. Sudhakar and his colleagues have studied the influence of modifier oxide (viz., PbO, CaO and ZnO) on spectroscopic and thermoluminescence characteristics of Sm^{+3}-doped $Sb_2B_2O_6$ glasses and found that ZnO mixed glasses has high non-radiative losses among three glasses [69]. Hayder Obayes et al., have reported the improved thermoluminescence and kinetic parameters of the new Sr/Cu-doped LB glass system in the dose range 0.5–100Gy; the material has excellent reproducibility and low fading useful for dosimetry applications [70].

Ono et al. have reported the preparation of Tb^{+3}-doped $CaAl_2B_2O_7$ glasses; studied the thermoluminescence properties by X-ray irradiation which found to show good linearity and sensitivity with dynamic range[71]. Ismail Mohammed et al., studied the effect of ZnO co-dopant on the thermoluminescence properties of Cu_2O-doped lithium borate glass and found that the TL properties of the dosimeter has enhanced in terms of sensitivity by 4 times, TL intensity by 3 times, fading, reproducibility, and minimum detectable dose which confirms that the dosimeter has potential to be used in dosimetry.[72]. Eman Mohammed et al. have studied the effect of gamma rays on Zn/Cu-doped $SrNa_2B_2O_5$ glass system for dosimetric applications in many fields such as food irradiation processing, irradiation applications, and medical sterilization [73]. Bahra Mohammed et al. have studied the thermoluminescence dosimetric properties and kinematic parameters of $ZnSiB_2O_6$ glass doped with Cu_2O and then co-doped with SnO_2 within the range 0.5–100Gy and concluded that 0.1Mol% SnO_2 co-doped glass is found to be useful in thermoluminescence dosimetry as it has high linearity, reproducibility, low thermal fading and minimum detectable dose [74]. El-Bayoumi et al. observed a well-resolved thermoluminescence peak at 168 ℃ observed in W-doped CdB_2O_3 glasses which are irradiated by gamma radiation in the range from 0.025 to 2kGy and found that 1.5Mol% of W-doped glass system could be valuable for the radiation dosimetry of perishable food items as it exhibited a good linearity and sensitivity in the range of 25 – 150Gy [75].

Furthermore, there have been many developments in phosphate glasses for thermoluminescence dosimetric applications. Ivascu et al. have investigated the FTIR, Raman spectra, and thermoluminescence properties of the $P_2Li_2BaO_7$ glasses in the high dose range <10Gy and concluded that the addition of Li_2O to the base glass $BaO–P_2O_5$, has not shown satisfactory in terms of linearity and sensitivity but the base glass sample has shown good linearity in the dose range up to 100Gy [76]. Swamy and his colleagues have reported the influence of Cu and Mn on thermoluminescence properties of boron phosphate glasses by exposing different gamma-ray doses in the range 250–1000Gy and the dose response of MnO-doped glass sample revealed that it exhibit a good linearity and an adequate sensitivity for the measurement of high doses when compared to commercially available dosimeter $CaSO_4$:Dy phosphor [77, 78]. Barna Biro et.al. investigated the thermoluminescence properties of yttrium-doped silica phosphate vitro ceramics and concluded that 30 Mol% Y_2O_3-doped vitro ceramic exhibited good reproducibility, low thermal fading, and acceptable homogeneity which recommends this material for dosimetry applications [79].

Anwar et al. have reported the improvement in thermoluminescence characteristics of $Li_2O–P_2O_5$ glasses and observed linearity up to the dose 200Gy and concluded that the addition of appropriate transition metal to the base sample can enhance the TL properties such as linearity and fading [80]. Kalpana et.al. has studied the influence of alumina in photoluminescence and thermoluminescence characteristics of Gd^{+3}- and Tb^{+3}-doped boron phosphate glasses and observed that TL linearity obtained in the dose range of 0.5–4kGy which concluded that the glass material has potential use in dosimetric applications in this range [81, 82]. Tanaka et.al. has studied the radio photoluminescence (RPL) properties of Ag-doped mixed phosphate glasses and found that the peak intensity of RPL increase with exposure except in Bi/Na–Ag [83].

Vallejo and his colleagues have studied the photoluminescence and thermoluminescence properties of Dy^{+3}-doped phosphate glasses containing silver nanoparticles which increase the TL intensity and can be used in solid-state illumination and retrospective dosimetry [84]. Sunil Thomas et.al. reported the thermoluminescence of β-irradiated K–Mg–Al–Zn fluorophosphate glasses and found that the glasses exhibit superlinear in the dose range of 1–190Gy, fading is 11% in 15h and the activation energy for higher temperature peak was evaluated as 1.31eV and that of lower temperature is 0.47eV [85]. Amany El-Kheshon and his colleagues have investigated La-doped phosphate glass and revealed that the glasses have high reproducibility and linearity in the wide range of radiation and found that the minimum detectable dose of 27.3μGy which confirms the use dosimetry as beta dosimeter [86, 87]. Anwar et al. have studied the thermoluminescence characteristics of a newly developed glass of composition $40P_2O_5$-50BaO-$2.5Na_2O$-2.5MgO-$5TiO_2$ and concluded that it has minor sensitivity up to 10Gy, linearity in the dose range 10–500Gy which recommends a vital role in the environmental dosimetry at high radiation doses [88].

El Mesady and his colleague have studied the optical and luminescence properties of Si-doped alumino-phosphate-sodium glass system and concluded that $APCNSi_5$ sample shows good linearity and sensitivity in the selected UV region and this type of glass is useful material for UV as well as γ-dosimetry [89]. Hirano et.al. has evaluated the photoluminescence (PL) and thermally stimulated luminescence (TSL) properties of Sn-doped zinc sodium Phosphate glasses and identified that 0.5% Sn-doped glass sample exhibited highest sensitivity with good linearity among all the other samples and TSL fading is also evaluated [90]. The thermoluminescence characteristics and dose response of Gd^{+3}, Dy^{+3}, and Tb^{+3}-doped alumino-phosphate glasses was studied by Gesiorowski et al., and observed that 0.5Mol% Tb_2O_3-doped glass sample has shown high TL efficiency, good linearity and sensitivity which makes this as a demanding material for electron and gamma-ray dosimetry [91–93].

The feasibility of the Mg–phosphate glasses as a thermoluminescent dosimeter in a high dose has been investigated by Abdou et al. and observed that the dosimeter is having TL linearity in the dose range 5–1000Gy and no significant fading is observed after 60 days of normal storage [94].

Rubalajyothi and colleagues have studied the thermoluminescence characteristic studies and anti-bacterial activity of $Ba_{1-x}Ca_xSO_4$: Dy, Er glasses and found that Dy and Er-doped glasses have sensitivity in radiotherapy and medical environment from 10 to 500Gy and 900Gy to 2kGy, respectively [95]. Vinod Kumar et al. investigated the thermoluminescence properties of Pr^{+3}-doped $SrBPO_5$ glasses and the TL properties are enhanced by the addition of UO_2^{+2} and the dose response was recorded in the range of 1mGy–1kGy and concluded that the dosimeter exhibited the linearity in the dose range 100mGy–100Gy [96]. Raja et al., have prepared a novel fluoroperovskite $RbCaF_3$: Sm^{+3} phosphors for radiation dosimetry and orange–red LED applications and observed that 0.6Mol% Sm^{+3} phosphor exhibited good linearity and low fading of 10% of the TL signal up to 50 days and almost stable later [97].

Muniratnam et al. have studied the effect of Mn on thermoluminescence properties of $Na_3Y(PO_4)_2$:Dy phosphors irradiated by gamma rays for dosimetry applications and observed that 0.07Dy-doped phosphor exhibited linearity in the dose range 50Gy–1.5kGy and the glow curves exhibited second-order dynamics which confirms that the phosphor is having potential applications in TL dosimetry to measure low irradiation [98]. Li et al. has reported the synthesis and optical properties of novel Gd^{+3}-doped $BaZn_2(PO_4)_2$ glass ceramics and found that 0.5 mol% Gd-doped glass sample exhibited good linearity in the dose range 0.3–500Gy, good reusability and the minimum detectable dose is 0.675 mGy [99]. The synthesis of Nd^{+3}-doped NaMgBSi glasses has been reported by Kaur et al., [100] and observed that 0.08mol% Nd-doped dosimeter exhibited a good linearity and low fading. Alazab et al. have studied the thermoluminescence properties of bioglass and observed that the glass dosimeter is slightly sublinear in the dose range 25–1000Gy which indicates that the glass also is useful for high dose dosimetry [101]. Anil Kumar et al. have reported the preparation of $Zr_xCa_{30-x}P_{70}$ bioglass and studied its thermoluminescent properties under different gamma radiation doses with and without immersing in a simulated body fluid(SBF) and observed that the TL intensity decreases when immersed in SBF which is useful to modulate bio-behavior in term of hydroxyapatite layer growth on the glass surface [102].

This overview demonstrates that many researchers worldwide are showing interest in the preparation of various materials for radiation dosimetric applications. At present, nanocrystalline phosphors are being used for TLD materials but as they are failing to hold the high dosage of radiation, there is a need to develop the nanomaterials as TL dosimeters. In the present review, the application of glass materials as thermoluminescence dosimeters in radiation dosimetry is presented.

2 Materials and methods used in glass preparation

Different methods can be employed for the synthesis of luminescent materials such as glasses in microcrystalline and nanocrystalline forms. Mostly, the melt-quenching method, combustion method, and sol–gel method have been used as described below.

2.1 Melt-quenching method

The melt-quenching technique is the most convenient method to prepare the glasses in which the molten form of the materials is cooled so quickly to avoid crystal formation. In this method, the raw materials are thoroughly mixed and are melted at the required temperature by placing them in a muffle furnace. The melt is then poured onto a stainless mould and pressed quickly with another plate which is at annealing temperature to avoid crystal formation. Therefore, transparent glass material is obtained. Different factors affect the color and formation of the glasses, such as the type of dopant added and the rate of quenching. The faster the rate of quenching, the better the formation of the glasses. Borosilicate glass with the composition (60-x) B_2O_3-$20SiO_2$-xBi_2O_3-12ZnO-8BaO (x = 0,2, 4, 6, 8, 10 and 12 mol%) [103], Ge-doped calcium borate glasses with the composition (30-x) CaO-$70B_2O_3$: $xGeO_2$ where x = 0.1,0.2,0.3, 0.4 and 0.5mol% [104] and lead borate and lead aluminum borate glasses with composition 4.5PbO-$1.9H_3BO_3$ and 11.1PbO-$2.9H_3BO_3$-$0.2Al_2O_3$ [105] have been synthesized using melt-quenching method Fig. 1.

2.2 Combustion method

The combustion method is a low-cost and effective method for preparing glass nanocrystals. In this method, all the raw materials are taken in stoichiometric ratio, and fuel is taken

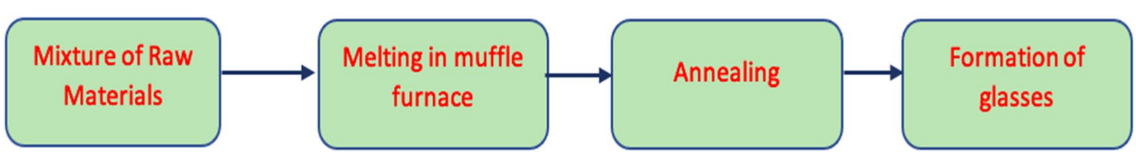

Fig. 1 Flow chart for melt-quenching technique

to cause the combustion such as urea, citric acid, glycine, etc. By taking all the raw materials in a crucible and it is to be placed in a preheated furnace at a high temperature at which the combustion of the materials can take place. The phosphor with the composition $Li_2B_4O_7$: $Ag_{1\%,}La_{(x\%)}$ (x = 0.1, 0.5, 1 and 3 wt%) [106], $NaBaBO_3$: Ce^{+3} [53] have been synthesized using combustion method Fig. 2.

2.3 Sol–gel method

The sol–gel method is a very simple and economical method for the preparation of glasses. In this method, first, we need to take the precursors of high purity in an aqueous solution form which is having a constant pH value (generally >7), and then add the solvent drop-wise till the gelatinous precipitate is formed Table 1. Filter this precipitate using a filter paper and transform this precipitate into a crucible which has to be put in the muffle furnace which is maintaining a high temperature for the formation of glasses Fig. 3. Dy-doped strontium borate glasses (SrB: Dy) have been prepared by the sol–gel method [43].

3 Few recently developed highly sensitive TLD glass materials

3.1 $MgLi_2B_2Cu_2O_6$: Sr

The $MgLi_2B_2Cu_2O_6$: Sr glass was synthesized by melt-quenching method and investigated the effect of different concentrations of Strontium (SrO) on TL characteristics at a dose of 50Gy and found that the optimum TL response with 0.003 Mol% of Sr concentration with TL intensity of $3.6\times10^5 nCg^{-1}$. The TL glow curve for 0.003Mol% Sr is shown in Fig. 4. The maximum peak temperature of glow curve for all the glass samples of different concentrations of Sr was observed between 170 and 200 ℃ [59].

3.2 $BaZnSiB_2O_{10}$: Bi_2O_3

The synthesis of $BaZnSiB_2O_{10}$: Bi_2O_3 was carried out by melt-quenching technique and has given the detailed studies of thermal, mechanical, radiation shielding, and thermoluminescence (TL) properties by D'Souza et al [103]. The TL study was done to assess the suitability of prepared glasses as a radiation dosimeter in the gamma dose range of 0.25–30kGy. Figure 5 shows the TL glow curve of powdered ZnBiB glass samples with gamma dose of 5kGy. It is observed that the addition of Bi_2O_3 decreases the TL intensity of the glass samples because, with the addition, Zn^{+2} ions reduced to Zn^+ ions which do not form Si–O–Zn linkage to form glass network.

3.3 $Ba_{1-x}Ca_xSO_4$: Dy^{3+}, Er^{3+}

Barium calcium sulfate ($Ba_{1-x}Ca_xSO_4$: Dy^{3+}, Er^{3+}) phosphor material was prepared by combustion method for thermoluminescence characteristics [95]. In this study, the authors reported the TL properties of Dy^{3+}- and Er^{3+}-doped glass matrix for low and high dose response. The TL study was done for the glass samples in the gamma dose range of 10–500Gy for Dy^{3+} and 900Gy–2kGy for Er^{3+}. Figure 6 shows the TL glow curves for 0.5Mol% Dy- and 1.0Mol% Er-doped glass sample with the gamma dose of 10Gy, 500Gy and 900Gy, 2kGy, respectively. From this study, it is also clear that the TL peaks have second-order active peaks and the dysprosium and erbium are found to be suitable for radiation therapy and medical environment in the range 10–500Gy and 900–2000Gy, respectively, and the frequency factors are found to be from $5.95\pm0.01 \times 10^7$ to $1.89\pm0.03 \times 10^{18}$ and $0.5\pm0.05 \times 10^9$ to $1.43\pm0.01 \times 10^{18}$, respectively.

4 Future scope

There is a need to prepare high-efficient, high-precision, and high-quality materials for in vivo dosimetry applications which are biologically compatible and eco-friendly. Under reduce–reuse–recycle theme for ecological balance, one needs to prepare a glass material that is re-usable and should have high-level scalability and applications in many fields of science like space applications, nuclear testing, and shielding applications, solar testing, X-ray testing, and even as neutron detectors also. As the

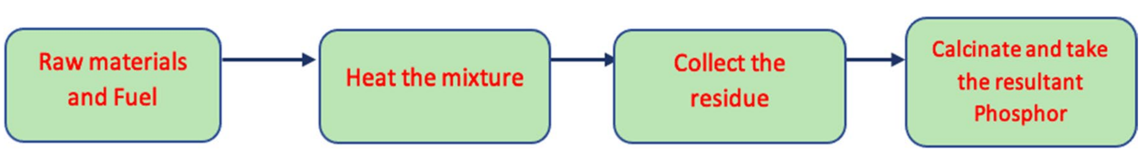

Fig. 2 Flow chart for combustion method

Table 1 Some recently studied glass materials for TLD applications

Glass Composition	Used precursors	Technique used for the synthesis	Doping materials	Range of TL response dose	Year of publication [Ref]
B_2O_3-Li_2O-ZnF_2	H_3BO_3 Li_2CO_3 ZnF_2	Melt-quenching	–	200–1000 Gy β-radiation	2017 [107]
xCeO_2-30MgO-20Al_2O_3-50B_2O_3 X = 0 – 10% wt	CeO_2 $MgCO_3$ $Al_2(CO_3)_3$ H_3BO_3	Melt-quenching	Ce	1 – 10 Gy X – rays	2017 [54]
(90-x) H_3BO_3 -10 Li_2CO_3 -x $CaCO_3$ X = 5, 10, 15, 20, 25, 30, 35 Mol% (80-y) H_3BO_3 -10 Li_2CO_3 -10 $CaCO_3$-y Cu_2O Y = 0.005, 0.01, 0.02, 0.04, 0.06,0.08, 0.1 M0l%	H_3BO_3 Li_2CO_3 $CaCO_3$ Cu_2O	Melt-quenching	Cu	0.5 – 100 Gy γ-rays (Co^{60})	2017 [58]
30 ˚CaO-(70-x) B_2O_3-x Dy_2O_3 (0.01 ≤ x ≤ 0.4) Mol%	H_3BO_3 $CaCO_3$ Dy_2O_3	Melt-quenching	Dy	0.5 – 40 Gy Photon	2017 [108]
30Li_2O-70 B_2O_3: Dy_2O_3	H_3BO_3 Li_2CO_3 Dy_2O_3	Melt-quenching	Dy	0.5 – 5 kGy γ-rays (Co^{60})	2017 [47]
(30-x) Li_2O -20Al_2O_3-50 B_2O_3-2 × CeO_2	H_3BO_3 Li_2CO_3 $Al_2(CO_3)_3$ CeO_2	Melt-quenching	Ce	0.01 – 100 Gy X-rays	2017 [109]
$Li_2B_4O_7$: Cu	$LiNO_3$ H_3BO_3 NH_4NO_3 NH_2CONH_2	Combustion method	Cu	1-1000 kGy Proton beam	2018 [60]
MgB_4O_7: Dy (0.4 Mol%)	$MgCO_3$ H_3BO_3 Na_2CO_3 Dy_2O_3	Melt-quenching	Dy	–	2018 [49]
10ZnO-5 Na_2O -10 Bi_2O_3-74.3 B_2O_3-0.7Eu_2O_3	ZnO $Bi_2(CO_3)_3$ H_3BO_3 Na_2CO_3 Eu_2O_3	Melt-quenching	Eu	0.25 – 3 kGy γ-rays (Co^{60})	2018 [68]
10ZnO-5 Na_2O -10 Bi_2O_3-(75-x) B_2O_3-0.7 Pr_6O_{11}	ZnO $Bi_2(CO_3)_3$ H_3BO_3 Na_2CO_3 Pr_6O_{11}	Melt-quenching	Pr	0.25 – 5 kGy γ-rays (Co^{60})	2018 [110]
`15Al_2O_3-35 P_2O_5-25CaO-25 Na_2O	$Al_2(CO_3)_3$ Na_2CO_3 P_2O_5 $CaCO_3$	Melt-quenching	SiO2	–	2018 [89]
x SnO_2-50$Zn_3(PO_4)_2$-50 $NaPO_3$ (x= 0, 0.1, 0.2, 0.5, 1.0 Mol%)	$Zn_3(PO_4)_2.4H_2O$ $NaPO_3$ SnO_2	Melt-quenching	Sn	0.1–10^3 mGy X-rays	2018 [90]
(70-x) B_2O_3-20 Li_2O -10MgO-x Dy_2O_3 0.05 < x < 0.7 Mol%	H_3BO_3 Li_2CO_3 MgCO3 Dy_2O_3	Melt-quenching	Dy	1 – 100 Gy Photon beam	2019 [50]

Table 1 (continued)

Glass Composition	Used precursors	Technique used for the synthesis	Doping materials	Range of TL response dose	Year of publication [Ref]
$35CaO-15\ Al_2O_3-50\ B_2O_3-x\ Tb_4O_7$ x= 0.25, 0.5, 1.0, 2.0, 5.0 Mol%	$CaCO_3$ $Al_2(CO_3)_3$ H_3BO_3 Tb_4O_7	Melt-quenching	Tb	$0.1–10^3$ mGy X-rays	2019 [71]
$Li_2B_4O_7$: $Ag_{1\%}$, $La_{x\%}$ x= 0.1, 0.5,1. 3wt%	$LiNO_3$ H_3BO_3 CH_4N_2O AgNO3 $La(NO_3)_3.6H_2O$	Solution combustion synthesis	Ag, La	0.1–10 Gy	2020 [106]
$NaBaBO_3$	$NaNO_3$ $Ba(NO_3)_2$ H_3BO_3 NH_4NO_3 $CO(NH_2)_2$	Combustion method	Ce	0.1–10 Gy β radiation	2020 [53]
$LiMgBO_3$: Dy	$CH_3COOLi.2H_2O$ $Mg(NO_3)_2.6H_2O$ H_3BO_3 $C_6H_8O_7$ $(CH_2OH)_2$ Dy_2O_3	Sol–gel method	Dy	Neutron (1mSV) Gamma (100 mGy)	2020 [52]
10BaO-20ZnO-20LiF-(50-x) B_2O_3-x Er_2O_3 x= 0, 0.1, 0.5, 0.7, 1 Mol%	$BaCO_3$ $Zn(NO_3)_2$ LiF H_3BO_3 Er_2O_3	Melt-quenching	Er	0.25 – 30 kGy γ-rays (Co^{60})	2020 [111]
(1-x)MnO-29K2O-70 B_2O_3-x Er_2O_3 x= 0, 0.2, 0.4, 0.6, 0.8, 1 Mol%	$MnCO_3$ K_2CO_3 H_3BO_3 Er_2O_3	Melt-quenching	Er	50–5000 Gy	2020 [64]
60 B_2O_3-4 °CdO	H_3BO_3 CdO WO_3	Melt-quenching	W	0.25 – 2 kGy γ-rays (Co^{60})	2020 [75]
x Bi_2O_3-(60-x) B_2O_3-20 SiO_2 -12ZnO-8BaO x= 0, 2, 4, 6, 8, 10, 12 Mol%	$Bi_2(CO_3)_3$ H_3BO_3 $Zn(NO_3)_2$ SiO_2 $BaCO_3$	Melt-quenching	Bi	0.25 – 30 kGy γ-rays (Co^{60})	2021 [103]
(60-x) B_2O_3-20SiO_2 -10Na_2O-10MgO-x Ce_2O_3 x= 0, 0.2, 0.4, 0.6, 0.8, 1 Mol%	H_3BO_3 Na_2CO_3 SiO2 $MgCO_3$ Ce_2O_3	Melt-quenching	Ce	500 Gy – 10 kGy γ-rays (Co^{60})	2021 [112]
25 Li_2O -(70-x) B_2O_3-5MgO-xCuO x= 0, 5, 10 Mol%	Li_2CO_3 H_3BO_3 $MgCO_3$ CuO_2	Melt-quenching	Cu	1–100 Gy	2021 [57]
$Na_3Y(PO_4)_2$: Dy	Na_2CO_3 Dy_2O_3 Y_2O_3 $NH_4H_2PO_4$ $MnCO_3$	Solid-state reaction method	Dy and Mn	50 Gy–1.5 kGy	2021 [98]
45P_2O_5-15BaO-25ZnO-15 B_2O_3	$NH_4H_2PO_4$ $BaCO_3$ $ZnCO_3$ H_3BO_3 Gd_2O_3	Melt-quenching	Gd	0.3–500 Gy	2021 [99]

Table 1 (continued)

Glass Composition	Used precursors	Technique used for the synthesis	Doping materials	Range of TL response dose	Year of publication [Ref]
(1-x)MnO-29K_2O-70B_2O_3-x Sm_2O_3 x= 0, 0.2, 0.4, 0.6, 0.8, 1 Mol%	$MnCO_3$ K_2CO_3 H_3BO_3 Sm_2O_3	Melt-quenching	Sm	10 Gy – 10 kGy γ-rays (Co^{60})	2022 [65]

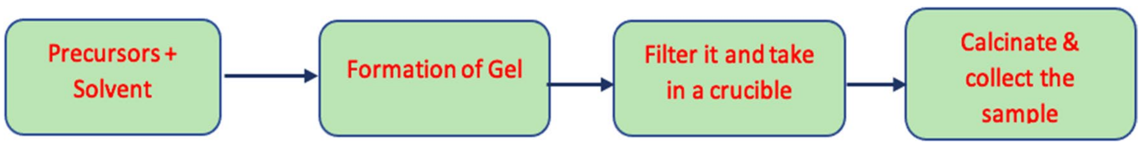

Fig. 3 Flow chart for sol–gel method

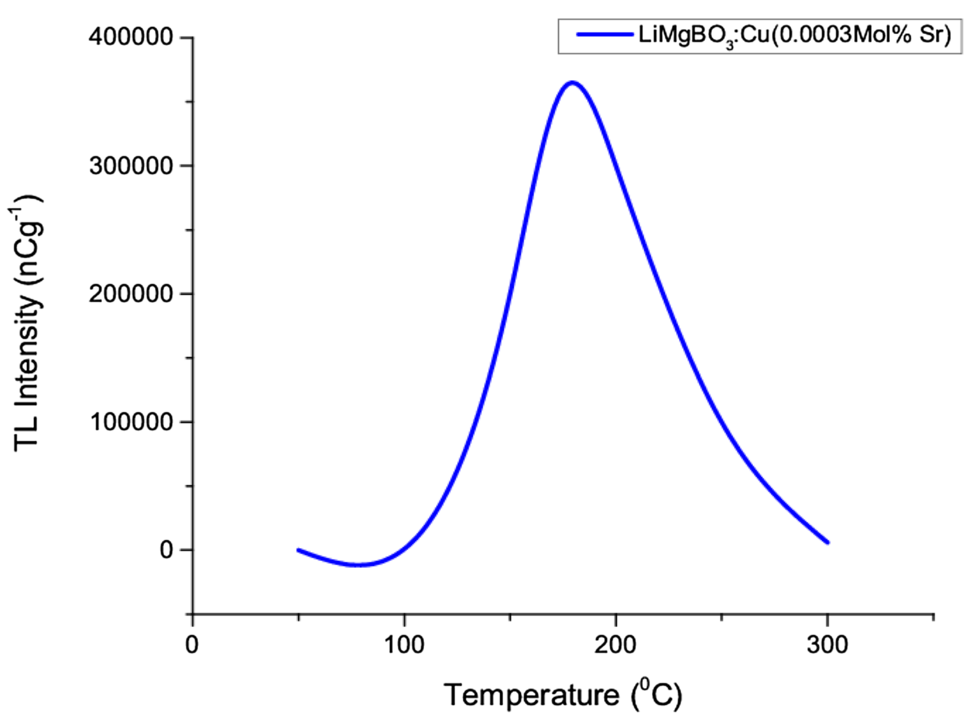

Fig. 4 TL glow curve of $MgLi_2B_2Cu_2O_6$: 0.003 Mol% Sr (Reproduced from ref. [59], Open access under Common Creative Attribution Non-Commercial 4.0 International (CC-BY-NC 4.0) https://creativecommons.org/licenses/by-nc/4.0/)

tailoring of the glass materials is possible, one can synthesize the materials in any geometrical structure according to the need of the application. For all the materials which are customized, there is a lot to explore in terms of characterization, physical and chemical properties, and especially in the field of in vivo dosimetry.

5 Conclusions

Different TLD materials in the form of glasses have been reviewed with a special focus on lithium borate glasses. It can be concluded that the studies on the TL dosimetry materials mainly focus on the development of more efficient glass

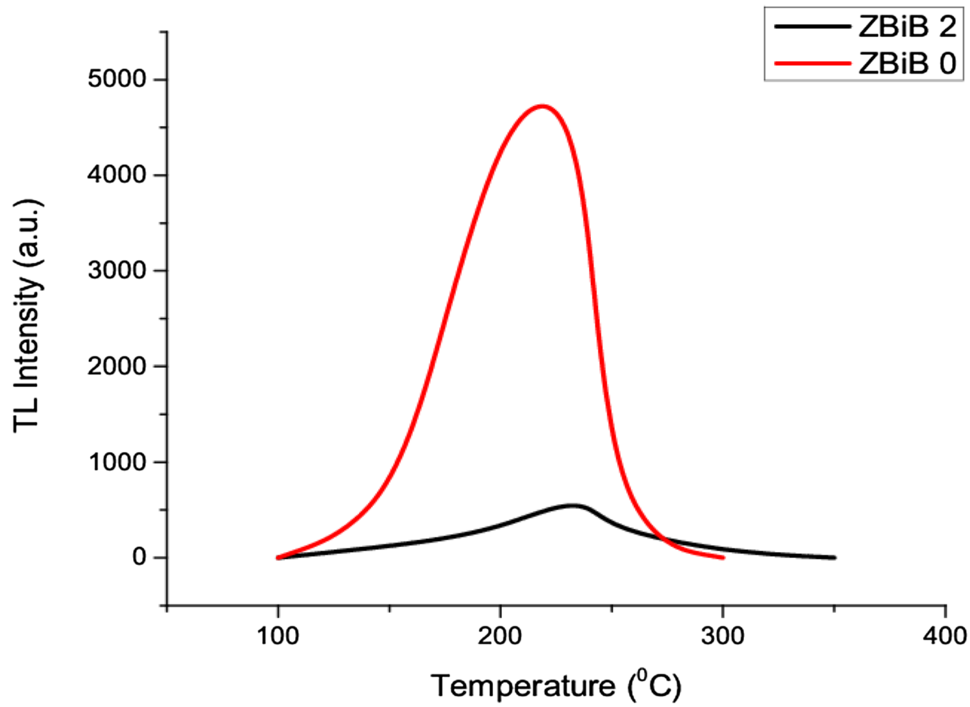

Fig. 5 TL glow curve of $BaZnSiB_2O10$: Bi_2O_3 of 0 and 2 Mol% (Reproduced from ref. [104], Open access under Common Creative Attribution 4.0 International (CC-BY 4.0) https://creativecommons.org/licenses/by/4.0)

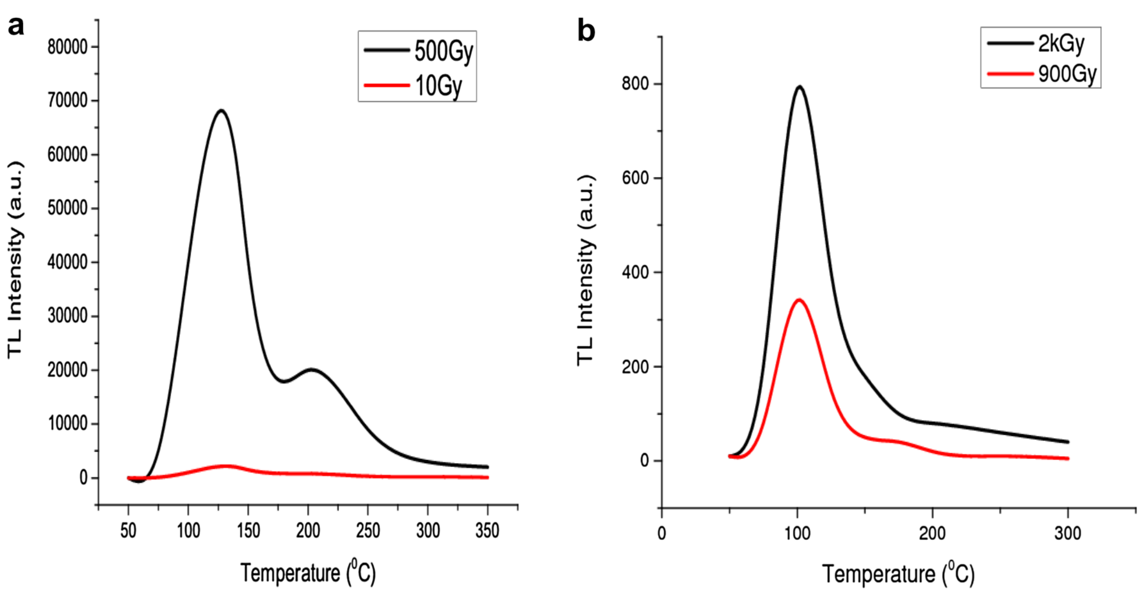

Fig. 6 TL glow curve of (**a**) 0.5 Mol% Dy^{3+} and (**b**) 1.0 Mol% Er^{3+} doped $Ba_{1-x}Ca_xSO_4$ (Reproduced from ref. [95], open access under Common Creative Attribution 4.0 International (CC-BY 4.0) https://creativecommons.org/licenses/by/4.0)

materials, more consistency, easily preparable/reproduceable, high durability for radiation damage and biocompatible or 100% environment friendly, over the existing materials. The search for new materials should aim to produce the materials with simple and good linearity in the TL dose curves and low fading. Furthermore, it is very important to consider the TL mechanism before developing the new glass materials for the applications in in vivo dosimetry.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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