Towards improved cover glasses for photovoltaic devices

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Abstract
For the solar energy industry to increase its competitiveness, there is a global drive to lower the cost of solar-generated electricity. Photovoltaic (PV) module assembly is material-demanding, and the cover glass constitutes a significant proportion of the cost. Currently, 3-mm-thick glass is the predominant cover material for PV modules, accounting for 10%–25% of the total cost. Here, we review the state-of-the-art of cover glasses for PV modules and present our recent results for improvement of the glass. These improvements were demonstrated in terms of mechanical, chemical and optical properties by optimizing the glass composition, including addition of novel dopants, to produce cover glasses that can provide (i) enhanced UV protection of polymeric PV module components, potentially increasing module service lifetimes; (ii) re-emission of a proportion of the absorbed UV photon energy as visible photons capable of being absorbed by the solar cells, thereby increasing PV module efficiencies and (iii) successful laboratory-scale demonstration of proof of concept, with increases of 1%–6% in I_{sc} and 1%–8% in I_{pm}. Improvements in both chemical and crack resistance of the cover glass were also achieved through modest chemical reformulation, highlighting what may be achievable within existing manufacturing technology constraints.

KEYWORDS
chemical properties, cover glass, mechanical properties, optical properties, photoluminescence, PV modules, strengthening of glass

1 | INTRODUCTION

Solar energy is often seen as the ultimate renewable energy because of the abundance of solar irradiation available for solar energy generation. In only 90 min, the Earth receives enough energy from the sun to provide its entire annual energy requirements.1 Chapin, Fuller and Pearson invented the first practical photovoltaic (PV) cell in 1954,2 and since the year 2000, installed PV capacity has experienced an almost exponential growth.3 The installed PV capacity can be regulated politically but that is largely achieved on a national level and may be subject to change within just a few years. The growth of the solar energy market has been driven by the reduction of costs. For solar or any other renewable energy source, it has been a necessity to compete on an economical level (i.e., reaching so-called grid parity), and...
thereby renewable energy has now become a real competitor to nonrenewable energy sources. Grid parity has been achieved by several countries, for example, Japan, Australia, Germany, Italy, Greece, Turkey, Spain and Argentina. The comparison of costs for different energy sources is known as the ‘levelized cost of electricity’ (LCOE) and provides a good benchmark to different energy sources. The LCOE for PV energy has decreased rapidly in the last 10 years and is now competitive, in the range of US$32–42/MWh.

In the PV industry, the measure of the direct current peak power rating ($W_p$) is a conventional benchmark among PV modules, which reflects the system efficiency under standardized conditions. The cost, expressed as either LCOE or cost per Watt peak ($W_p$), is a driving factor for maintaining the exponential trend for installed PV capacity. As shown in Ray, the LCOE reduction has flattened out and so has the cost per $W_p$; therefore, the PV industry and market need new innovations to further reduce costs. The reduction of costs will primarily be achieved by (i) increasing solar device efficiency, (ii) reducing balance of system costs and (iii) minimizing the module cost. The properties of PV module materials are of great importance to ensure optimal light capture and module lifetime as well as ultimately reducing the cost. Although these figures are a few years old, they provide a useful guide to the importance of the fractional cost of cover glass within PV modules. The cover glass constitutes about 25% of the cost of Si thin-film modules and about 10%–15% of the cost of crystalline Si (c-Si) modules as compared with the grid-parity aim (US$0.5–0.7/Wp). At the time of writing, the spot market price is about US$0.3/Wp for polycrystalline-Si and slightly lower for mono-Si modules; thus, the glass fractional cost is increasing as the cost per $W_p$ is decreasing. Improving the cover glass and reducing its cost thus become increasingly important, and the three main approaches for reducing material costs are identified as (i) reducing material thickness, (ii) replacing expensive raw materials and (iii) reducing material waste. The market share from the PV energy industry in global flat glass production was less than 2% in 2015, but the growth of installed PV capacity increases annually, with prognoses even claiming that the PV industry will demand an expansion of global flat glass production in the near future. The flat glass industry thus has rapidly growing interest in this field.

Today, mono- and poly-crystalline Si solar cells dominate the PV market, balancing the state of the art and economy; see Figure 1 for the Shockley–Queisser theoretical limit as a function of bandgap wavelength. The costliest module components are the active semiconductor material (Si) and the glass cover. Typical dimensions of a domestic PV module are $1.4–1.7\ m^2$, with $>90\%$ covered by soda-lime-silica (SLS) float glass. The glass alone weighs $\approx 20–25\ kg$ since the density of SLS glass is $\approx 2520\ kg/m^3$. This presents engineering challenges as current solar panels are rigid and need strong, heavy support structures. Rigidity and weight confuse exploitation of portable PV products, and the production of high volumes of glass carries both energy and environmental costs, contributing to global CO2 emissions. Service lifetimes and efficiencies of solar cell components are limited by solar UV radiation damage, which induces degradation of laminate materials, the most frequently used being ethylene vinyl acetate (EVA), eventually leading to delamination and module failure, although in recent years, ‘transparent EVA’ or T-EVA, with a UV cut-off wavelength of $\approx 300\ nm$, has been developed, reducing this effect. However, discolouration and delamination of T-EVA can still arise at the backsheet interface in PV modules, as recently discussed by Adothu et al. They also demonstrated discolouration and photobleaching of T-EVA in c-Si PV module tests, with yellowness indices, following UV exposure, that were approximately one-quarter those of traditional UV-cutting EVA (C-EVA). Although a significant improvement, the yellowness index of the T-EVA was still nonzero. Moreover, the environmental stability of the T-EVA encapsulant is still not known. Consequently, although T-EVA represents an important step forward and enables increases in PV module efficiency by comparison with C-EVA, T-EVA does not necessarily present a panacea for environmental degradation of PV module encapsulants. Undoubtedly, there remains room for further improvement.

There is a genuine and growing need to reduce the thickness (= weight) of the glass cover while improving PV module service lifetimes and efficiencies. Today, commercial 3-mm-thick toughened PV glass provides only limited benefits: Low-iron content is used to improve solar transmittance; see Figure 1. The Fe$^{2+}$/Fe$^{3+}$ redox ratio in the glass may be controlled through the use of oxidizing agents in glass raw materials mixtures (batches), providing a degree of chemical decolourization. Also, the glass surface may be patterned or coated so that some light can be guided back towards the solar cell, or to reduce reflection losses at glass-air interfaces via antireflective (AR) coatings. Even small increases in solar light
transmission through the cover glass can have a significant commercial advantage, for example, a 5\% increase in solar transmittance could result in up to 10\% improvement in energy collection efficiency.\textsuperscript{25} Here, we review the current state of the art for optical and mechanical properties of PV module cover glasses, and we present research on how development of the cover glass composition, and the use of novel dopants therein, may provide pathways to improve the efficiency, service lifetime and weight of PV modules, in addition to providing a perspective on the challenges that remain.

1.1 Optical properties of cover glasses for PV applications

Current commercial float glasses transmit $\sim 90\%$ of incident light, with the primary sources of loss being absorption and reflection. If the glass is AR-coated, it is possible to achieve $\sim 98\%$ light transmission. Here, we focus on the bulk glass material itself, and coatings or nanopatterning are beyond the scope. For an introduction to AR coatings, the reader is referred to Deubener et al\textsuperscript{21} and for nanopatterned glass to Gombert et al.\textsuperscript{26} Cover glass can be sensitive to corrosive media (e.g., acid rain) and water,\textsuperscript{27,28} and lowiron cover glass has only limited capability to block the UV radiation that damages both the active semiconductor materials\textsuperscript{29} and the EVA laminate\textsuperscript{15} within a PV module, with the latter being the dominating degradation mechanism. However, as noted in Section 1, recent developments on EVA laminate chemistry to develop T-EVA have rendered EVA partly transparent to UV with a cut-off wavelength of $\sim 300\, \text{nm}$,\textsuperscript{16} which is approximately the same wavelength as the UV cut-off for low-iron glass (c.f. Figure 1). Despite the availability and recent application of these new EVA materials (see, e.g., Vogt et al\textsuperscript{15} and Adothu et al\textsuperscript{17}), they remain susceptible to UV- and temperature-induced discoloration and delamination (see Section 1), and it remains important to have an appropriate level of UV blocking, otherwise degradation of the laminate is a major limiting factor of the service lifetime and lifetime efficiency of PV modules. For traditional C-EVA, this could lead to annual degradation of 0.6\%–2.5\% in PV module efficiency because of degradation of the C-EVA, depending on service conditions and manufacturer.\textsuperscript{15,30,31} The main effect is discoloration of the EVA layer due to UV damage, resulting in reduced light transmission and thus contributing to reduced module efficiency.\textsuperscript{32} The mechanisms and chemical species involved in this discoloration were recently summarized by Adothu et al.\textsuperscript{17} In addition to its effects on the polymeric encapsulant materials, UV degradation can also impact on the efficiency of the solar cell material itself. This was demonstrated by Shamachurn and Betts,\textsuperscript{33} who observed deterioration of solar cell efficiency for bare Si solar cells, which they attributed in part to degradation of the antireflective coating on the cell material. This further underlines the need for an appropriate level of UV protection for PV module materials, ideally provided by the first ‘barrier’, that is, the glass cover sheet.

The incorporation of small quantities of iron oxide (Fe$_2$O$_3$) into the SLS cover glass shifts the UV absorption edge strongly towards longer (visible) wavelengths. This arises because of strong oxygen-metal charge transfer (OMCT) bands centred in the deep UV, which exhibit tails to longer wavelengths,\textsuperscript{34} and also characteristic absorption bands between $\sim 360$ and $\sim 460\, \text{nm}$ arising from $d-d$ transitions of Fe$^{3+}$ ions.\textsuperscript{35} Both Fe$^{2+}$ and Fe$^{3+}$ ions typically occur in commercially manufactured float glass, and the presence of Fe$^{2+}$ parasitically absorbs photons within the nIR and red-visible region with a strong, broad absorption band centred at approximately 1000 nm,\textsuperscript{34} which particularly affects the efficiency of Si PV modules. Even low quantities of Fe$_2$O$_3$ (e.g., 0.01 mol%) in SLS glass result in a loss in PV module output power of 1.1\% and with 0.10-mol\% Fe$_2$O$_3$ present in the glass, this results in a 9.8\% loss.\textsuperscript{35} However, although minimizing the Fe$_2$O$_3$ content of the glass provides obvious improvements in PV efficiency, it reduces the protection against UV degradation afforded to the other PV module components. This presents engineers with somewhat of a dilemma—balancing the need to improve efficiencies in the short term while maintaining module efficiencies and service lifetimes in the longer term. A combination of reducing the concentration of iron oxide species within the glass front sheet, while providing sufficient absorption of UV photons to protect the EVA and/or other polymeric species, is thus of paramount importance for developing more efficient and longer lasting PV modules.

A suggested solution has been to dope the low-Fe glass with active optical centres that, unlike Fe, do not produce visible or nIR absorption bands, but do absorb UV photons and, moreover, re-emit a proportion of the absorbed energy as photons of visible light. This process is frequently called down-conversion or down-shifting, depending on the type of electronic transition involved (see Figure 2).\textsuperscript{36,37} This aspect of photoluminescence has been considered since the 1970s\textsuperscript{38–41} and is still receiving attention.\textsuperscript{37,42,43} By using down-conversion\textsuperscript{44,45} or down-shifting, the solution is two-fold as the doped glass both absorbs harmful UV photons but also re-emits some of this absorbed energy as photons of visible light that can be captured and converted by the solar cell. Thus, it can increase the PV module service lifetime while enhancing the module efficiency. Fluorescent glasses have been widely studied and most lanthanide-containing glasses fluoresce at visible wavelengths.\textsuperscript{46} A detailed treatment of the use of different lanthanide cations as spectral converters for PV cells was provided by van der Ende et al.\textsuperscript{47} The fluorescent components can either be doped directly into the bulk glass during manufacture, or they can be applied as coatings on the surface of the glass using post-processing steps such as sol-gel,\textsuperscript{48,49} spray-pyrolysis\textsuperscript{50} or nanoparticles\textsuperscript{51} via ion exchange.\textsuperscript{52,53} Luminescent materials have also been considered for use in solar collector concentrators\textsuperscript{54} where the light can be wave guided (by internal total reflection) to the sides of a window where solar cells are located.\textsuperscript{55,56}

Selection of glass dopant cations that produce no absorption bands at visible or near-IR energies is essential, otherwise any benefits for UV protection are likely to be outweighed by the negative impact on light transmission of the cover glass and thus solar cell efficiencies. The large majority of first-row transition metals, when doped into glasses, suffer this limitation.\textsuperscript{34,35,57–60} Other metal ions can also absorb UV photons and provide down-shifted or down-converted
fluorescence at visible wavelengths and recently Bi\(^{3+}\)-doped glasses have been suggested as promising materials for solar spectral conversion.\(^{51,62}\) Ion incorporation of Cu\(^+\) by exchange has also shown promise.\(^{52}\) In addition, recent research by some of the present authors\(^{63,64}\) has demonstrated that a number of second- and third-row transition metal dopants which adopt the \(d^0\) electronic configuration in glasses (Ti\(^{4+}\), Zr\(^{4+}\), Hf\(^{4+}\), Nb\(^{5+}\), Ta\(^{5+}\), Mo\(^{6+}\) and W\(^{6+}\)),\(^{65}\) and also heavy metal cations such as Sb which exhibit far-UV absorption bands from \(s \rightarrow p\) electronic transitions\(^{66}\) can also provide down-shifting of UV photons in silicate glasses with negligible visible absorption.\(^{65}\) Moreover, some of the present authors have also shown that adding Gd\(^{3+}\) or other lanthanides as a co-dopant with Bi\(^{3+}\) can provide enhanced luminescence intensity compared with Bi\(^{3+}\) doping alone.\(^{64}\)

In terms of luminescence mechanisms, down-conversion and down-shifting from UV to visible wavelengths have been the most commonly studied approaches, but up-conversion\(^{37,66}\) from the IR range to visible wavelengths is also an alternative; see Figure 2. Up-conversion\(^{37,67,68}\) could also provide benefits in terms of enhanced solar cell efficiency, as most solar cells decrease in efficiency with increased temperature; therefore, up-converting glass constituents could absorb IR photons and moderate solar cell temperature, in addition to the benefit of providing more nIR and visible light with energy greater than the semiconductor bandgap energy available for conversion by the solar cell. Dopants responsible for producing up-conversion in glasses have typically been lanthanides (see, e.g., Dejneka et al\(^{66}\)). However, the conversion efficiency of up-conversion in glasses is low, even in exotic glass chemistries that are greatly different to commercial SLS glasses and unsuited to low-cost, high-volume manufacture. Furthermore, the majority of studies of up-conversion in glasses have relied on laser light sources to enable measurable levels of up-conversion. Development of new low-cost silicate glasses with economically viable up-conversion with sufficient efficiency improvements remains a considerable research challenge.

Given the above evidence, in this study, we have focused on the development of new down-shifting glass formulations, with selection of nontoxic Bi\(^{3+}\) coupled with Gd\(^{3+}\) as dopants for further development and testing in lab-scale PV modules. Research considering other dopants capable of providing combinations of down-shifting, down-converting and up-converting mechanisms including, but not limited to those dopants listed above, is planned for future research.

### 1.2 | Mechanical performance of glass for PV applications

In addition to optical and environmental performance, the mechanical performance of PV modules is also of vital importance, and with the glass front sheet constituting a high proportion of the mass of PV modules, it also impacts on mechanical properties of the PV module composite. Consequently, it is important to develop new glasses with enhanced or improved strengths and toughness compared with existing glasses, particularly in light of the drive towards thinner glasses to reduce weight and costs (see Section 1). The strength of glass is an extrinsic property that depends to a major extent on the surface of the glass rather than of the bulk glass.\(^{69}\) In the linear elastic fracture mechanics theory, that brittle materials obey, the critical stress intensity factor (\(K_{\text{IC}}\)), which is a material property\(^{70}\) for when a material fractures (\(K_{\text{I}} \geq K_{\text{IC}} = \) Fracture Toughness), where \(K_{\text{I}}\) is the stress intensity factor. By prestressing the glass surface with residual compressive stresses, it is possible to increase the fracture toughness by the failure criterion \(K_{\text{IC}} + K_{\text{IV}}\).\(^{71}\)

Thermal toughening of PV cover glass is the most conventional route to meet the standard IEC 61215 on impact resistance that is aimed to simulate hailstorms. In this process, the glass is rapidly quenched with dry or humid pressurized air from temperatures \(\sim 75^\circ\text{C}\) above the glass transition temperature (\(T_g\)).\(^{72}\) Initially, the glass surface starts to cool and contract more rapidly than the interior; the interior will be in compression, whereas the surface is in tension. At \(T_g\), the glass surface becomes an elastic solid, whereas the hotter interior still is a viscoelastic body that can undergo structural and stress relaxation.\(^{72}\) As the glass continues to cool, the glass surface will contract much less than the interior, and the glass surface will therefore be placed in a state of compression while the interior develops balancing tensile stresses. The residual stress profile is often of parabolic type (Figure 3A), and the central tensile stresses are approximately half the value of the compressive stresses at the surface.\(^{75}\)

In practice (Figure 4), the glass is cooled within a few tens of seconds from a temperature higher than 600°C to ambient temperatures. During the first few seconds, the temperature decreases at the
surface by more than 150°C. Thermal strengthening depends greatly on the thermal expansion coefficient, \( \alpha \), of the glass and has been theoretically described by Narayanaswamy and Gardon.\(^7\) Thus, not all glasses are suitable for thermal toughening, for example, glasses that have lower \( \alpha \) do not thermally toughen well in practice, for example, Pyrex borosilicate glass (\( \alpha = 3.3 \times 10^{-6} \text{ K}^{-1} \)). Thermal toughening of glass depends not only on \( \alpha \) but also on the quality of the parent glass and the maximum cooling rate that is practically achievable. SLS glass (\( \alpha = 9 \times 10^{-6} \text{ K}^{-1} \)) is the most commonly used glass in PV, as well as architectural applications (EN 572-2). Thermally toughened glass is also called safety glass because it fractures into small fragments, which are in general much less sharp and dangerous than the large dagger-like pieces of broken annealed glass. One drawback of thermally toughened glass is that it suffers from a spontaneous cracking problem as nickel sulphide (NIS) can be introduced into the glass as a contaminant from the raw materials. This is not a frequent occurrence, at most in 1 out of 500 glasses, and there is a method to eliminate this problem called the heat soak test.\(^77,78\) Nevertheless, a number of high-profile cases of spontaneous failure of architectural glass, which have ultimately been identified as originating from NIS inclusions, have been reported in the media.

Theoretically, the highest cooling rates enable the highest compressive stresses to develop in the glass surface and thus for thinner glass to be toughened. Upon too rapid cooling, however, the initial thermal gradient and surface tensile stresses can become so large as to cause glass fracture. The temporary tensile stresses that develop at the glass surface during cooling from the initial temperature \( T_i \) to \( T_g \) is described by Gulati et al.\(^79\) With conventional cooling rates, the temporary tensile stresses are \( \sim \)40 MPa. The residual stresses depend on the thickness of glass, the thinner glass; the greater cooling rates are needed to achieve same magnitude of residual stresses. Similarly, for a given thickness, the magnitude of the residual stresses is a function of the cooling rate. Therefore, it has previously been a critical limit of the thickness of the glass that can be thermally toughened by conventional processes. Traditionally, 3 mm was considered the minimum thickness, but with an improved process, 2 mm or thinner glass has recently been toughened. In this state-of-the-art process, the rollers are replaced by gas flotation systems in the furnace (e.g., the HZL technology of the LiSEC group and Glaston’s GlastonAir™).\(^74\) In this respect, eliminating the ceramic rollers is very important because they readily introduce surface defects onto the glass such as roller waves or scratches, thereby
increasing the susceptibility to fracture, and they may also act as heat sinks during the quenching giving inhomogeneous toughening.

Another type of toughened glass that has received much interest recently is chemically toughened glass. This is based on thermally assisted ion exchange below \( T_g \) and involves incorporation of larger ions into the glass surfaces that induce compressive stresses. Compared with thermally toughened glass, higher compressive stresses can be achieved (Figure 3B) but at a considerably higher cost. Chemically toughened glass has found wide usage as cover materials for electronic devices but recently also in architectural and automotive applications.\(^{80}\) Chemical toughening of glass has recently been extensively reviewed.\(^{75,81-84}\) The price of chemically toughened glass compared with thermally toughened glass is a factor of about two to six times. It has been used for more demanding PV applications such as space PV panels.\(^{85}\) Recently, a chemically toughened cover glass for the PV industry, LeoFlex™, has been released.\(^{86}\)

Surface defects determine the strength of glass as given from the Griffith criterion for brittle materials.\(^{87}\) Therefore, besides toughening, there are also other ways to increase the inherent toughness and strength of the glass; for example, by increasing its resistance to scratches and cracks during handling. This has often been studied by indentation technology techniques.\(^{88}\) Damage resistance of glasses has traditionally been described by the brittleness of glass,\(^{89}\) which has often been described as the ratio of the hardness of the material and the indentation fracture toughness.\(^{90}\) SLS glasses are optimized to a large extent based on the cost, melting and viscosity behaviour, especially the float glass composition is optimized to suit the float process.\(^{91}\) However, even by small changes of the composition, it is possible to modify the surface mechanical properties.\(^{91-96}\)

### 1.3 The LIMES project

The LIMES project (Light Innovative Materials for Enhanced Solar Efficiency) was a Solar-ERA.NET project that ran from 2014 to 2017, which investigated cover glass properties for PV applications. Solar-ERA.NET was an EU FP7 funded network that since 2013 has launched joint calls to strengthen the competitiveness and innovativeness of European industry. In these calls, one of the key topics has been ‘Solar glasses and encapsulation materials’. The LIMES project addressed several aspects that are relevant for PV cover glasses and investigated optical,\(^{63}\) mechanical and chemical properties of glass as well as novel thermal toughening methods\(^{97}\) and also the addition of antireflective and self-cleaning capabilities to the glass surface.\(^{98,99}\) The glasses made in laboratory experiments were used for proof-of-concept studies by making the 70 x 70 mm PV modules discussed here. These aspects were addressed in order to give the opportunity to make thinner cover glasses that give enhanced efficiency and increased lifetime of PV modules. This paper gives an overview of some of the results and knowledge gained from this project and since.

### 2 EXPERIMENTAL PROCEDURES

#### 2.1 Glass synthesis

In the LIMES project, several different glass synthesis routes were used in order to optimize given properties within each subset of glasses. These are described below.

| Oxide | 1st DoE | 2nd DoE |
|-------|---------|---------|
| SiO\(_2\) | 71.36 to 66.36 | 70.76 |
| Al\(_2\)O\(_3\) | 0 to 5 | 0.59 |
| B\(_2\)O\(_3\) | 0 to 5 | 0 |
| Na\(_2\)O | 13.93 | 13.93 |
| CaO | 9.24 | 5 to 14.71 |
| MgO | 5.47 | 0 to 8. |
| TiO\(_2\) | - | 0 to 5 |
| BaO | - | 0 to 5 |
| ZnO | - | 0 to 5 |
| ZrO\(_2\) | - | 0 to 5 |
| SrO | - | 0 to 2.5 |
| La\(_2\)O | - | 0 to 2 |
2.1.1 | Glass synthesis for optimizing mechanical and chemical properties

Glass was produced using high-purity (>99.9% purity) raw materials from Glasma AB (MAM1s Sand, Al(OH)3, Na2B4O7·5H2O, Na2CO3, CaMg(CO3)2, CaCO3, MgO, SrCO3, BaCO3, Na2SO4, TiO2, ZnO, ZnSO4 and La2O). Glass melting was performed in Pt/Rh crucibles using an electrically heated Super Kanthal furnace at 1450 °C for 2 h, homogenization by stirring at 1400 °C for 1 h, conditioning for 1.5 h at 1450 °C and finally 0.5 h at 1480 °C to improve pourability. The glass was poured into stainless steel moulds with rectangular shape (ca. 50 × 40 × 10 mm) and was annealed from 540 °C for 1 h and then cooled to ambient temperature. The software MODDE from UMETRICS was used for the design of experiments (DoEs). In the first DoE, 12 glasses evaluate the network formers SiO2, B2O3 and Al2O3, whereas MgO, CaO and Al2O3 were kept constant; see Table 1. In the second DoE, the network modifiers were evaluated in 15 glass melts. The relative component influence on the different evaluated properties described in Sections 2.2 and 2.3 was then evaluated based on the authors’ collective glass technological expertise.

2.1.2 | Glass synthesis for optimizing optical properties

Raw materials were high purity (<100 ppm Fe) silica sand, and ≥99.9% purity aluminium hydroxide (Al(OH)3), sodium carbonate (Na2CO3), calcium carbonate (CaCO3), magnesium carbonate (MgCO3), bismuth oxide (Bi2O3), gadolinium oxide (Gd2O3) and sodium sulphate (Na2SO4). All raw materials were dried at 110 °C before batch preparation. Batches to produce 100 g of glass of the compositions shown in Table 2 were prepared using a three-decimal place balance, mixed thoroughly and then melted in a zirconia grain stabilized platinum (ZGS-Pt) crucible in an electric furnace for 5 h at 1450 °C. Glasses were then poured into a steel mould that was preheated to 550 °C, as illustrated in Figure 5. The inclusion of nearly 2 mol% Li2O in each glass composition was found to be necessary to reduce the viscosity sufficiently to enable reproducible forming of the 7 × 7 cm plates that were needed for solar performance testing. Although this compositional change represents a slight departure from current float glass compositions, the manufacture of similar glass compositions has been successfully trialled and demonstrated at commercial scale, supporting the applicability of the glass compositions studied here. Here, during forming, excess glass passed through the overflow channels. Once the plates were formed, the mould was removed, and the glass was subsequently annealed at 530 °C for 1 h before cooling slowly to room temperature. Samples for optical absorption measurements were ground with SiC paper with progressively smaller particle sizes to 1 μm, then polished using a 1 μm CeO2 polishing slurry.

2.1.3 | Flat glass synthesis for solar cells and solar cell efficiency measurements

Raw materials were high purity (100 ppm Fe) silica sand, and ≥99.9% purity aluminium hydroxide (Al(OH)3), sodium carbonate (Na2CO3), calcium carbonate (CaCO3), magnesium carbonate (MgCO3), bismuth oxide (Bi2O3), gadolinium oxide (Gd2O3) and sodium sulphate (Na2SO4). All raw materials were dried at 110 °C for 24 h prior to batch preparation. Batches to produce 100 g of glass of the compositions shown in Table 3 were prepared using a three-decimal place balance, mixed thoroughly and then melted in a zirconia grain stabilized platinum (ZGS-Pt) crucible in an electric furnace for 5 h at 1450 °C. Glasses were then poured into a steel mould that was preheated to 550 °C, as illustrated in Figure 5. The inclusion of nearly 2 mol% Li2O in each glass composition was found to be necessary to reduce the viscosity sufficiently to enable reproducible forming of the 7 × 7 cm plates that were needed for solar performance testing. Although this compositional change represents a slight departure from current float glass compositions, the manufacture of similar glass compositions has been successfully trialled and demonstrated at commercial scale, supporting the applicability of the glass compositions studied here. Here, during forming, excess glass passed through the overflow channels. Once the plates were formed, the mould was removed, and the glass was subsequently annealed at 530 °C for 1 h before cooling slowly to room temperature. Samples for optical absorption measurements were ground with SiC paper with progressively smaller particle sizes to 1 μm, then polished using a 1 μm CeO2 polishing slurry.

### Table 2: Glass compositions (mol%) and measured densities

| Sample name | SiO2  | Al2O3 | MgO  | CaO  | Na2O  | SO3  | Bi2O3 | Fe2O3 | Density (g/cm³) ± 0.002 |
|-------------|-------|-------|------|------|-------|------|-------|-------|--------------------------|
| Base glass  | 70.51 | 0.59  | 5.48 | 9.25 | 13.95 | 0.22 | 0.00  | 0.00  | 2.484                    |
| Base glass’ | 72.00 | 0.48  | 5.01 | 9.13 | 13.20 | 0.18 | <0.10 | <0.10 |                          |
| 0.01        | 70.50 | 0.59  | 5.48 | 9.25 | 13.95 | 0.22 | 0.01  | 0.00  | 2.485                    |
| 0.025       | 70.485| 0.59  | 5.48 | 9.25 | 13.95 | 0.22 | 0.025 | 0.00  | 2.487                    |
| 0.05        | 70.46 | 0.59  | 5.48 | 9.25 | 13.95 | 0.22 | 0.05  | 0.00  | 2.497                    |
| 0.10        | 70.41 | 0.59  | 5.48 | 9.25 | 13.95 | 0.22 | 0.10  | 0.00  | 2.502                    |
| 0.15        | 70.36 | 0.59  | 5.48 | 9.25 | 13.95 | 0.22 | 0.15  | 0.00  | 2.513                    |
| 0.20        | 70.31 | 0.59  | 5.48 | 9.25 | 13.95 | 0.22 | 0.20  | 0.00  | 2.518                    |
| 0.20/0.01   | 70.30 | 0.59  | 5.48 | 9.25 | 13.95 | 0.22 | 0.20  | 0.01  | 2.518                    |
| 0.20/0.05   | 70.26 | 0.59  | 5.48 | 9.25 | 13.95 | 0.22 | 0.20  | 0.05  | 2.519                    |
| 0.20/0.10   | 70.21 | 0.59  | 5.48 | 9.25 | 13.95 | 0.22 | 0.20  | 0.10  | 2.523                    |

Note. All are nominal compositions except where noted, as analysed by XRF.

*Analysed by XRF.*
base glass (LIMES A) similar to float glass (with the aforementioned Li2O additions to enable forming) was prepared, and seven further glasses containing different levels of Bi2O3 and Gd2O3 (see Allsopp et al64) were prepared, as shown in Table 3.

2.2 | Glass characterization

2.2.1 | Mechanical property, density and compositional analyses

Densities were measured on solid bulk glass samples (with mass 10–30 g) using the Archimedes method and a four-decimal place balance with deionized water at 20°C. The measured densities presented in Table 2 are averages of three independent measurements. Densities, presented in Table 2, are consistent with other experimental values95 and the Fluegel model,101 indicating the compositions is similar to the nominal compositions, also shown in Table 2.

Mechanical properties were investigated using nanoindentation/microindentation. The employed instrument was an Anton Paar Micro Combi tester equipped with a CPX-NHT2 nanoindenter. Vickers indenter tip was used for the microindentation measurements and for the nanoindentation a Berkovich tip. Average hardness and reduced elastic modulus from 20 indents were measured using the nanoindentation. Indentation fracture toughness and crack resistance (CR) were measured using microindentation by collecting 10 and 15 indents, respectively. We followed the conventional scheme of indentation fracture toughness102 and CR.103,104

X-ray fluorescence (XRF) analyses were carried out using a Philips Magix Pro XRF spectrometer and a Panalytical Axios Fast fluorescence spectrometer using a 1:10 sample to lithium tetraborate flux ratio as fused beads. Beads were melted in a Pt/5%Au crucible at 1065°C for 15 min then cooled in the air to room temperature. Scans were carried out on the SuperQ 3-IQ + software in the oxide setting. XRF analysis of the base glass, shown in Table 2, corresponds to the expected values from the nominal composition.

2.2.2 | Chemical resistance and weathering analysis

The chemical resistance was determined by the powder method, standardized as ISO 719, commonly called P98. It is a hydrolytic method involving cooking of 1-g glass powder with fractions in the range of 100–300 μm for 1 h at 98°C. The water is then titrated with 0.01 N HCl and the result expressed as consumed ml of 0.01 N HCl per g of glass.

Climate chamber tests were conducted in a climate box to verify the P98 results. The method employed involved subjecting the samples to 50°C with approximately 100% relative humidity for 3 weeks. UV–Vis spectrophotometry was used for evaluating the results. The glass samples (ca. 40 × 20 × 10 mm) were mounted in the metal holder for grading and polishing. The smaller side was polished with three different grades of diamond grading wheels (125, 320 and 600 μm) for 2 min each. Final polishing used a diamond paste (1 μm) for 6 min. In order to calculate the visible light transmittance of the glass Tv, Equation 1 was adopted from EN 410:2011. The term Dλτλ (Equation 1) was given in tabular form in the EN 410:2011.

\[
T_v = \sum_{\lambda=380nm}^{780nm} \frac{D_{\lambda} \tau_{\lambda} \lambda}{\sum_{\lambda=380nm}^{780nm} D_{\lambda} V(\lambda) \lambda} 
\]

The transmission was measured between 380 and 780 nm with a PerkinElmer UV–VIS spectrophotometer (Lambda 25) using a scan speed of 480 nm/min, collecting interval 10 nm and a slit width of 1 nm. The light source switch between UV–VIS occurs at 326 nm. The transmission was measured before and after treatment in a climate chamber.
2.2.3 | Thermal property analyses

Thermal expansion behaviour was determined using a dilatometer from room temperature to the softening temperature with a speed of 25 K/min. The determined parameters are thermal expansion (α), transformation temperature (Tₜ), and softening temperature (Mₛ). A glass rod of 40- to 50-mm length and a diameter of 5 mm was used.

For determining the liquidus temperature, the glass was crushed and sieved to the fractions 1-3 mm and placed on a platinum ship. The liquidus temperature was determined in a gradient furnace in the temperature interval of 930–1200 °C for 8 h. The resulting amount of crystals was controlled in a polarized light microscope.

Theoretical calculations of the high-temperature viscosity of given glass compositions were performed using the Lakatos factors for the SLS system for the base glass and the crystal glass system for the others. The results are displayed as the parameters of the Vogel–Fulcher–Tammann equation, \( T = T₀ + B/(\log \eta + A) \) and as \( (\log (\eta/d\text{Pas})) \) versus temperature (°C).

2.2.4 | Optical property analyses

Optical absorption UV–Vis–nIR spectra were measured between 200 and 1100 nm using a Varian Cary 50 spectrophotometer, at a rate of 60 nm/min and with a data interval of 0.5 nm. UV–Vis–nIR fluorescence measurements were carried out using a Varian Cary Eclipse spectrophotometer with all samples placed at 30° to normal incidence. Excitation and emission measurements were made using a 120-nm/min scan rate and 1-nm data interval with slit widths of 20 or 10 nm, and a detector voltage of 400 V.

2.3 | Solar cell manufacturing and solar cell efficiency characterization

Solar modules exemplified by that shown in Figure 6 were prepared at Solar Capture Technologies Ltd, Blyth, UK. Wafers of c-Si (ALBSF Monocrystalline 20.2% efficiency, size 20 x 11 mm, eight cells in series) were tabbed using an Ag PV tabbing ribbon (width 1.2 mm), Tedlar backsheet (Feron CPx 1000), EVA glue (EVASA Solarcap FC100011E 0.46-mm thickness) and glass front sheet (as described in Section 2.1.3). These were cured to form test modules such as that shown in Figure 6. The exact details of the temperature, time and pressure for lamination of the PV modules are the propriety technology of Solar Capture Technologies and are not available within this manuscript. To enable comparison of the candidate glasses against a benchmark, commercially available float glass was obtained and prepared into a module in the same way as the candidate glasses. Electro-luminescence measurements were carried out to identify damaged areas. Solar efficiency measurements were performed on each test module using solar simulator device, SPI-SUN SIMULATOR 240A, with 1.5 AM illumination (Global terrestrial conditions), as described in previous studies. The solar simulator was using a pulsed Xenon light source that closely matches the solar spectrum that with filtering meets ASTM E-927 spectral distributions. The SUN SIMULATOR provides in addition to an I-V curve display, a parametric evaluation of the solar module, which include open-circuit voltage (VₒC), short-circuit current (I SCC), peak power at load (PV(MAX)), peak voltage at load (V(LD)), peak current at load (I(LD)), cell or module efficiency (EF), fill factor (FF), peak power (P(MAX)), voltage at peak power (V(MAX)), current at peak power (I(MAX)), shunt resistance (R(SH)), series resistance (R(S)), the results were corrected to standard testing conditions (1000 W and 25°C). The perimeter of the module was masked and placed in the same location in the centre of the solar simulator that was calibrated before use. Both strings (unlaminated with EVA and cover glass) and modules (laminated with EVA and cover glass) were measured to enable comparison of differences arising during processing.

3 | RESULTS AND DISCUSSION

3.1 | Glass results

3.1.1 | Optimization of glass compositions for use as cover glass for PV modules

Two different glass series have been manufactured, based on modifying the base glass composition that is similar to conventional float glass compositions (see Table 4), thus remaining technologically relevant while enabling exploration of potentially achievable compositional modifications (see, e.g., Wallenberger and Bingham). In total 27 different glasses were developed through a DoEs program to evaluate the varied components effect on the properties; see Table 1 and Section 2.1.1 for details. The DoEs resulted in information on the relative influences of each component on the different properties. The DoE information was then used for proposing three different
compositions (A, B and C), which were then evaluated separately. The decision was made by a trade-off between glass processing and the improvement in properties based partly on the DoE and partly on our collected glass technological know-how. The proposed glass compositions (A, B and C) mechanical properties were investigated using nanoindentation/microindentation (results are shown in Table 5). Hardness and elastic modulus (stiffness) were found to be relatively constant, whereas the parameter CR103 was significantly increased for the optimized compositions, most notably compositions A and B that represent ageing of the glass and the climate test more akin to testing and P98 show comparable trends in the results. The methods presented in Table 5, the climate chamber tests (expressed as ΔT%, before and after climate testing) and the P98 results are shown. The optimized glasses (A, B and C) give approximately a factor of two performance improvement compared with conventional float glass. In order to simulate 30 years of environmental exposure, an empirical equation developed by Lyle108 was used to calculate the parameters of the climate chamber tests. The optimized glasses being tested for 30 years of usage show longer service lifetime than float glass (approximately a factor of 2). Alumina is known to have a positive effect on the chemical resistance.109,110 Besides that, based on previous literature are Sn, Ag, Bi, Ti, Ba, Sr, La, Zn, Mg and Zr interesting oxides for the improvement of the chemical durability.111–113 Based on the results in Table 5, glass B shows the most promising results.

Optimization of the mechanical and chemical properties is of course interesting and important from a PV perspective; however, the thermal properties remain the most important from the perspective of being able to manufacture the glass. In order to estimate the feasibility of glass production, a number of basic thermal properties were measured (see Table 6) and the viscosity calculated (see Table 7). The thermal expansion coefficients of glasses A, B and C were measured and the viscosity calculated (see Table 7). The thermal expansion coefficients of glasses A, B and C were measured as it is an important property for the thermal strengthening of glass, the lower the thermal expansion coefficient is, the lower the strengthening degree will become for a given quench rate.114 The thermal

| Sample name | Hardness (GPa) | Reduced elastic modulus (GPa) | Crack resistance (N)103 | P98 (ISO 719) | Climate chamber treatment in ΔT% |
|-------------|----------------|-----------------------------|------------------------|----------------|-------------------------------|
| Commercial float glass | 6.9 ± 0.1 | 73.7 ± 0.4 | 0.5 ± 0.1 | 1.20 ± 0.1 | - |
| Base glass | 7.3 ± 0.1 | 73.3 ± 0.7 | 1.0 ± 0.1 | 0.85 ± 0.1 | -2.5 ± 0.5 |
| Glass A | 7.1 ± 0.1 | 71.9 ± 0.4 | 1.3 ± 0.1 | 0.47 ± 0.1 | 0.23 ± 0.5 |
| Glass B | 7.3 ± 0.1 | 72.4 ± 0.6 | 1.5 ± 0.1 | 0.43 ± 0.1 | 0.04 ± 0.5 |
| Glass C | 7.3 ± 0.1 | 73.4 ± 0.3 | 0.6 ± 0.1 | 0.46 ± 0.1 | -1.76 ± 0.5 |

Note: P98 is given with the unit ml 0.01 N HCl per gramme glass.

| Sample name | a25–300 \(10^{-6} \text{K}^{-1}\) | Tg (°C) | Mg (°C) | TLiq (°C) |
|-------------|-------------------------------|--------|---------|-----------|
| Base glass | 8.90 ± 0.1 | 554 ± 5 | 615 ± 5 | 1120 ± 20 |
| Glass A | 7.02 ± 0.1 | 569 ± 5 | 630 ± 5 | 1080 ± 20 |
| Glass B | 8.27 ± 0.1 | 554 ± 5 | 605 ± 5 | No crystals |
| Glass C | 8.26 ± 0.1 | 554 ± 5 | 614 ± 5 | 1108 ± 20 |

Note: a25–300 is the thermal expansion coefficient; Tg, the dilatometric glass transition temperature; Mg, the dilatometric softening temperature and TLiq, the liquidus temperature.

| Sample name | \(\eta = 2\) (dPas) | \(\eta = 3\) (dPas) | \(\eta = 5\) (dPas) |
|-------------|-----------------|-----------------|-----------------|
| Base glass | 1435 C | 1181 C | 902 C |
| Glass A | 1466 C | 1180 C | 901 C |
| Glass B | 1469 C | 1193 C | 903 C |
| Glass C | 1439 C | 1174 C | 892 C |

Note: a25–300 is the thermal expansion coefficient; Tg, the dilatometric glass transition temperature; Mg, the dilatometric softening temperature and TLiq, the liquidus temperature.
expansion coefficients are slightly lowered compared with the base glass but still sufficiently high for thermally strengthen the glass.\textsuperscript{74} The results of the glass transition temperature (\(T_g\)), liquidus temperature (\(T_{\text{Liq}}\)) and viscosity are similar to the base glass composition. Measured thermal expansion coefficients of glasses A, B and C are similar to conventional float glass, which is sufficient for the possibility to thermally strengthen these compositions.

### 3.1.2 Doping of optically active components for UV down-shifting

As shown in Figure 7, compare Table 2, the UV–Vis–nIR absorption spectra of SLS glasses doped with 0- to 0.2-mol\% Bi\(_2\)O\(_3\) all show a strong UV absorption edge, even in the Bi\(_2\)O\(_3\)-free glass. This UV absorption in the Bi\(_2\)O\(_3\)-free glass is due to the Si–O network and network modifying cations, with contributions from parts-per-million levels of Fe\(^{2+}\) and Fe\(^{3+}\) occurring as impurities from the raw materials used to make the glasses. The incorporation of Bi in the glasses has the effect of shifting the UV absorption to lower wavenumbers (longer wavelengths). This is attributable to \(^1\text{S}_0 \rightarrow ^3\text{P}_0\) and \(^1\text{S}_0 \rightarrow ^3\text{P}_1\) transitions of Bi\(^{3+}\); causing strong, broad absorption bands centred in the deep UV with tails to lower wavenumbers. Similar behaviour was recently observed for \(s \rightarrow p\) transitions of Sb\(^{3+}\)-doped float-type SLS glasses\textsuperscript{65}; however, the nontoxicity of Bi renders it preferable to Sb from a health and safety perspective. Increasing Bi concentrations thus increase the intensity of these UV absorption bands and hence shift the UV edge to lower wavenumbers (longer wavelengths). The addition of only 0.01-mol\% Bi\(_2\)O\(_3\) shifts the UV edge by 1200 cm\(^{-1}\) (11 nm) compared with the Bi-free (base) glass. The dotted line shown in Figure 7 is reproduced from Yang et al\textsuperscript{115} and extended using data from Fix et al\textsuperscript{116} and provides the absorption profile of C-EVA. This can change, depending on composition and age of the C-EVA\textsuperscript{117} or T-EVA (see Section 1) and older; more strongly irradiated EVA will exhibit a shift in its absorption profile to lower wavenumbers (longer wavelengths).

The effects on optical absorption spectra of doping SLS glasses with different levels and combinations of Bi\(_2\)O\(_3\) and Fe\(_2\)O\(_3\) are shown in Figure 8, with compositions given in Table 2. Increasing levels of Fe\(_2\)O\(_3\) shift the UV edge to lower wavenumbers (longer wavelengths) as expected. The narrow absorption band at 26 220 cm\(^{-1}\) (381 nm) is attributed to the \(^4\text{A}_1(S) \rightarrow ^4\text{E}(D)\) transition of Fe\(^{3+}\) cations in tetrahedral and octahedral sites within the glass structure.\textsuperscript{34,58-60} The broad absorption band centred at 10 000 cm\(^{-1}\) (1000 nm) is attributed to the \(^5\text{T}_2(D) \rightarrow ^5\text{E}(D)\) transition for Fe\(^{2+}\) ions in octahedral sites, which decreases transmission of photons close to the bandgap of c-Si solar cells (1.14 eV or 1087 nm), thereby deleteriously affecting solar cell efficiency.

Fluorescence excitation and emission spectra are shown in Figure 9. The emission spectrum arises from excitation at 33 300 cm\(^{-1}\) (300 nm). It can be observed that emission intensity increases with increasing Bi\(_2\)O\(_3\) concentration throughout the series studied, and consequently, we can conclude that concentration quenching did not strongly impact upon emission intensity within the range of Bi\(_2\)O\(_3\) additions studied here. The emission band is broad (half-width half-maximum is estimated to be approximately 2500 cm\(^{-1}\)) and centred at 23 700 cm\(^{-1}\) (430 nm), with a second, weak band centred at 12 800 cm\(^{-1}\) (780 nm). The two excitation spectra (shown as dotted lines in Figure 9) illustrate that the two emission bands have different origins and are centred at approximately 33 000 cm\(^{-1}\) (300 nm) and 30 500 cm\(^{-1}\) (328 nm), respectively.

Fluorescence emission spectra (Figure 10) show the emission, as a function of excitation wavenumber, for Sample 0.20, as given in Table 2. Within the deep UV, there are inefficiencies of absorption because of the photons having higher energy than the bandgap of Bi\(^{3+}\).
+, between 35 700 cm\(^{-1}\) (280 nm) and 33 300 cm\(^{-1}\) (300 nm) shows the greatest emission intensity.

Figure 11 shows the effects on fluorescence emission spectra from the 0.20-mol% Bi\(_2\)O\(_3\)-doped SLS glass (Sample 0.2 from Table 2) as a function of increasing added Fe\(_2\)O\(_3\) (mol%). Through a combination of competitive absorption of UV photons and fluorescence quenching, the total intensity of the Bi\(^{3+}\) emissions decreases strongly with increasing Fe\(_2\)O\(_3\) concentration, illustrating the need to minimize Fe\(_2\)O\(_3\) content to enable maximum visible fluorescence from Bi\(^{3+}\).

Optical measurements were carried out on flat and polished glass samples with thickness 8 ± 0.1 mm. The UV absorption edge in glasses is characterized by a cut-off wavelength corresponding to photon energies high enough to induce absorption.\(^{118}\) To enable comparative study, we have set this here to the wavenumber corresponding to absorption of 1.0. From Figure 8, we show that increasing additions of Fe\(_2\)O\(_3\) to the glass cause a shift in the UV edge towards the visible region. The addition of only 0.01-mol% (100 ppm) Fe\(_2\)O\(_3\) to silicate glass as a PV module cover glass has been shown to reduce the module output by 1.1% because of the visible and IR absorptions at 26 220 and 11 000 cm\(^{-1}\) (381 and 909 nm) of Fe\(^{3+}\) and Fe\(^{2+}\), respectively.\(^{35}\) By comparison, the addition of Bi\(_2\)O\(_3\) to these glasses can provide a degree of UV protection to the C-EVA and the T-EVA glue, as shown in Figure 7, but without any of the deleterious visible or nIR absorption bands, shown in Figure 8, that arise from doping the solar glass with Fe\(_2\)O\(_3\).

C-EVA strongly absorbs photons with wavenumbers above 26 666 cm\(^{-1}\) (wavelengths below 375 nm),\(^{115}\) with damage arising from absorption of photons with higher energies than this. Similarly, and as discussed in Section 1, T-EVA also suffers, albeit to a lesser extent than C-EVA, from damage due to high-energy photons. For C-EVA, which remains widely used in the PV industry, the National Renewable Energy Laboratory (NREL) carried out a study of the yellowing index of EVA glues in Si-based PV modules.\(^ {119}\) In their...
study, the module was covered with a standard SLS glass, with UV edge at 33 900 cm$^{-1}$ (295 nm). They observed that the yellowing index was 81.9 after 35 weeks of accelerated ageing. They also studied PV modules covered with two SLS glasses, doped with 0.3- and 1.0-mol% CeO$_2$ respectively, which had been added to the glass to move the UV edge to lower wavenumbers of 30 770 cm$^{-1}$ (325 nm) and 30 300 cm$^{-1}$ (330 nm). The two glasses presented yellowing indices of 23.8 (0.3-mol % CeO$_2$) and 17.8 (1.0-mol% CeO$_2$), under the same accelerated ageing conditions. It is believed that the Bi$_2$O$_3$-doped glasses studied here may be suitable to achieve similar or greater levels of UV solar protection, given appropriate optimization. These glasses also require lower concentrations of Bi$_2$O$_3$ than the CeO$_2$ glasses. Control of the UV absorption edge to even more effectively match the C-EVA absorption ‘edge’ would require considerably higher doping concentrations than those that we have studied here and may produce undesirable visible absorption bands centred at 20 000 cm$^{-1}$ (500 nm) and 14 300 cm$^{-1}$ (700 nm), as shown for other glasses doped with 1.0-mol% Bi$_2$O$_3$. However, T-EVA now represents a number of apparent improvements over C-EVA in terms of its UV transparency. Consequently, lower levels of cover glass dopants such as Bi$^{3+}$ than are necessary to fully protect C-EVA may be sufficient to provide protection of T-EVA components of PV modules, which could in turn render the economic considerations for using such glasses even more favourable.

As demonstrated in Figure 10, there is a large variation in emission intensity as a function of excitation wavelength. The peak is consistently centred at 23 700 cm$^{-1}$ (420 nm) with little variation. Although at sea level there are few photons with high energies in the deep UV (>33 000 cm$^{-1}$, <300 nm), there is strong absorbance of these highly damaging photons as shown in Figure 7 because of the transition of $^1$S$_0$ → $^3$P$_1$. Bi$^{3+}$ ion has a 6s$^2$ electronic configuration and has the ground state $^1$S$_0$. After an electron has been promoted to a vibrational level in the $^3$P$_1$ state, the electron will relax to the lower $^3$P$_0$ through a nonradiative transition at lower temperatures (4.2 K), and the forbidden $^3$P$_0$ → $^1$S$_0$ emission state is predominantly observed. However, at room temperature, the electron in the $^3$P$_1$ state directly radiates to the $^1$S$_0$ state and is the preponderant emission. Xu et al demonstrated that concentration quenching of Bi$^{3+}$ ions in borate glasses occurs above 0.25-mol% Bi$_2$O$_3$ and leads both to a reduction in emission intensity and to a shift to longer wavelengths of the peaks. This has been attributed to the self-absorption of Bi$^{3+}$, that is, photons emitted through UV-induced fluorescence are significantly more likely to be reabsorbed because of the higher quantity of Bi$^{3+}$ centres. Within this study, the doping concentration of Bi$_2$O$_3$ has been maintained below 0.20 mol% to both prevent deleterious visible absorptions and to minimize self-absorption effects.

Figure 11 displays the effect of increasing Fe$_2$O$_3$ concentration on the fluorescence emission of Bi$^{3+}$ excited at 33 300 cm$^{-1}$ (300 nm). The total emission rapidly diminishes with increasing quantities of Fe$_2$O$_3$. As shown in Figure 8, the UV absorption of Fe$_2$O$_3$/Bi$_2$O$_3$-doped is shifted further towards the visible than the corresponding Bi$_2$O$_3$ and base glass. This is attributed to the $^6$A$_1$(S) → $^4$T$_2$(D) transition of Fe$^{3+}$ with a peak position at 25 190 cm$^{-1}$ (396 nm) and the $^4$A$_1$(S) → $^4$E(D) with a peak position at 27 250 cm$^{-1}$ (366 nm). Although Fe$_2$O$_3$ more strongly shifts the UV edge and therefore better protects the EVA from damage, the visible and IR bands deleteriously impact PV module efficiency, up to 9.8% loss with a 0.10-mol% Fe$_2$O$_3$-doped glass front sheet. The authors postulate small doping concentrations (up to 0.20 mol%) of Bi$_2$O$_3$ may protect the EVA from UV-induced degradation without the visible and IR bands associated with Fe$_2$O$_3$.

### 3.1.3 Thermal strengthening of glass and in situ chemical vapor deposition

In a previous publication, we have demonstrated the combination of thermal strengthening of glass and the application of amorphous Al$_2$O$_3$ coating onto the glass. This was demonstrated using MOCVD and Al (ac-ac)$_3$ as the precursor with the purpose to increase the surface mechanical properties and tentatively also the chemical durability. The latter has however not been studied. The elaborated process produced thermally strengthened glass of similar strengthening level as conventional tempered glass, that is, 80–110 MPa. The Al$_2$O$_3$ content was quantified being at least doubled at the surface and having an increased Al$_2$O$_3$ content at least 0.5 μm into the glass surface. These mechanical properties were characterized using the CR method, showing a value of 1.3 N compared with 0.8 N for traditional thermal strengthening.

### 3.2 Solar cell efficiencies as a function of glass composition

A float glass PV module is shown in Figure 12 (left), the electroluminescence of before defined as string (centre) and after lamination defined as module (right), and a typical I/V curve is shown in...
Although efforts were made to prepare fully homogenous flat glasses, this proved difficult with the compositions of glass used for previous sample preparation. As the redox of the glass would be affected strongly by increasing the temperature to lower the viscosity for amenable pouring, it was decided to incorporate 2-mol% Li$_2$O into the glass in replacement of Na$_2$O (see Section 2.1.3). This reduced the high-temperature viscosity of the molten glass through two mechanisms, the mixed alkali effect and reduced connectivity of the silicate network, because of the partial replacement of Na$_2$O by Li$_2$O.$^{124}$ However, incorporation of Li$_2$O also affects the refractive index of the glass by increasing the polarizability of the constituents relative to a glass containing the equivalent quantity of R$_2$O such as Na$_2$O or K$_2$O.$^{125}$

There is an increase in the short-circuit current between the string and module because of lower reflection losses and a minor index matching corresponding to the C-EVA and glass layers. The difference in refractive indices is lower in the module than in the string, as the C-EVA acts as an index matching layer when bonded together. There are several abbreviations in Table 8 that are explained below.

$V_{oc}$ is the open-circuit voltage, the maximum voltage available from a PV module that occurs at zero current. On the $I/V$ curve shown in Figure 13, this is where the curve touches the x-axis where the y-axis (current) is equal to zero. $I_{sc}$ is the short-circuit current; this is the maximum current available when the voltage across the PV module is zero. On the $I/V$ curve shown in Figure 13, this is where the curve touches the y-axis where the x-axis (voltage) is equal to zero. $R_{series}$ is the series resistance in a PV module. This is a measure of the movement of current across the emitter and base of the module, the resistance across the metal contacts and the silicon (or other PV active material) and the resistance of the top and rear contacts. This results in inefficiencies within the module and reduces the $V_{oc}$ and $I_{sc}$. $R_{shunt}$ is the shunt resistance of a PV module. Low shunt resistance causes power loss in a module as the propagation of the current may follow an alternative path than that designed. Larger values therefore

| Property       | Float | LIMES BG A | LIMES BG B | LIMES BG C | LIMES B2G A | LIMES B2G B | LIMES B2G2 | LIMES B2 |
|----------------|-------|-----------|-----------|-----------|-----------|-----------|-----------|--------|
| Irradiance (W/m$^2$) | ±20   | 1044      | 1041      | 1062      | 1057      | 1040      | 1040      | 1051   | 1043   | 1051   |
| Corrected (W/m$^2$) | ±20   | 1000      | 1000      | 1000      | 1000      | 1000      | 1000      | 1000   | 1000   | 1000   |
| Module temp (°C)  | ±1    | 23.4      | 24.0      | 24.0      | 23.8      | 21.8      | 22.2      | 23.1   | 23.2   | 22.9   |
| Corrected to (°C) | ±1    | 25        | 25        | 25        | 25        | 25        | 25        | 25     | 25     | 25     |
| $V_{oc}$ (V)      | ±0.3  | 5.07      | 4.97      | 4.98      | 5.01      | 4.99      | 4.97      | 5.05   | 5.03   | 4.97   |
| $I_{sc}$ (A)      | ±0.003| 0.113     | 0.062     | 0.070     | 0.113     | 0.115     | 0.114     | 0.117  | 0.111  | 0.115  |
| $R_{series}$ (mΩ) | ±10   | 45.20     | 7.06      | 85.16     | 11.18     | 6.18      | 15.51     | 14.37  | 18.50  | 5.95   |
| $R_{shunt}$ (Ω/cm$^2$) | ±100 | 626.67    | 6460.12   | 4206.23   | 986.97    | 4838.96   | 504.53    | 1004.53| 576.77 | 983.19 |
| $P_{max}$ (W)     | ±0.02 | 0.445     | 0.241     | 0.284     | 0.434     | 0.467     | 0.465     | 0.437  | 0.446  | 0.446  |
| $V_{pm}$ (V)      | ±0.4  | 4.33      | 4.66      | 4.35      | 4.17      | 4.28      | 4.13      | 4.27   | 4.25   | 4.15   |
| $I_{pm}$ (A)      | ±0.005| 0.103     | 0.052     | 0.065     | 0.104     | 0.109     | 0.104     | 0.109  | 0.103  | 0.107  |
| Fill factor       | ±0.05 | 0.78      | 0.79      | 0.82      | 0.77      | 0.81      | 0.76      | 0.79   | 0.78   | 0.78   |

Figure 13. Although efforts were made to prepare fully homogenous flat glasses, this proved difficult with the compositions of glass used for previous sample preparation. As the redox of the glass would be affected strongly by increasing the temperature to lower the viscosity for amenable pouring, it was decided to incorporate 2-mol% Li$_2$O into the glass in replacement of Na$_2$O (see Section 2.1.3). This reduced the high-temperature viscosity of the molten glass through two mechanisms, the mixed alkali effect and reduced connectivity of the silicate network, because of the partial replacement of Na$_2$O by Li$_2$O.$^{124}$ However, incorporation of Li$_2$O also affects the refractive index of the glass by increasing the polarizability of the constituents relative to a glass containing the equivalent quantity of R$_2$O such as Na$_2$O or K$_2$O.$^{125}$

There is an increase in the short-circuit current between the string and module because of lower reflection losses and a minor index matching corresponding to the C-EVA and glass layers. The difference in refractive indices is lower in the module than in the string, as the C-EVA acts as an index matching layer when bonded together. There are several abbreviations in Table 8 that are explained below.

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![Figure 13](image-url)
minimize the difference between theoretical maximum power output and realized power output of a PV module. $P_{\text{MAX}}$ is the maximum power (W) of a PV module and is calculated by multiplying the $V_{\text{OC}}$, $I_{\text{SC}}$, and fill factor of the module together.

$V_{\text{PM}}$ is the voltage at maximum power of a PV module, similar to $I_{\text{PM}}$, which is the current at maximum power within a PV module. Fill factor is a measure of the quality of a given PV module and is calculated by dividing the maximum power point by the product of $V_{\text{OC}}$ and $I_{\text{SC}}$.

From Tables 8 to 10, the $I_{\text{sc}}$ and $I_{\text{pm}}$ are shown for each prepared glass and that of a commercially available float glass, and the relative enhancement of the glass is shown in Figure 14. Note that in those samples, in which the cells have cracked during lamination, the total area available for PV conversion is lowered, and therefore, the relative enhancement appears to be lower. This is an artefact of the broken cells rather than being significantly lower efficiency. In samples without significant damage to the cells, there is an increase in $I_{\text{sc}}$ and $I_{\text{pm}}$ indicating higher efficiency from the dopants, as illustrated in Figure 14; however, repeated experiments to provide full confirmation of this may be prudent.

It is postulated that the enhancement of the $I_{\text{sc}}$ and $I_{\text{pm}}$ is due to the addition of fluorescent dopants. The wide variation is due to slight sample differences; not all glasses were able to be prepared to the

**TABLE 9** Electrical data for cell strings

| Property          | Uncertainty | Float | LIMES A | LIMES BG A | LIMES BG B | LIMES BG C | LIMES B2G A | LIMES B2G B | LIMES B2G2 | LIMES B2 |
|-------------------|-------------|-------|---------|------------|------------|------------|------------|------------|------------|-----------|
| Irradiance (W/m²) | ±20         | 1043  | 1039    | 1049       | 1048       | 1063       | 1055       | 1040       | 1065       | 1044      |
| Corrected to (W/m²): | ±20         | 1000  | 1000    | 1000       | 1000       | 1000       | 1000       | 1000       | 1000       | 1000      |
| Module temp (°C)  | ±1          | 25.0  | 24.9    | 24.6       | 24.2       | 24.2       | 24.5       | 25.4       | 25.3       | 23.8      |
| Corrected to (°C): | ±1          | 25    | 25      | 25         | 25         | 25         | 25         | 25         | 25         | 25        |
| $V_{\text{oc}}$ (V) | ±0.3        | 5.03  | 4.96    | 4.91       | 4.98       | 4.98       | 4.95       | 5.02       | 5.03       | 4.96      |
| $I_{\text{sc}}$ (A) | ±0.003      | 0.102 | 0.098   | 0.097      | 0.100      | 0.100      | 0.099      | 0.102      | 0.104      | 0.099     |
| $R_{\text{series}}$ (mΩ) | ±10        | 12.67 | 8.60    | 12.86      | 9.85       | 8.06       | 14.66      | 12.51      | 11.46      | 24.19     |
| $R_{\text{shunt}}$ (Ω/cm²) | ±100       | 2274.31 | 1403.03 | 1249.74    | 1198.94    | 3304.78    | 2112.79    | 1012.15    | 1869.49    | 2448.08   |
| $P_{\text{max}}$ (W) | ±0.02      | 0.405 | 0.381   | 0.376      | 0.391      | 0.394      | 0.380      | 0.398      | 0.405      | 0.384     |
| $V_{\text{pm}}$ (V) | ±0.4        | 4.22  | 4.38    | 4.13       | 4.18       | 4.18       | 4.11       | 4.19       | 4.22       | 4.15      |
| $I_{\text{pm}}$ (A) | ±0.005      | 0.096 | 0.087   | 0.091      | 0.094      | 0.094      | 0.093      | 0.095      | 0.096      | 0.093     |
| Fill factor       | ±0.05       | 0.79  | 0.78    | 0.79       | 0.78       | 0.79       | 0.78       | 0.78       | 0.78       | 0.78      |
to C-EVA, its yellowing index is nonzero,
and hence, enhanced performance of T-EVA in PV modules has not yet been fully investigated. However, in terms of its application in PV modules, there remains room for improvement. In the current paper, we have reviewed the state of the art and conclude that improvements to PV modules can be made by optimizing the cover glass composition. We have shown that it is possible to increase the CR of cover glass from 0.5 N for conventional SLS float glass to 1.5 N (glass LIMES B) and to increase the chemical resistance by a factor of about 3 as measured using P98 (ISO 719). This has been demonstrated for glass compositions that have similar hardness, reduced elastic modulus and thermal properties as for conventional SLS float glass. Iron, when present in float glass, produces a broad d-d absorption band in the nIR (Fe2+) and narrow d-d bands in the visible (Fe3+), collectively resulting in a significant loss in transmission. However, removal of iron from the glass to increase transmission creates a problem in terms of increased UV transmission, which more rapidly ages the polymeric C-EVA or T-EVA leading to reduced PV module service lifetimes. We have shown here that doping the SLS float glass with Bi2O3 and Gd2O3 can effectively reduce the UV transmission while keeping the glass essentially free from absorption in the visible and nIR ranges. This is augmented by broadband down-shifting of absorbed UV photons and re-emission as visible photons available for conversion by the solar cell. The compound effect of these compositional changes to the cover glass thereby enables both increased efficiency and increased lifetime of PV modules. This was also demonstrated for laboratory-scale PV modules in terms of measured $I_{sc}$ and $I_{lum}$; however, further measurements to confirm the results are advisable. Thermal strengthening is the predominant technique for providing protection to hailstorms for PV modules; however, this process can be effectively improved in terms of CR by combining with CVD in a one-step process providing a thin film of Al2O3.

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