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**Oxidation protective glass coating for magnesium silicide based thermoelectrics**

Fabiana D'Isanto[1*], Federico Smeacetto[1], Michael John Reece[2], Kan Chen[2], Milena Salvo[1]

[1]Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129, Turin, Italy

[2]School of Engineering & Materials Science and Nanoforce Technology Ltd, Queen Mary University of London, Mile End Road, London E1 4NS, United Kingdom

*Author to whom the correspondence should be addressed: fabiana.disanto@polito.it; Tel +39 011 0904567

**Abstract**

A $Mg_2Si$-$Mg_2Sn$ based thermoelectric material (TE), with composition of $Mg_2Si_{0.487}Sn_{0.5}Sb_{0.013,}$ produced by ball-milling combined with spark plasma sintering, is successfully coated with a new silica-based glass, which is specifically designed, characterised and tested as an oxidation protective coating for mid-temperature range (up to 500 °C) applications. Despite the relatively high coefficient of thermal expansion (CTE) of $Mg_2(Si,Sn)$ based materials, very good thermo-mechanical compatibility between the substrate and the coating material is obtained. Oxidation tests, performed at 500 °C for 120 hrs in air, demonstrate the effectiveness of the glass coating for the protection of Sb doped $Mg_2(Si,Sn)$ thermoelectric materials.

**Keywords:** Oxidation protective coatings; thermoelectric materials; glasses; magnesium silicides

## 1. Introduction

Magnesium silicide is a n-type semiconductor belonging to the $Mg_2X$ (X = Si, Ge, Sn and Pb) family of intermetallic compounds [1,2]. Thanks to their good thermoelectric performance, low-toxicity, low-cost and light-weight [3–5], they have been proposed as good candidates for thermoelectric modules for waste heat recovery. In order to improve its thermoelectric performance, i.e. the figure of merit (zT), $Mg_2Si$ was doped with Bi, thus achieving a zT of ~ 0.9 at 600 °C [6]. Furthermore, to reduce the thermal conductivity, n-type solid solutions of $Mg_2Si$ with $Mg_2Sn$ [7–10] and/or $Mg_2Ge$ [11,12] have been investigated; one of the best results in terms of zT has been reported for $Mg_{2.08}Si_{0.364}Sn_{0.6}Sb_{0.036}$ with a value of 1.5 at 450 °C [13].

The stability and oxidation resistance of thermoelectrics over time at high temperature are critical issues; their oxidation leads to a reduction in generated power and significantly limits the long-term reliability and efficiency of TE modules [14,15]. Most of the common thermoelectric materials, such as tellurides and silicides, are easily oxidized at high temperature [16]; e.g. magnesium silicide and its solid solutions cannot be used above ~ 400 °C in air. Sondergard et al. [17] investigated the thermal stability in air of $Mg_2Si_{0.4}Sn_{0.6}$ and $Mg_2Si_{0.6}Sn_{0.4}$ up to 400 °C, reporting the formation of Sn-rich $Mg_2Si_{1-x}Sn_x$ and MgO phases for powders heated in air, while sintered pellets showed higher stability. Furthermore, Skomedal et al. [18] studied the degradation of $Mg_2Si_{1-x}Sn_x$ with $0.1 < x < 0.6$, demonstrating a slow oxidation rate for temperatures below 430 °C, while in the temperature range between 430-500 °C all of the alloys exhibited breakaway oxidation. This study explained that the breakaway behaviour

was due to of the formation of a non-protective MgO layer, which led to the formation of a Mg depleted phase and a Sn rich liquid phase at the alloy/interface.

It is therefore clear that in order to develop thermoelectric modules that can be used over a wide temperature range for waste heat regeneration (steel industry, incinerators, automobiles), an anti-oxidation technology is needed[19]. Several solutions have been proposed and evaluated to protect TEs, for example, hermetic sealing under vacuum or in an inert gas such as argon [20] or in aerogels [21–24]. Most studies in the field of protective coatings for silicide based TEs have only focused on $Mg_2Si$, which has a much lower CTE (~$11 \cdot 10^{-6}$ $K^{-1}$ [25]) than that of Sb doped $Mg_2(Si,Sn)$ based materials (17-17.5$\cdot 10^{-6}$ $K^{-1}$). Tani et al [26] studied the effect of magnetron sputtered β-FeSi on $Mg_2Si$, observing that it improved oxidation resistance up to 600 °C. Furthermore, YSZ showed potentially good oxidation suppression characteristics for $Mg_2Si$ after thermal cycling from room temperature to 600 °C [19]. Recently, $Mg_2Si$ has been coated using the dip-coating method with a silane-based amorphous coating (produced using sol- gel method); this oxidation protective coating was only effective up to 450 °C, probably due to the differences in CTEs between the coating, thermoelectric material and oxidation products [27].

As mentioned above, very little information can be found in literature on protective coatings Sb doped $Mg_2(Si,Sn)$ based materials. Yin et al [28] proposed and studied the effect of a BN coating for Sb substituted $Mg_2Si_{0.3}Sn_{0.7}$, which can effectively protect the material up to 500 °C. As another example, hybrid coatings were successfully used to

protect a magnesium silicide with composition $Mg_{2.1}Si_{0.487}Sn_{0.5}Sb_{0.013}$ against oxidation at 500°C [29].

In this work, a new silica-based glass coating has been developed to protect a Sb doped $Mg_2(Si,Sn)$ based material ($Mg_2Si_{0.487}Sn_{0.5}Sb_{0.013}$) from oxidation up to 500°C.

## 2. Experimental

The thermoelectric (TE) material studied in this research was a Sb doped $Mg_2(Si,Sn)$ with composition $Mg_2Si_{0.487}Sn_{0.5}Sb_{0.013}$. Starting powders of $Mg_2Si$ (≥ 99 %, 20 mesh, Sigma-Aldrich), Sn (99.8 %, < 45 μm particle size, Sigma-Aldrich), Mg (99.8 %, 325 mesh, AlfaAesar) and Sb (99.5 %, 200 mesh, AlfaAesar) were loaded into a stainless steel jar with stainless steel balls and sealed in an inert atmosphere of argon. The mixed powders were ball-milled using a commercial planetary ball-milling machine (P5 Fritsch, FRITSCH GmbH, Idar-Oberstein, Germany) and then sintered as 15 mm diameter discs using a Spark Plasma Sintering furnace (FCT HPD 25, FCT Systeme GmbH, Rauenstein, Germany) with sintering conditions of 720 °C/50 MPa/5 min (heating and cooling rate of 100 °C/min). The density of some as-sintered Sb doped $Mg_2(Si, Sn)$ samples were measured using the Archimede' s method.

The glass coating developed in this work (referred to as M3 glass) was produced by the conventional melting and casting method. It has the following composition (wt %): $SiO_2$ (purity 99.5%, Sigma Aldrich) 44.05, $K_2O$ (precursor $K_2CO_3$, purity 99.5%, Sigma Aldrich) 24.07, $Na_2O$ (precursor $Na_2CO_3$, purity 99.5%, Sigma Aldrich) 13.63, CaO (precursor $CaCO_3$, purity 99%, Sigma Aldrich) 3.41, MgO (precursor $MgCO_3$, purity 99.9%, Sigma Aldrich) 1.47, $Al_2O_3$ (purity 99.9%, Alfa Aesar) 3.03 and $B_2O_3$ (precursor $H_3BO_3$, purity

99.99%, Sigma Aldrich), 10.33. This composition was designed with the help of the SciGlass® software (Science Serve GmbH, Sciglass 6.6 software, Newton, Massachusetts, USA), in order to obtain the desired thermophysical properties of the glass, i.e. the glass transition temperature ($T_g$) and softening point, and a coefficient of thermal expansion (CTE) as close as possible to that of the TE substrate. The glass composition included a high content of alkaline oxides, such as $K_2O$ and $Na_2O$, to increase the CTE, and MgO to hinder the diffusion of Mg from the TE substrate towards the glass coating. A $T_g$ lower than 500 °C was the target in order to ensure an adequate viscosity of the glass during the coating process that should not exceed the sintering temperature of the TE substrate (720°C). All of the raw material powders were mixed in the proper ratios for 24 hrs, before the melting process, which was carried out in an electric furnace (Nabertherm LHT418PN2, Lilienthal/ Bremen, Germany), using a Pt-Rh crucible, in air. The melting process was conducted at 1200 °C for 1 h and subsequently at 1250°C for 30 minutes, and finally the glass was cast and quenched on a brass plate. The M3 glass was milled in a $ZrO_2$ ball mill and then sieved to obtain powders with a particle size of ≤ 38 µm. The differential thermal analysis (DTA) (DTA 404 PC, Netzsch, Selb, Germany) of the M3 powders was carried out from room temperature to 810 °C with a heating rate of 10 °C/min. Furthermore, the sintering behaviour of the glass powders was investigated using hot stage microscopy (HSM, EM 301, Hesse Instruments, Harzgerode, Germany), with a heating rate of 10 °C/min, from room temperature to 820 °C.

The parameters of the M3 deposition thermal treatment were chosen on the basis of the results of the HSM analysis: 550 °C for 1 h under flowing Ar (heating rate of 10

°C/min). A small quantity of a slurry paste composed of ethanol (70 wt %) and glass powder (30 wt %), was manually deposited with a spatula onto the Sn-Sb doped magnesium silicide substrate and allowed to dry for a few minutes. The coating process was carried out in a tubular furnace (STF 16/ 180, Carbolite Gero, Hope Valley, UK) under continuous flowing Ar. The same heat treatment was also used to produce glass pellets (referred to as M3 550 °C 1h); M3 glass powder (≤ 38 µm) was uniaxial pressed (100 bar) for 15 seconds, and then sintered at 550 °C.

The X-ray diffraction analysis was carried out on as-sintered TE sample, coated samples and M3 sintered pellets between 20° and 70° using a X'Pert Pro MRD diffractometer with Cu Kα radiation (PANalytical X'Pert Pro, Philips, Almelo, The Netherlands), with the aid of the X-Pert HighScore software; the phases were identified using JCPDS data base provided by ICDD (International Centre for Diffraction Data, Newton Square, Pennsylvania, USA).

A field emission scanning electron microscope (FE-SEM, Merlin electron microscope, ZEISS, Oberkochen, Germany) with energy dispersive X-ray spectroscopy (EDS, Zeiss Supra TM 40, Oberkochen, Germany) was used to characterise the morphology of the samples, which were previously polished using SiC papers (grit size 600-4000) and coated with Cr.

The CTE measurements were carried out in a dilatometer (DIL 402 PC/4, Netzsch, Selb, Germany) equipped with an alumina sample holder, at a heating rate of 5°C/min, applying a constant compressive force, between the sample and the piston, of 0.25 N.

The oxidation resistance of uncoated and coated thermoelectric materials was assessed by heating the samples at 500 °C for 120 hrs in a muffle oven (Manfredi OVMAT 2009, Pinerolo, Italy) in static air. After that, FE-SEM and EDS analysis were carried out to assess the microstructure of the coated sample after the oxidation tests. X-ray diffraction analysis was carried out both on the uncoated/coated samples, as well as on the M3 pellet prepared at 550 °C for 1h, after the oxidation test at 500 °C for 120 hrs (for the coated sample, the surface coating was removed before the analysis).

## 3. Results and discussion

The solid-state reaction, occurring during the ball milling of the elemental powders, produced a single phase of $Mg_2Si_{0.487}Sn_{0.5}Sb_{0.013}$, with crystal structure similar to that of $Mg_2Si_{0.4}Sn_{0.6}$ as identified by the PFD card 01-089-4254, as can be seen in the XRD pattern shown in Figure 1a.

The XRD analysis of the as-sintered TE (Figure 1b), produced by SPS with sintering conditions of 720°C/50 MPa/5 min, showed that no phase separation occurred during the heat treatment, while a peak at 2Θ~43° can be correlated to a slight amount of MgO (identified with the PDF card n. 01-075-1525), already found in previous works [30,31].

The average density of some sintered $Mg_2Si_{0.487}Sn_{0.5}Sb_{0.013}$ pellets, measured using the Archimede's method is 3.00 g/ $cm^3$. This value is higher than the theoretical value of the $Mg_2Si_{0.5}Sn_{0.5}$ (2.89 g/ $cm^3$ [32]) because of the presence of MgO, which has a theoretical density of 3.58 g/ $cm^3$ [33].

The dilatometric analysis on the Sb doped $Mg_2(Si,Sn)$ was carried out in order to characterise its thermo-mechanical behaviour and to identify a compatible glass-based coating, thus avoiding the presence of high residual stresses at the TE/coating interface. The CTE was extrapolated from the slope of the linear portion of the curve (Figure 2, green curve) between 50 °C and 300 °C and was found to be $17.6 \cdot 10^{-6}$ $K^{-1}$. Furthermore, the dilatometric analysis, carried out on the as-cast glass, is reported in Figure 2 (black curve); the CTE between 150 °C and 300 °C is $16.8 \cdot 10^{-6}$ $K^{-1}$ and the dilatometric softening temperature, $T_d$, was found to be at 429 °C.

In order to choose the optimal coating thermal treatment, it is necessary to obtain a suitable densification of the glass-based coating. The sintering behaviour of the M3 glass was evaluated from HSM and DTA analyses and the resultant plots are presented in Figure 3.

The DTA recorded the onset of the glass transition temperature ($T_g$) at 420°C and the onset of the melting ($T_m$) at ~760°C, while no evidence of crystallization peaks was detected. Furthermore, the hot stage microscopy of the shape of the sample (reported on the top of the graph in Figure 3) was observed, and some characteristic fixed viscosity points of the glass were identified, which correspond to specific temperatures [34]: first shrinkage temperature ($T_{FS}$), maximum shrinkage temperature ($T_{MS}$), deformation temperature (DT), sphere temperature (ST), half-sphere temperature (HT), flow temperature (FT). A significant shrinkage of the sample started at ~ 438 °C ($T_{FS}$); reaching a shrinkage of around 35% at ~ 534 °C ($T_{MS}$). The method proposed by M. J. Pascual et al. [34] was adopted to predict the viscosity vs T behaviour of the glass

at fixed viscosity points. Figure 4 shows the results obtained by plotting the characteristic temperatures and fitting a trend line to predict the viscosity of the system vs temperature. A value of viscosity of ~ $10^{6.5}$ Pa s was obtained at a temperature of 550 °C. This value is considered as appropriate to allow good glass flow and bonding with the thermoelectric substrate. On the basis of the HSM analysis, the thermal treatment to obtain the glass-based coating was chosen as 550 °C for 1h under flowing Ar.

Figure 5a shows the XRD pattern of M3 after the deposition heat treatment, no evidence of crystalline phases was found. The results of the dilatometry on sintered M3 after the heat treatment are reported in Figure 2 (blue curve); the CTE of the cast and sintered M3 glass are similar, ~ $17 \cdot 10^{-6}$ $K^{-1}$ (150-300 °C). This value is slightly lower than that of the $Mg_2Si_{0.487}Sn_{0.5}Sb_{0.013}$ substrate ($17.6 \cdot 10^{-6}$ $K^{-1}$), which led to a moderate compression state in the coating [14,15], thus making the coated $Mg_2Si_{0.487}Sn_{0.5}Sb_{0.013}$potentially more resistant to the propagation of cracks during the cooling process or under thermal cycling.

Figure 6 (a, b) shows SEM images of the cross-section of the M3 glass coated Sb doped $Mg_2(Si,Sn)$. It can be seen that the coating is well adhered to the substrate, and no cracks or delamination are visible at the coating/TE interface after the deposition treatment. The absence of cracks indicates good thermo-mechanical compatibility between the coating and the thermoelectric substrate, thus confirming the results obtained with the dilatometric analysis. Furthermore, no oxidation/reaction layers are visible at the interface. The M3 coating showed a low amount of closed porosity,

probably due to the manual deposition method of the slurry (glass powders with ethanol). No crystalline phases were detected, consistent with the XRD pattern (Figure 5).

Based on the above results, M3 glass-based coated TE and uncoated samples were submitted to an oxidation test at 500 °C (a temperature lower than M3 deformation temperature, DT) for 120 hrs in air.

Figure 7 shows the samples before and after the oxidation test. The uncoated sample was completely oxidised and turned into powder, while the coated one appeared unaffected, and it is clear that the glass-based coating was effective in protecting the thermoelectric substrate in an oxidative atmosphere.

The XRD pattern of the uncoated $Mg_2Si_{0.487}Sn_{0.5}Sb_{0.013}$ after the oxidation test (Figure 1c) shows that the thermoelectric substrate decomposed into a mixture of compounds: MgO (PDF card n. 01-075-1525), $SnO_2$ (PDF card n. 01-077-0447), SnO (PDF card n. 01-078-1913), Sn (PDF card n. 01-089-2761) and Si (PDF card n. 00-026-1481), as already reviewed by Skomedal et al.[35].

The XRD analysis of the coated sample after the oxidation test (after removing of the outer layers to reveal pristine Sb doped $Mg_2(Si,Sn)$ is shown in Figure 1d, which is identical with that of the as-sintered sample (Figure 1b), thus validating the efficacy of the M3 glass-based coating to protect the TE material. The small amount of MgO, corresponding to the peak at 2Θ~43°, was already present in the as-sintered Sb doped $Mg_2(Si,Sn)$ before the oxidation test (Figure 1b).

Figure 8 shows the cross-section of a M3 glass coated $Mg_2Si_{0.487}Sn_{0.5}Sb_{0.013}$ sample after the oxidation test. It can be seen that the excellent adhesion of the coating to the thermoelectric material was maintained after the long exposure to severe conditions.

The interface between the coating and the thermoelectric substrate was characterised by an absence of cracks or delamination, and no reaction layers were visible. The EDS analysis presents the atomic % of the elements in the glass-based coating (Spectrum1) and in the $Mg_2Si_{0.487}Sn_{0.5}Sb_{0.013}$substrate (Spectrum 2), and a good correspondence to the nominal composition of the glass composition was found. No diffusion of elements between the $Mg_2Si_{0.487}Sn_{0.5}Sb_{0.013}$ and the glass coating was detected. In fact, in the substrate only the elements Mg, Si and Sn were identified, while in the coating all of the chemical elements belonging to the glass composition were found. The presence of Sb could not be detected due to a lack of sensitivity of the EDS. In order to evaluate the thermodynamic stability of the M3 glass-based coating after the oxidation test, the X-ray diffraction analysis was performed (Figure 5b); the glass is still completely amorphous since devitrification did not occur.

A difference of 50°C between the deposition temperature and the oxidation test temperature was found to be effective to avoid glass flowing and to protect the substrate from oxidation. These results are in line with those of our previous studies [36,37] where we have discussed that some glass systems can be used as effective protection at a temperature higher than their dilatometric softening point. Similarly, this work confirmed that, at the oxidation test temperature, the viscosity of the M3

glass (~ $10^{7.6}$ Pa s from Figure 4) is still sufficient to hinder the diffusion of oxygen through the coating.

## 4. Conclusions

The novelty of this research is in the design of a new oxidation protective glass-based coating with a low deposition temperature (500 °C) and high coefficient of thermal expansion (~$17 \cdot 10^{-6}$ $K^{-1}$), similar to that of the thermoelectric substrate. In fact, the development of a thermo-mechanically compatible glass-based coating for $Mg_2Si_{0.487}Sn_{0.5}Sb_{0.013}$ plays a key role in the manufacture of reliable, efficient and durable TE devices. The morphological characterization of the M3 glass coated Sb doped $Mg_2$(Si,Sn) showed good compatibility between the coating and the thermoelectric substrate; no cracks and delamination were visible before and after oxidation testing at 500 °C for 120 hrs in air. Furthermore, XRD analysis on the coated sample after the oxidation testing confirmed that the thermoelectric substrate was unchanged, thus demonstrating the effectiveness of the glass coating during long exposure to severe conditions. These finding suggest that the M3 glass-based coating is a promising candidate for protecting $Mg_2$(Si,Sn) based thermoelectric materials against oxidation.

Future work will focus on the measurement of electrical properties of the as-sintered and coated $Mg_2Si_{0.487}Sn_{0.5}Sb_{0.013}$ (after oxidation test at 500°C for 120 hrs in air). The Seebeck coefficient, the electrical resistivity, the power factor and the figure of merit (zT) will be evaluated in order to confirm the effectiveness and the reliability of the M3 glass-based oxidation resistant coating for Sb doped $Mg_2$(Si,Sn) thermoelectrics.

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**Conflicts of interest**: The authors declare no conflicts of interest.

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**Figure captions**

Figure 1: XRD patterns of $Mg_2Si_{0.487}Sn_{0.5}Sb_{0.013}$ (a) after ball milling, (b) as-sintered, (c) after the oxidation test at 500°C for 120 hrs in air without coating, (d) M3 glass coated after the oxidation test at 500°C for 120 hrs in air, and (e) PDF card (number: 01-089-4254) of $Mg_2Si_{0.4}Sn_{0.6}$.

Figure 2: Dilatometry curves of (1) $Mg_2Si_{0.487}Sn_{0.5}Sb_{0.013}$, (2) M3 as-cast glass and (3) M3 glass sintered at 550°C 1h under flowing Ar.

Figure 3: DTA (black curve) and HSM (blue curve) analyses with characteristic temperatures for M3 glass powders (≤ 38 µm), both recorded at 10 °C/min.

Figure 4: log η vs Temperature curve for the M3 glass obtained by fitting the characteristic fixed viscosity points and related temperatures [34], calculating the constant of the equation $y= ax^b$ and the R-square value, by non-linear regression.

Figure 5: XRD pattern of (a) M3 glass after the deposition heat treatment at 550 °C 1h under flowing Ar and (b) M3 glass coating after the oxidation test at 500 °C for 120 hrs in air.

Figure 6: SEM image of the cross-section of a M3 glass coated $Mg_2Si_{0.487}Sn_{0.5}Sb_{0.013}$ sample (deposition heat treatment at 550°C, 1h, under flowing Ar).

Figure 7: Uncoated $Mg_2Si_{0.487}Sn_{0.5}Sb_{0.013}$ and M3 glass coated $Mg_2Si_{0.487}Sn_{0.5}Sb_{0.013}$, before and after the oxidation test at 500°C for 120 hrs in air.

Figure 8: SEM image and EDS analysis of cross-section of M3 glass coated $Mg_2Si_{0.487}Sn_{0.5}Sb_{0.013}$ after oxidation test at 500°C for 120 hrs in air.