Gamma irradiation-induced defects in borosilicate glasses for high-level radioactive waste immobilisation

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Published version

RAUTIYAL, Prince, GUPTA, Gaurav, EDGE, Ruth, LEAY, Laura, DAUBNEY, Aaron, PATEL, Maulik, JONES, Alan and BINGHAM, Paul (2020). Gamma irradiation-induced defects in borosilicate glasses for high-level radioactive waste immobilisation. Journal of Nuclear Materials.

Figure S1. *XRD patterns for NaBaBSi and LiNaBSi pristine glasses.*

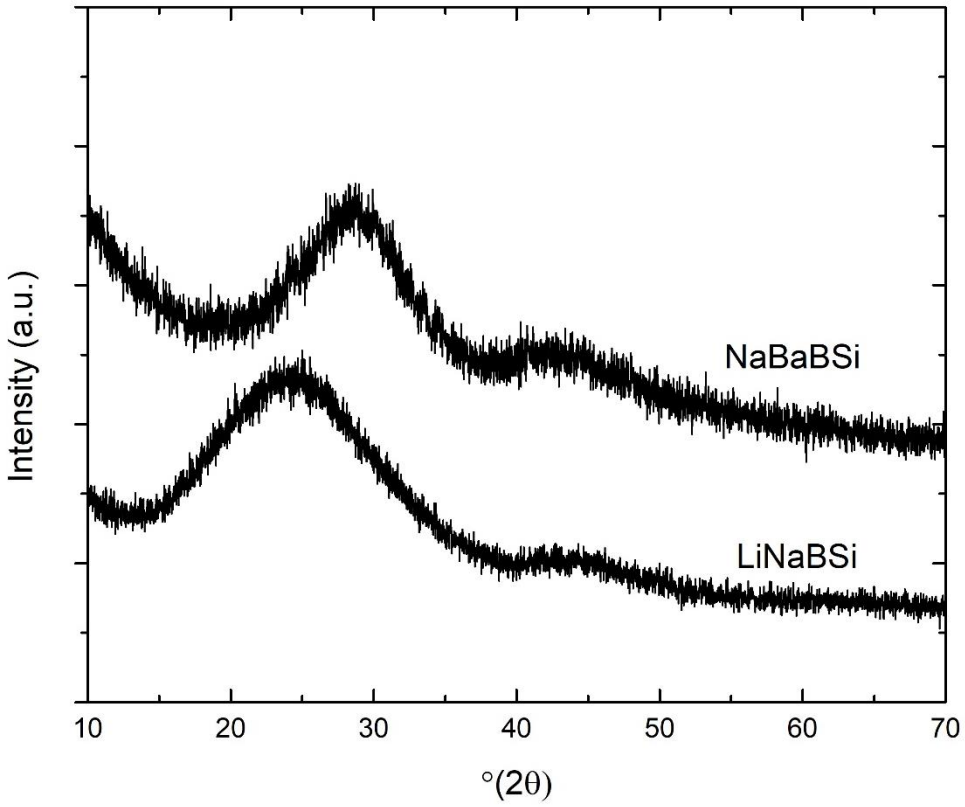

Figure S2. *Intensity-normalised first derivative EPR spectra for NaBaBSi glass irradiated with 0.5MGy annealed for 16 hours at different temperatures.*

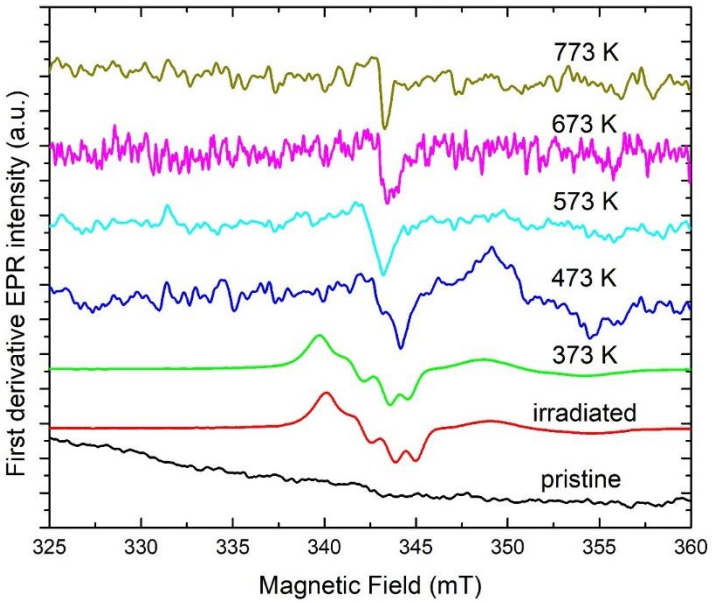

Figure S3. *Intensity-normalised second derivative EPR spectra for NaBaBSi glass irradiated with 0.5MGy annealed for 16 hours at different temperatures.*

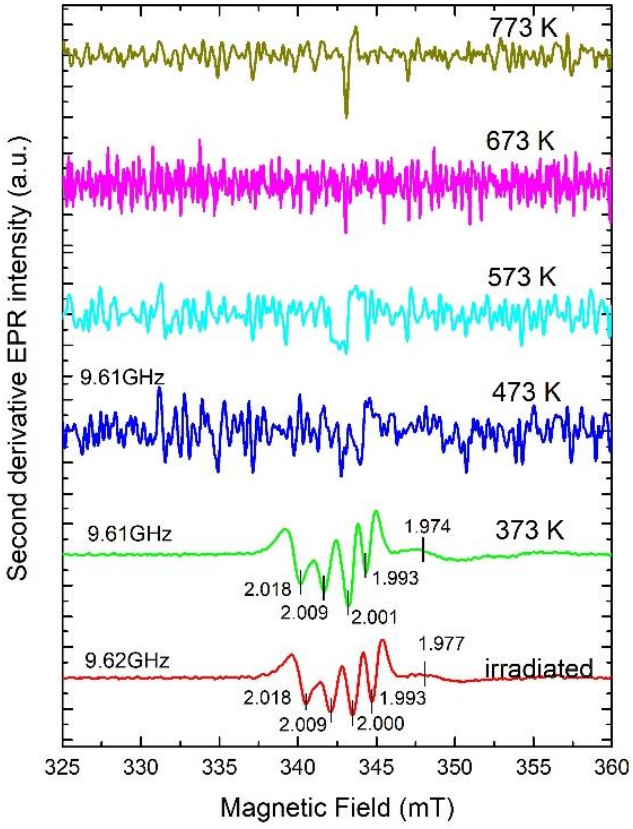

Table S1. *The g-values and defect types for NaBaBSi glass irradiated with 0.5MGy annealed for 16 hours at different temperatures.*

NaBaBSi 0.5 MGy 16 hrs									
373 K		**473 K**		**573 K**		**673 K**		**773 K**	
g-value	**defect**	**g-value**	**defect**	**g-value**	**defect**	**g-value**	**defect**	**g-value**	**defect**
2.019	BOHC/E^-	low S/N	-	low S/N	-	Annihilated/Recombined			
2.009	BOHC	low S/N	-	low S/N	-				
2.001	BOHC	low S/N	-	low S/N	-				
1.993	ET	low S/N	-	low S/N	-				
1.974	E-	low S/N	-	low S/N	-				

Note: Low S/N ratio means concentration of defects have become very low due to defect recombination/annihilation that the calculation of g-value was not possible.

Figure S4. *Intensity-normalised first derivative EPR spectra for NaBaBSi irradiated with 0.5MGy annealed for 24 hours at different temperatures.*

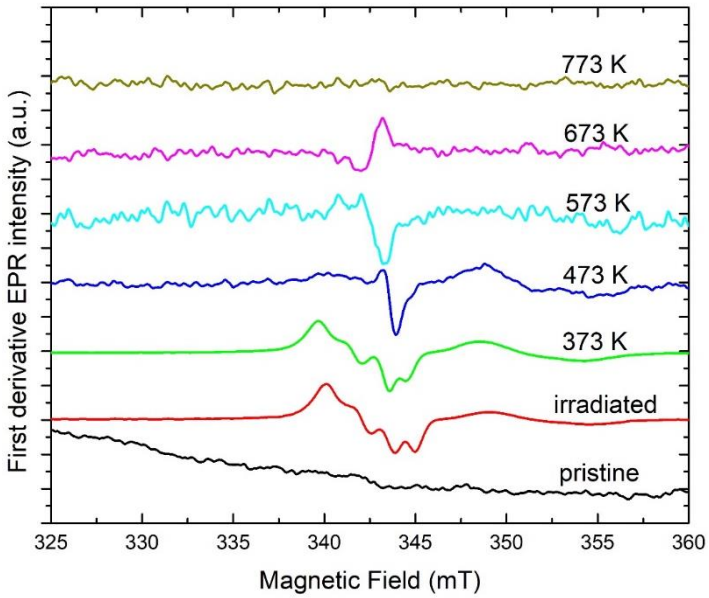

***Figure S5**. Intensity-normalised second derivative EPR spectra for NaBaBSi irradiated with 0.5MGy annealed for 24 hours at different temperatures.*

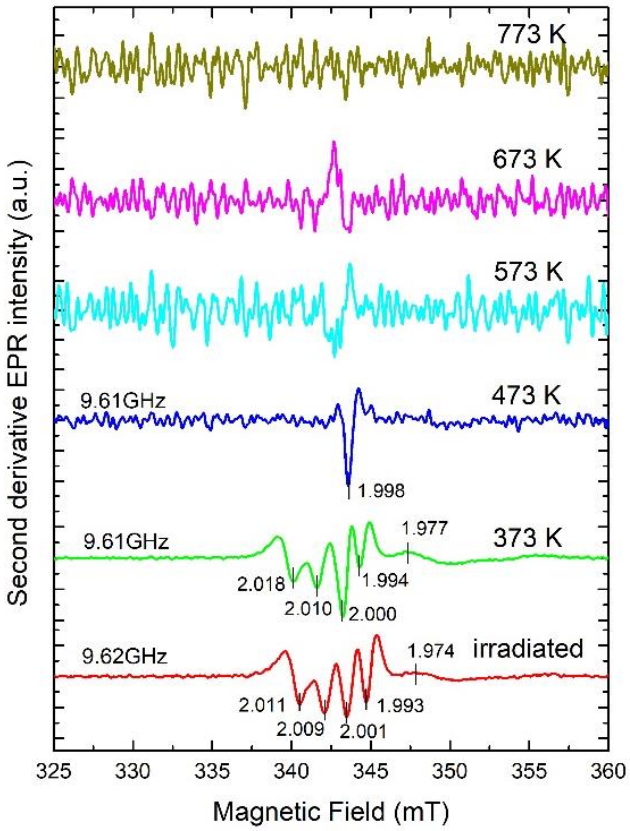

***Table S2.** The g-values and defect types for NaBaBSi glass irradiated with 0.5MGy annealed for 24 hours at different temperatures.*

NaBaBSi 0.5 MGy 24 hrs									
373 K		**473 K**		**573 K**		**673 K**		**773 K**	
g-value	**defect**	**g-value**	**defect**	**g-value**	**defect**	**g-value**	**defect**	**g-value**	**defect**
2.019	BOHC/E^-	1.998	E'	low S/N	-	Annihilated/Recombined			
2.010	BOHC	low S/N	-	low S/N	-				
2.000	BOHC	low S/N	-	low S/N	-				
1.994	ET	low S/N	-	low S/N	-				
1.977	E-	low S/N	-	low S/N	-				

Figure S6. *Intensity-normalised first derivative EPR spectra for NaBaBSi irradiated with 5 MGy annealed for 16 hours at different temperatures.*

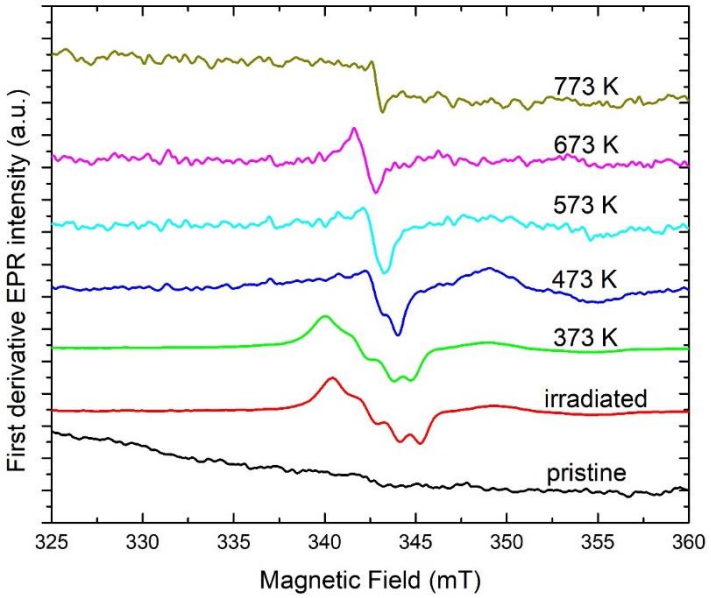

Figure S7. *Intensity-normalised second derivative EPR spectra for NaBaBSi glass irradiated with 5 MGy annealed for 16 hours at different temperatures.*

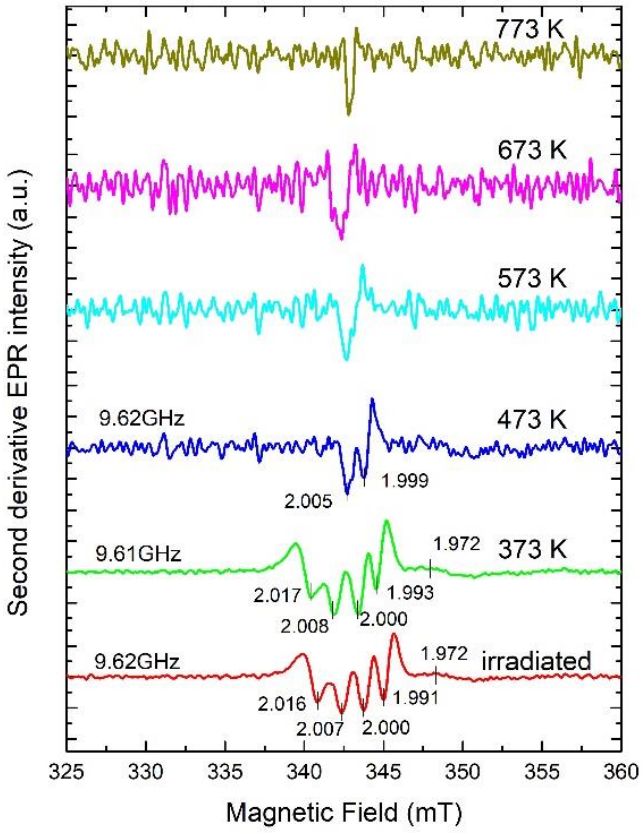

Table S3. *The g-values and defect types for NaBaBSi glass irradiated with 5 MGy annealed for 16 hours at different temperatures.*

NaBaBSi 5 MGy 16 hrs									
373 K		**473 K**		**573 K**		**673 K**		**773 K**	
g-value	**defect**	**g-value**	**defect**	**g-value**	**defect**	**g-value**	**defect**	**g-value**	**defect**
2.017	BOHC/E^-	2.005	POR	low S/N	-	Annihilated/Recombined			
2.008	BOHC	1.999	POR	low S/N	-				
2.000	BOHC			low S/N	-				
1.993	ET			low S/N	-				
1.972	E-			low S/N	-				

Figure S8. *Intensity-normalised first derivative EPR spectra for NaBaBSi irradiated with 5MGy annealed for 24 hours at different temperatures.*

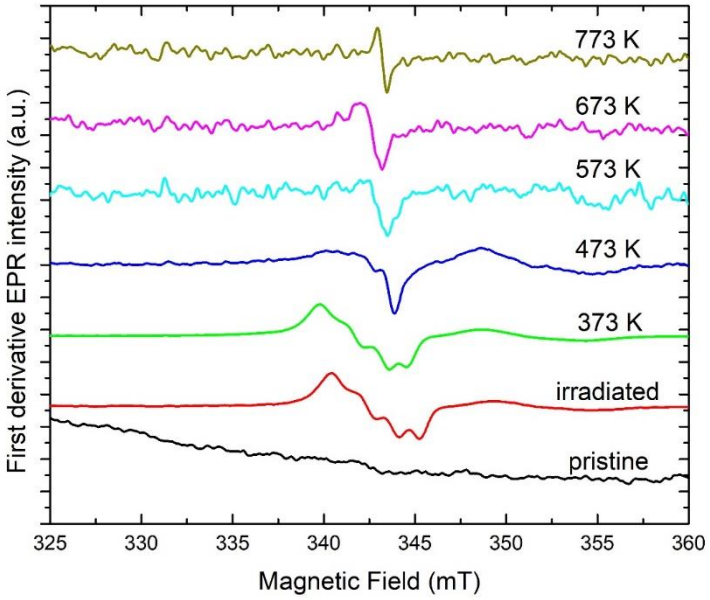

Figure S9. *Intensity-normalised second derivative EPR spectra for NaBaBSi irradiated with 5MGy annealed for 24 hours at different temperatures.*

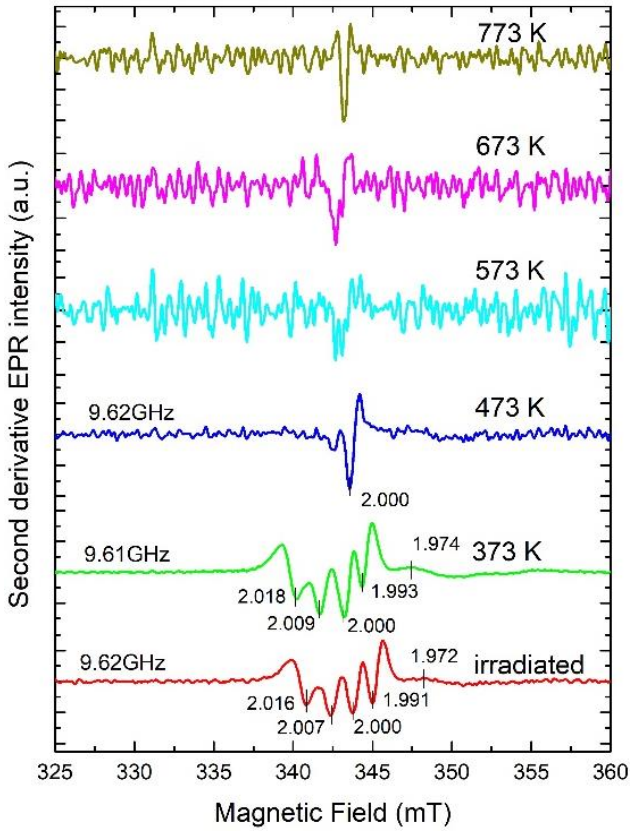

Table S4. *The g-values and defect types for NaBaBSi glass irradiated with 5 MGy annealed for 24 hours at different temperatures.*

NaBaBSi 5 MGy 24 hrs									
373 K		**473 K**		**573 K**		**673 K**		**773 K**	
g-value	**defect**	**g-value**	**defect**	**g-value**	**defect**	**g-value**	**defect**	**g-value**	**defect**
2.018	BOHC/E^-	2.000	POR	low S/N	-	Annihilated/Recombined			
2.009	BOHC			low S/N	-				
2.000	BOHC			low S/N	-				
1.993	ET			low S/N	-				
1.974	E-			low S/N	-				

Figure S10. *Intensity-normalised first derivative EPR spectra for LiNaBSi irradiated with 0.5MGy annealed for 16 hours at different temperatures.*

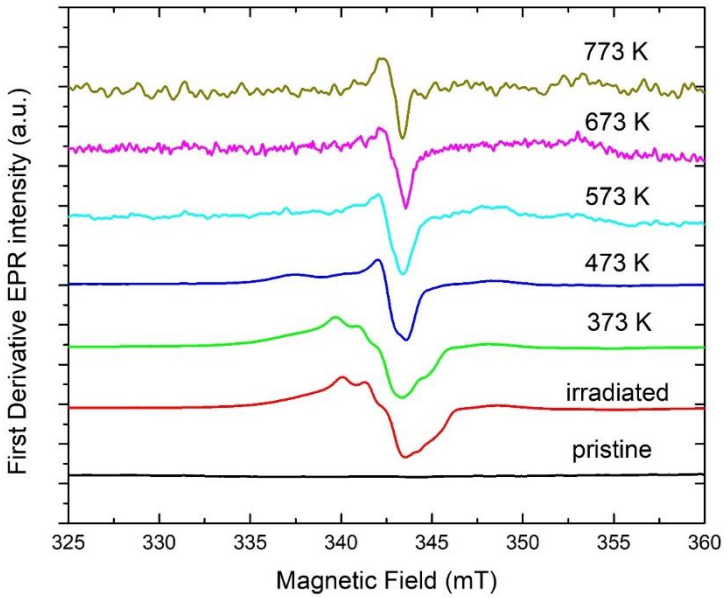

Figure S11. *Intensity-normalised second derivative EPR spectra for LiNaBSi irradiated with 0.5MGy annealed for 16 hours at different temperatures.*

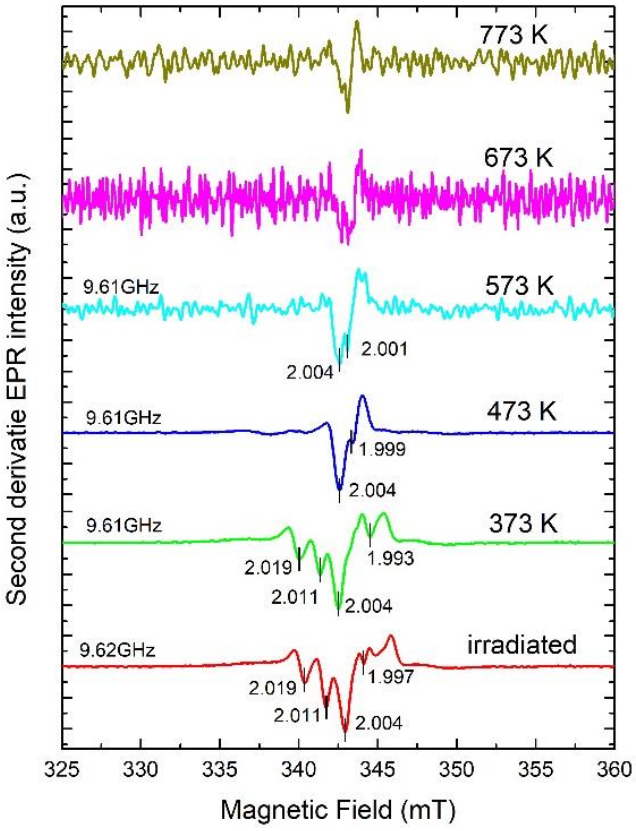

Table S5. *The g-values and defect types for LiNaBSi glass irradiated with 0.5 MGy annealed for 16 hours at different temperatures.*

LiNaBSi 0.5 MGy 16 hrs									
373 K		**473 K**		**573 K**		**673 K**		**773 K**	
g-value	**defect**	**g-value**	**defect**	**g-value**	**defect**	**g-value**	**defect**	**g-value**	**defect**
2.019	BOHC	2.004	PORs	2.004	POR	Annihilated/Recombined			
2.012	BOHC	1.999	PORs	2.001	POR				
2.005	BOHC	low S/N	-	low S/N	-				
1.993	ET	low S/N	-	low S/N	-				

Figure S12. *Intensity-normalised first derivative EPR spectra for LiNaBSi irradiated with 0.5MGy annealed for 24 hours at different temperatures.*

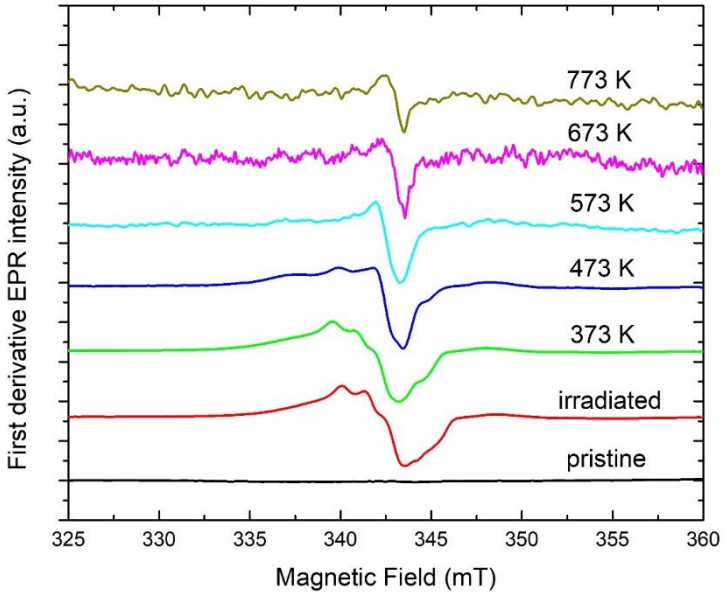

Figure S13. *Intensity-normalised second derivative EPR spectra for LiNaBSi irradiated with 0.5MGy annealed for 24 hours at different temperatures.*

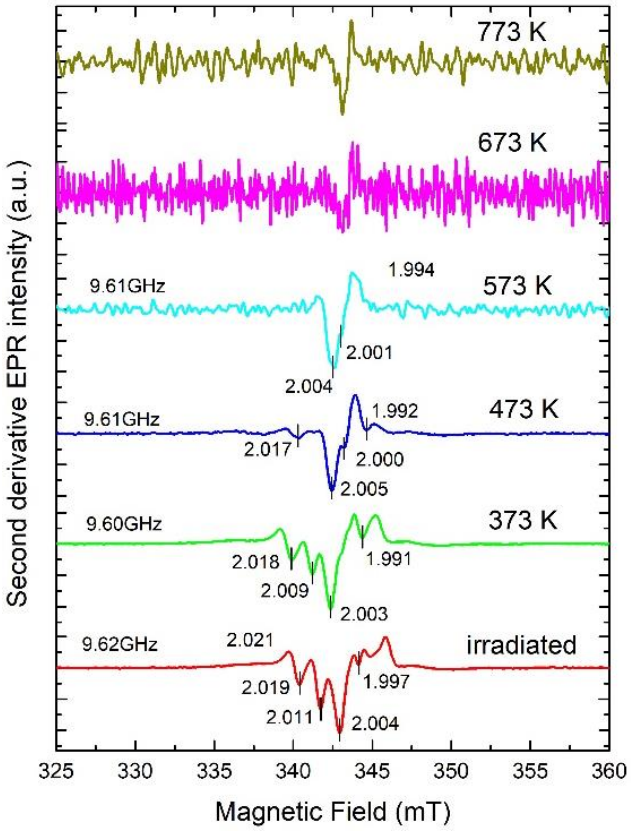

Table S6. *The g-values and defect types for LiNaBSi glass irradiated with 0.5 MGy annealed for 24 hours at different temperatures.*

LiNaBSi 0.5 MGy 24 hrs									
373 K		**473 K**		**573 K**		**673 K**		**773 K**	
g-value	**defect**	**g-value**	**defect**	**g-value**	**defect**	**g-value**	**defect**	**g-value**	**defect**
2.018	BOHC	2.017	POR	2.004	POR	Annihilated/Recombined			
2.009	BOHC	2.005	POR	2.001	POR				
2.003	BOHC	2.000	POR	low S/N	-				
1.991	ET	1.992	ET	low S/N	-				

Figure S14. *Intensity-normalised first derivative EPR spectra for LiNaBSi irradiated with 5MGy annealed for 16 hours at different temperatures.*

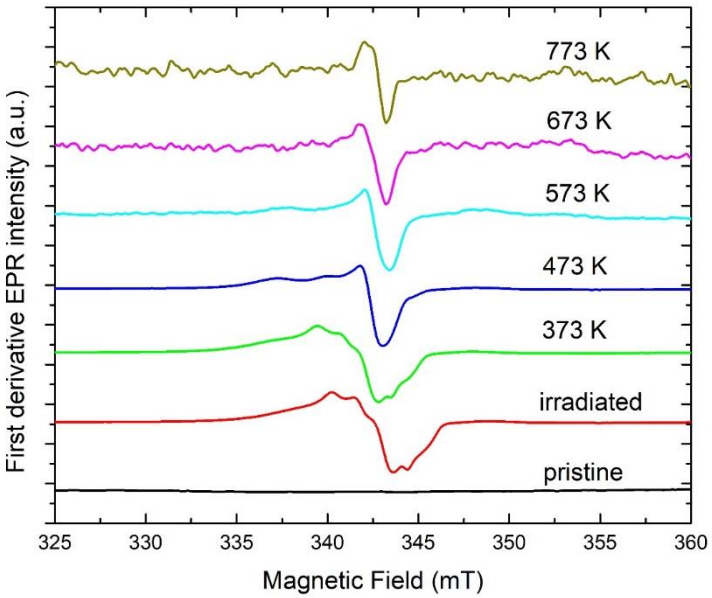

Figure S15. *Intensity-normalised second derivative EPR spectra for LiNaBSi irradiated with 5MGy annealed for 16 hours at different temperatures.*

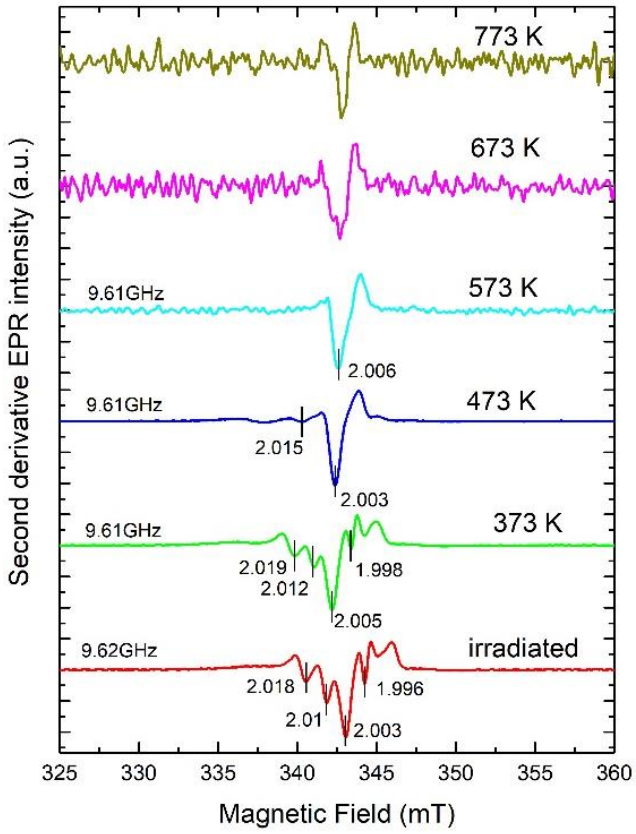

Table S7. *The g-values and defect types for LiNaBSi glass irradiated with 5 MGy annealed for 16 hours at different temperatures.*

LiNaBSi 5 MGy 24 hrs									
373 K		**473 K**		**573 K**		**673 K**		**773 K**	
g-value	**defect**	**g-value**	**defect**	**g-value**	**defect**	**g-value**	**defect**	**g-value**	**defect**
2.019	BOHC	2.015	POR	2.006	POR	Annihilated/Recombined			
2.012	BOHC	2.003	POR	low S/N	-				
2.005	BOHC	low S/N	-	low S/N	-				
1.998	ET	low S/N	-	low S/N	-				

Figure S16. *Intensity-normalised first derivative EPR spectra for LiNaBSi irradiated with 5MGy annealed for 24 hours at different temperatures.*

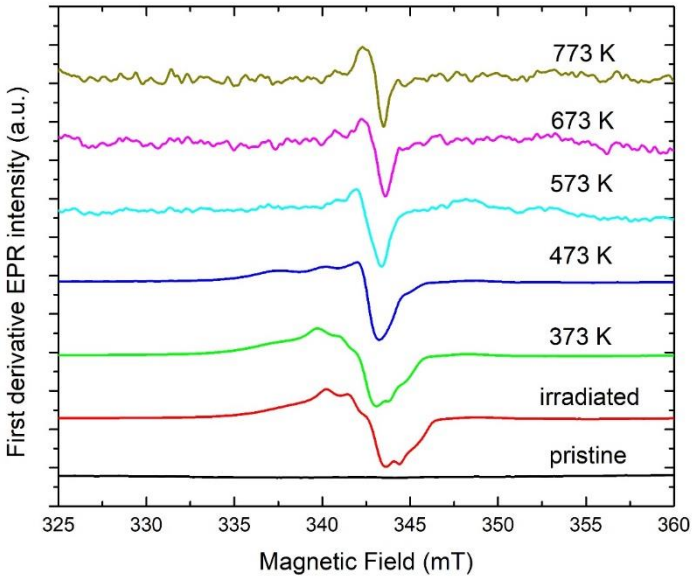

Figure S17. *Intensity-normalised second derivative EPR spectra for LiNaBSi irradiated with 5MGy annealed for 24 hours at different temperatures.*

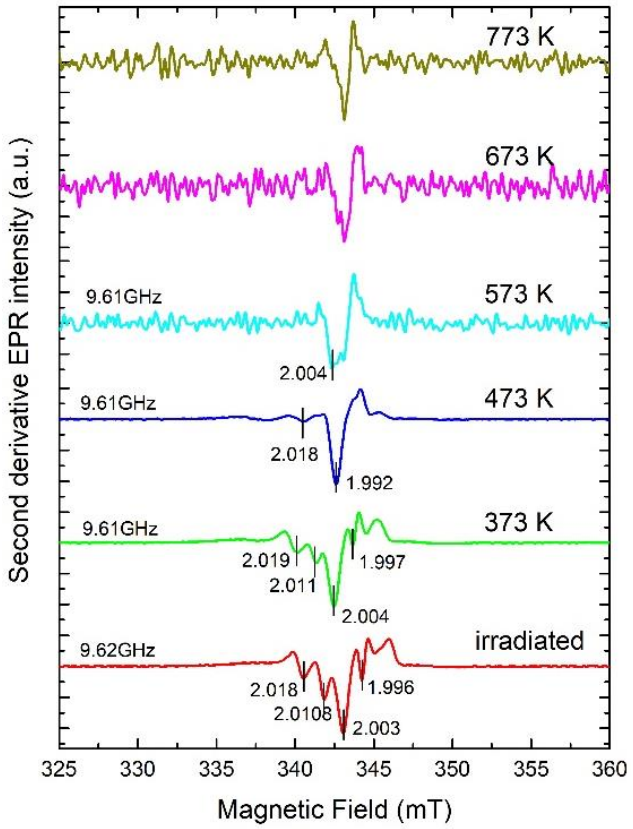

Table S8. *The g-values and defect types for LiNaBSi glass irradiated with 5 MGy annealed for 24 hours at different temperatures.*

LiNaBSi 5 MGy 16 hrs									
373 K		**473 K**		**573 K**		**673 K**		**773 K**	
g-value	**defect**	**g-value**	**defect**	**g-value**	**defect**	**g-value**	**defect**	**g-value**	**defect**
2.019	BOHC	2.018	POR	2.004	POR	Annihilated/Recombined			
2.011	BOHC	1.992	POR	low S/N	-				
2.004	BOHC	low S/N	-	low S/N	-				
1.997	ET	low S/N	-	low S/N	-				

Figure S18. *Temperature vs log area for the integral of the first derivative EPR intensity of 0.5 MGy NaBaBSi glass.*

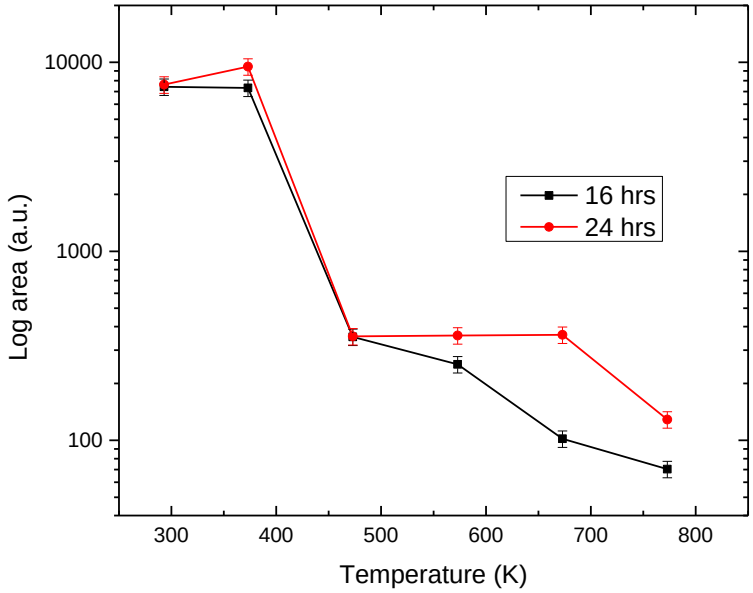

Figure S19. *Temperature vs log area for the integral of the first derivative EPR intensity of 5 MGy NaBaBSi glass.*

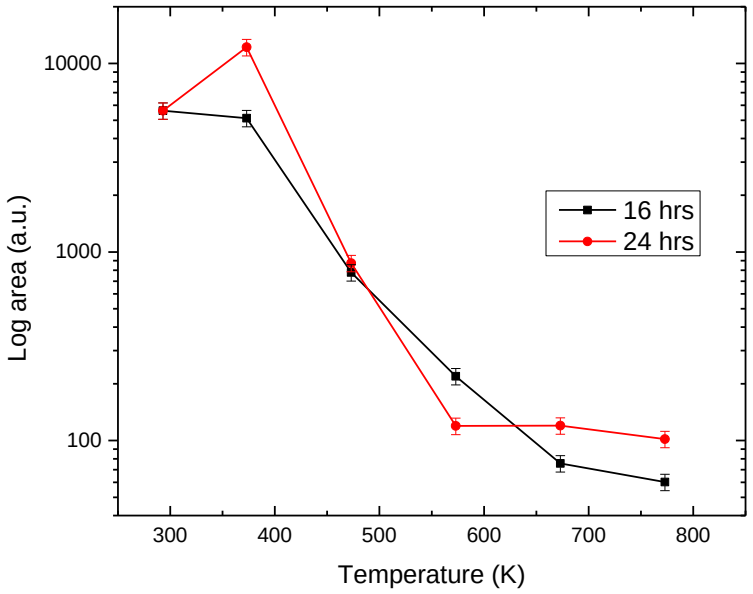

Figure S20. *Temperature vs log area for the integral of the first derivative EPR intensity 0.5 MGy LiNaBSi glass.*

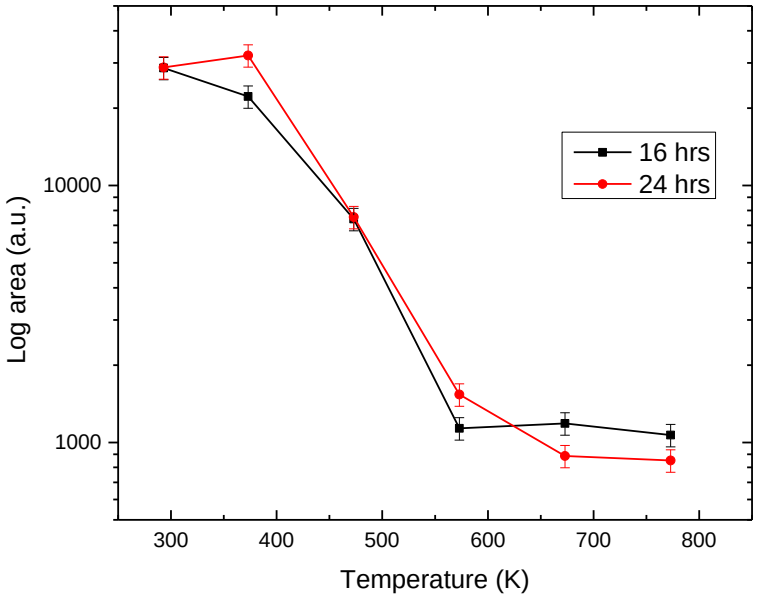

Figure S21. *Temperature vs log area for the integral of the first derivative EPR intensity 5 MGy LiNaBSi glass.*

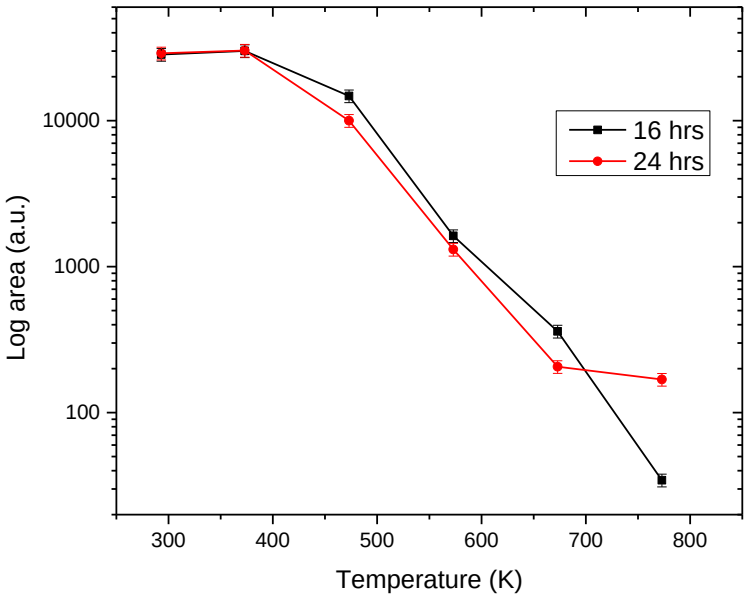

Figure S22. *Tauc plot for optical band gap for (i) pristine, (ii) 0.5 and (iii) 5 MGy irradiated NaBaBSi glass specimens.*

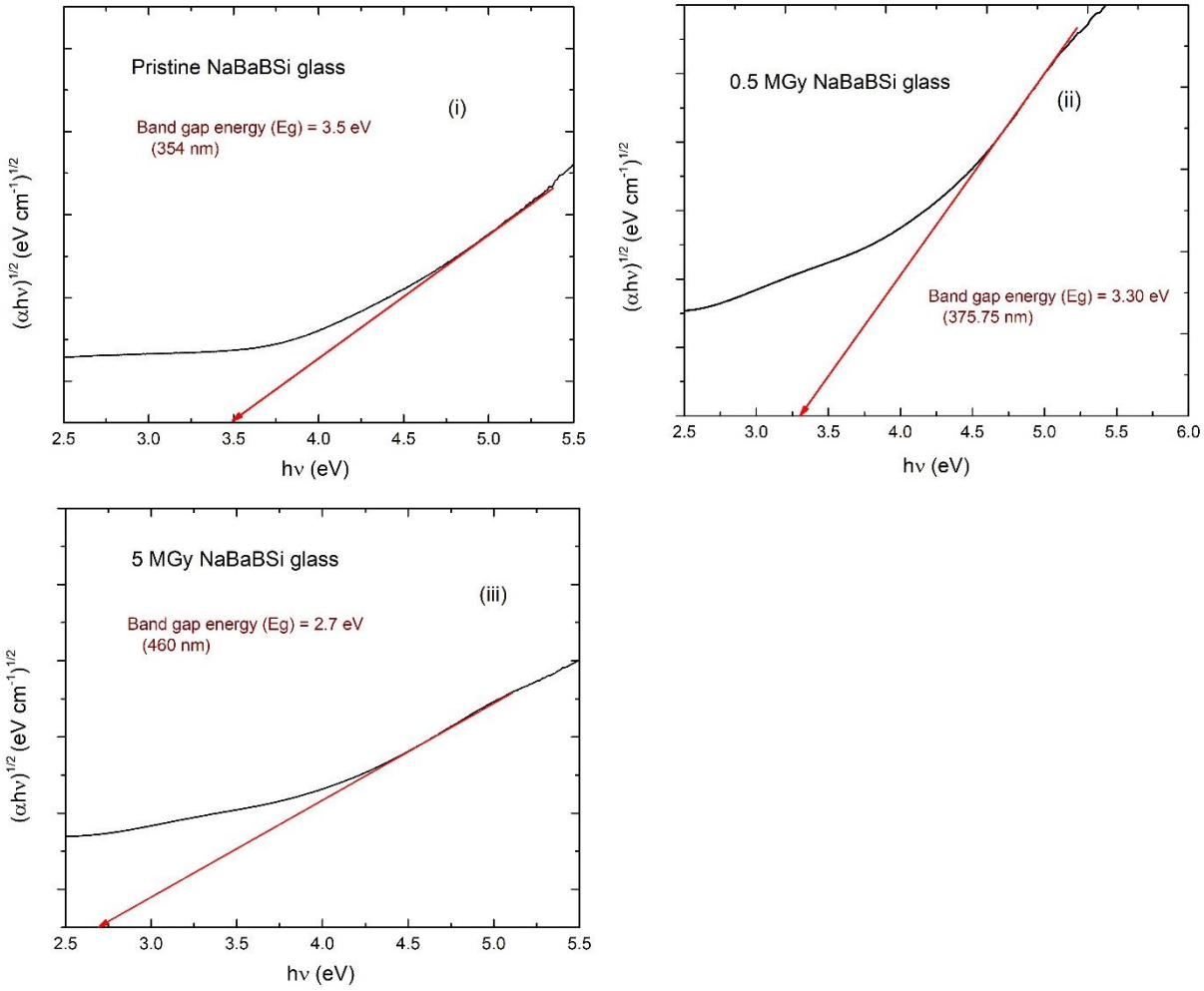

Figure S23. *Tauc plot for optical band gap for (i) pristine (ii) 0.5 and (iii) 5 MGy irradiated LiBaBSi glass specimens.*

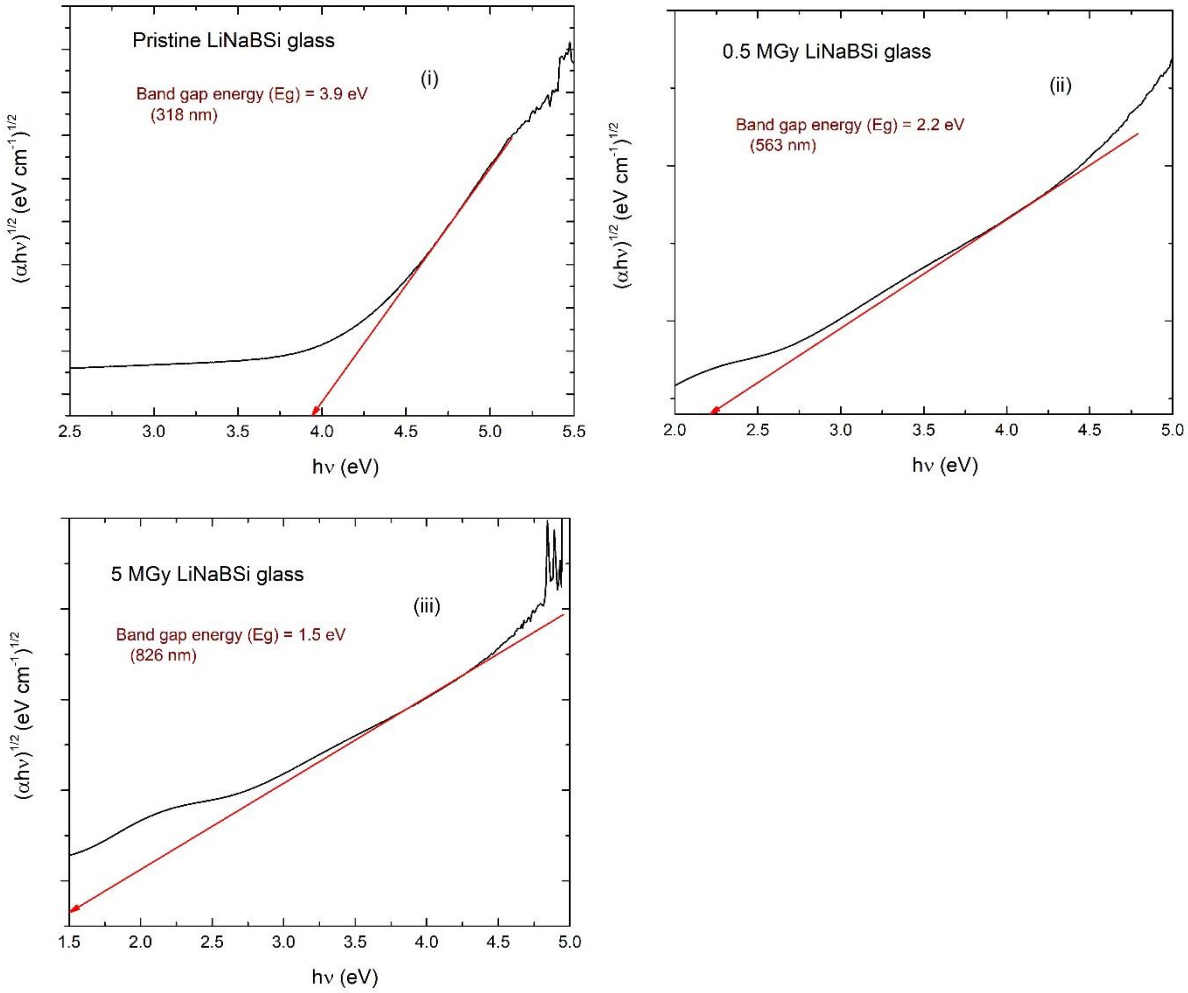

Table S9*. Deconvolution and fitting parameters for UV-Vis-nIR spectra.*

Parameter		**LiNaBSi**		**NaBaBSi**	
		0.5 MGy	**5.0 MGy**	**0.5 MGy**	**5.0 MGy**
Reduced χ^2		0.40202	0.24107	2.46828	4.50537
R^2		0.99629	0.9993	0.99962	0.99967
	v_1	17620 cm^{-1}	16084 cm^{-1}	15636 cm^{-1}	15224 cm^{-1}
	λ_1	568 nm (BOHC + peroxy radicals)	622 nm (BOHC)	639 nm (E- centre + peroxy radicals)	657 nm (E-centre + peroxy radicals)
	A_1	341412 (7.69%)	64983 (0.86%)	81602 (10.27%)	62725 (4.27%)
	Δv_1	5936 cm^{-1}	4380 cm^{-1}	4945 cm^{-1}	4444 cm^{-1}

	v_2	28274 cm^{-1}	16161 cm^{-1}	18969 cm^{-1}	17618 cm^{-1}
	λ_2	354 nm (BOHC)	551 nm (BOHC)	527 nm (BOHC)	568 nm (BOHC)
	A_2	2298160 (51.73%)	397338 (5.72%)	61154 (7.70%)	82003 (5.58%)
	Δv_2	12215 cm^{-1}	6145 cm^{-1}	7367 cm^{-1}	5864 cm^{-1}
	v_3	34580 cm^{-1}	26565 cm^{-1}	30883 cm^{-1}	31321 cm^{-1}
	λ_3	289 nm (Trapped electrons)	376 nm (BOHC)	324 nm (E- centre)	319 nm (E-centre)
	A_3	1397460 (31.46%)	1701740 (22.58%)	432366 (54.44%)	795898 (54.19%)
	Δv_3	7861 cm^{-1}	11194 cm^{-1}	14823 cm^{-1}	18375 cm^{-1}
	v_4	38002 cm^{-1}	36465 cm^{-1}	39388 cm^{-1}	40230 cm^{-1}
	λ_4	263 nm (Trace Fe impurity)	274 nm (Trapped electrons)	253 nm (Trace Fe impurity)	249 nm (Trace Fe impurity)
	A_4	405291 (9.12%)	5370910 (71.28%)	219076 (27.58%)	528043 (35.95%)
	Δv_4	4856 cm^{-1}	5661 cm^{-1}	6663 cm^{-1}	8588 cm^{-1}

Table S10. *Summary of materials, methods, and results from literature in which formation of metallic colloid sodium is discussed, and in which other radiation induced optical absorption bands are reported.*

Study	Material	Radiation type	Result	Analysis
Hassib *et al.* (1977) [85]	Sodalite	X-ray	Formation of colloidal aggregates (Na), blue coloration, EPR signal at 2.011	EPR, Optical transmission
Groote *et al.*(I) (1994) [86]	NaCl	Electron beam	F-defect centres T<65˚C, Na colloids at higher T, absorption band b/w 550-600nm	Optical absorption spectroscopy
Groote *et al.* (II) (1994) [90]	NaCl	Electron beam	Na colloids of different shape and size	Optical absorption spectroscopy
Groote *et al*. (III) (1994) [89]	NaCl	Electron beam	Different melting T is linked with different size of Na colloid	Differential scanning calorimetry
Wesełucha-Birczyńska *et al.* (2011) [92]	Single crystals of natural blue halite	N/A	Plasmon band at 629 for navy blue and 621 nm for blue samples	Optical absorption spectroscopy
Tsai *et al*. (2014) [93]	Silicate glass	Gamma	Absorption band in the range 360-540, HC1 and HC2 defect centre, EPR signal at 2.01	EPR, Optical transmission spectroscopy

Zatsepin *et al.* (2012) [37]	Sodium silicate glass	Gamma	HC1, HC2, and E^- centre (g~1.97)	EPR
Mahadik *et al*. (2018) [95]	Natural halite	N/A	F-centres, Na colloids	Photoluminescence, Micro-Raman spectroscopy
Jiang *et al.* (2008) [94]	Sodium silicate glass	Electron beam	Formation of metallic sodium identified by plasmon at 5.8 eV	Electron energy loss spectroscopy
Manara *et al.* (1984) [96]	Borosilicate glass	Electron beam	Na moves towards the periphery, concentrated in a possible colloidal form	Energy dispersive X-ray analysis
Fayad *et al.* (2018) [68]	Borosilicate glass doped with yttrium oxide	Gamma	Absorption band at 229 nm related to Fe impurities and visible band b/w 500-600 due to BOHC or NBOHC	XRD, FTIR, optical absorption spectroscopy
El-Alaily *et al*. (2018) [71]	Barium borosilicate glass doped with titanium oxide	Gamma and heat treatment	Absorption band at 240 nm due to trace Fe impurity	SEM, Infrared, optical absorption, and transmission spectroscopy
Kolobkova *et al.* (2015) [87]	Sodium fluorophosphate glasses	Heat treatment	Surface plasmon b/w 400-450 nm	Heat treatment
Bochkareva *et al.* (2016) [88]	Na containing silicate glasses	Electron beam and subsequent heat treatment	Na nanoparticles characterised by plasmon resonance band at 405-410 nm	Optical absorption spectroscopy
Jiang *et al.* (2007) [69]	Na silicate glasses	Electron beam	Bulk plasmon band at 5.8 eV (214 nm) and surface plasmon at 3.9 eV (318 nm)	TEM and EELS
Griscom *et al.* (1998) [66]	Fused silica	Gamma	Combination of band due to peroxy-radicals and NBOHC at ~620 nm	Differential optical absorption spectroscopy
Bishay (1969) [73]	Alkali silicate glass	Gamma	Hole centre at 590-620, 427-450 nm	EPR, Optical absorption spectroscopy
Mackey *et al.* (1966) [67]	Sodium silicate glass	X-ray	Absorption band b/w 600-730 nm (E- centre), 326-413 nm due to trapped holes	Optical absorption spectroscopy
Mackey *et al.* (1966) [70]	Sodium disilicate glass doped with Eu^{3+}	X-ray	Absorption band 305 nm trapped electrons, 460 and 620 nm due to trapped holes	Optical absorption spectroscopy