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Review paper

Coefficient of thermal expansion of bioactive glasses: Available literature data and analytical equation estimates

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Abstract

Bioactive glasses are able to develop a tenacious bond with human bone tissues and therefore they are largely used in orthopaedic and dental implants. However, due to their brittleness, they are mainly applied as coatings on tough substrates, such as titanium, alumina and zirconia. The reliability of bioactive glass coatings is deeply influenced by their thermodilatometric compatibility with the substrate, which may govern the development of dangerous thermal stresses at the interface. In spite of the technological relevance of the coefficient of thermal expansion (CTE) of bioactive glasses, few papers are specifically dedicated to such topic. In the present contribution, more than 70 bioactive glasses were reviewed in the literature, in order to investigate the relation existing between their composition and their CTE. Then four analytical models were applied to estimate the CTE of the same glasses and the calculated values were compared to the experimental results, in order to assess the reliability of the models and define an effective tool to predict the CTE. In particular, on the basis of the literature data and calculated values, the effect of modifier oxides and intermediate oxides, such as K_2O and MgO, on the CTE was discussed.

Keywords: C. Thermal expansion; D. Glass; E. Biomedical applications; Glass property modelling

Contents

1. Introduction

Bioactive glasses are a special subset of glasses that are able to bond to bone tissue when implanted into the human body [1]. In fact, when they are in contact with physiological fluids, they transform at the surface to hydroxy-carbonate apatite, which resembles the mineral component of human bones [2]. More specialized glasses are even able to develop tenacious bonds with soft tissues [3]. Moreover it has recently been demonstrated that, after implantation, bioactive glasses with proper compositions experience a controlled release of ions, such as silicon and phosphorous, which can regulate the gene transcription [4], promote the cell proliferation and hence the natural bone tissue regeneration [5]. As a consequence, bioactive glasses are increasingly diffused in orthopaedic, spinal, cranio-maxillofacial and periodontal applications [6]. Nevertheless, the use of bioactive glasses is severely limited by their relatively poor mechanical properties. In particular, their brittle behaviour impedes the development of reliable bulk-glass prostheses for load-bearing sites [7]. In order to overcome this drawback, bioactive glasses can be applied as coatings on mechanically stronger substrates, such as titanium and alumina

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Table 1
Available data in the literature on the CTE of bioactive glasses. For each glass, the composition (in wt%), the CTE and the reference are indicated, as well as the experimental conditions to determine the CTE (when available). The name of the glasses whose composition was converted from oxide mol% to wt% are written in italics. Double items are marked with colours.

Code	SiO_2	Na_2O	CaO	P_2O_5	MgO	K_2O	SrO	Li_2O	TiO_2	Al_2O_3	B_2O_3	CaF_2	CTE	REF.
Bioglass	45	24.5	24.5	6									15.1	[27]
6P44-a	44.2	23.6	12.6	6	7.1	6.5							15.6	(ΔT: 200-400°C)
6P44-b	44.2	17	18	6	10.2	4.6							13.0	
6P44-c	44.2	10.3	23.4	6	13.3	2.8							11.3	
6P50	49.8	15.5	15.6	6	8.9	4.2							12.2	
6P53-a	52.7	17	12.6	6	7.1	4.6							12.9	
6P53-b	52.7	10.3	18	6	10.2	2.8							11.5	
6P55	54.5	12	15	6	8.5	4							11.0	
6P57	56.5	11	15	6	8.5	3							10.8	
6P61	61.1	10.3	12.6	6	7.2	2.8							10.2	
6P64	64.1	9.8	11.1	6	6.3	2.7							9.1	
6P68	67.7	8.3	10.1	6	5.7	2.2							8.8	
Bioglass	45	24.5	24.5	6									15.1	[28]
6P57	56.5	11	15	6	8.5	3							10.8	(ΔT: 200-400°C)
6P68	67.7	8.3	10.1	6	5.7	2.2							8.8	
SCP	61.1	10.3	12.6	6	7.2	2.8							9	[29]
P8		15	20	65									16.1	[30]
P30		15	20	64.5						0.5			15.7	
P31		15	20	63						2			15.0	
SC	53.7		46.3										9	[31]
Ground coat	55	10	25							5	5		9.34	[32]
Cover glass	55.1	9.2	27.8	3.4								4.5	10.8	
Nom. Glass	34		44.7	16.2	4.6							0.5	?	[33]
Real Glass	33.3		48.2	13.3	1.92					1.9		0.03	10.08	(ΔT: 50-400°C)
BG1	47.0	47.0		6.0									17.4	[34]
BG2	47.0	37.6	9.4	6.0									16.9	(rate: 2°C/min)

BG3	47.0	32.9	14.1	6.0									15.2	
BG4	47.0	28.2	18.8	6.0									13.4	
BG5	47.0	23.5	23.5	6.0									12.3	
BG6	47.0	18.8	28.2	6.0									12.4	
BG7	47.0	14.1	32.9	6.0									12.0	
BG8	47.0	9.4	37.6	6.0									11.7	
BG9	47.0	4.7	42.3	6.0									?	
BG10	75.2	18.8		6.0									11.8	
BG11	65.8	18.8	9.4	6.0									11.7	
BG12	56.4	18.8	18.8	6.0									12.2	
BG13	37.6	18.8	37.6	6.0									?	
Bioglass	45	24.5	24.5	6									14.0	[35]
A-3	54.5	12	15	6	8.5	4							11.6	
A-5	56.5	11	15	6	8.5	3							8.5	
A-6	54.8	10.7	14.6	5.8	8.2	2.9			3				?	
6P61	61.1	10.3	12.6	6	7.2	2.8							10.2	[36]
6P64	64-1	9.8	11.6	6	6.3	2.7							9.1	
Bond coat	50-65	8-20	10-20	0-10				0-5	5-10	0-5	0-15	0-10	9.32	[37]
Top coat	30-40	0-5	40-55	3-10							0-5	0-5	9.58	
AWC	33.30		48.20	13.30	1.92					1.90		0.03	10	[38]
B18	6.0	11.9	30.1	2.2						5.5	44.3			[39]
H12	6.9	7.6	34.3	5.4						3.1	42.6			(ΔT: 100-500°C)
45S5	45.2	24.5	24.5	5.8										(rate: 3°C/min)
TSCB	47.6		46.4						3.0		3.0		?	[40]
SCN	50.4	26.0	23.5										16.6	
ICSW2	46.8	26.8	21.3	5.0									15.70	[41]
ICSW3	42.2	26.7	21.1	9.9									16.18	(ΔT: 25-400°C)
ICSW4	33.3	26.3	20.8	19.5									18.88	(rate: 5°C/min)
ICSW8	41.9	27.8	22.0	8.2									16.37	
ICSW10	38.4	28.1	22.3	11.3									16.54	
ICIE1	49.1	27.0	21.4	2.5	0.0								17	[42] (*)
ICIE1-25Mg	49.8	27.4	16.3	2.5	3.9								15.8	(ΔT: 25-400°C)
ICIE1-50Mg	50.6	27.8	11.0	2.6	7.9								16.3	(5°C/min)
ICIE1-75Mg	51.4	28.3	5.6	2.6	12.1								16.3	

ICIE1-100Mg	52.2	28.7		2.7	16.4							16.8	
LG208	48.9	27.0	21.3	2.8								16.9	[43] (*)
LG211	49.3	20.4	27.5	2.8								15.9	(rate: 5°C/min)
LG214	49.6	13.7	33.9	2.8								13.4	
LG223	49.9	6.9	40.4	2.9								12.1	
LG224	50.2		46.9	2.9								10.8	
SCK	51.7		42.5			5.8						9.5	[44]
1d	46.1	4.5	28.7	6.2	8.8						5.7	10.61	[45]
1d-a	41.8	4.5	32.8	6.2	8.9						5.7	11.04	
1d-b	37.5	4.6	37.1	6.3	8.9						5.7	11.71	
1e	43.5	4.5	30.4	7.2	8.7						5.6	10.84	
1e-a	43.1	4.4	30.2	9.2	8.7						4.5	10.66	
1e-b	42.7	4.4	29.9	11.1	8.6						3.3	10.45	
1e-c	42.3	4.4	29.6	13.0	8.5						2.2	9.74	
ICIE1	49.1	27.0	21.4	2.5								16.60	[46] (*)
ICIE1 Sr2.5	48.9	26.9	20.8	2.5			1.0					16.30	(ΔT: 40-460°C)
ICIE1 Sr10	48.2	26.5	18.9	2.5			3.9					16.35	(rate: 10°C/min)
ICIE1 Sr50	45.0	24.8	9.8	2.3			18.1					17.45	
ICIE1 Sr100	41.6	22.9		2.1			33.4					18.65	

(*) CTE values extrapolated from figure.

ones. Titanium and its alloys, in fact, are ideal substrates whenever a very high load carrying ability is needed [8,9]. Alumina is frequently used in orthopaedic and maxillofacial applications because it offers excellent wear resistance, fracture toughness and compressive strength [8]. An obstacle is represented by the sensible gap between the coefficient of thermal expansion (CTE) of typical bioactive glasses, usually in the 14–15 $\times 10^{-6}\,K^{-1}$ range [10], and that of the substrate, about 8–10 $\times 10^{-6}\,K^{-1}$ for titanium and its alloys [11,12], as well as for alumina [13]. Independently of the deposition technique applied, the thermal expansion mismatch is expected to induce high residual tensile stresses in the glass coating, which may cause both crack formation and scarce interface adhesion [14]. Several alternative approaches have been proposed to overcome this drawback, such as the introduction of a proper bond-coat [15] or the design of a functionally graded coating [16], however a strict control on the CTE of the glass, which depends on the glass composition and thermal history, is mandatory.

Broadly speaking, the CTE affects the thermal shock resistance of a glass, since glasses with a small CTE are usually able to withstand high thermal stresses [17]. The CTE is also determinant for optimizing the time-temperature cooling schedule of glassware and for designing special glass products that face varying temperature conditions [18]. Moreover the CTE plays a key role in many industrial applications, such as the lightning manufacture [18] and the fabrication of vitrified abrasive products [19], not to mention the glazing of ceramic tiles [20].

The prediction of the CTE of a glass, without resorting to direct experimental methods, which may be energy- and time-consuming, is extremely important. Several analytical methods are currently available to estimate the CTE of a glass on the basis of its composition, however they have been formulated for generic glasses and not specifically for bioactive glasses. Therefore the main purpose of the present contribution is to evaluate the effectiveness of such empirical models to predict the CTE of bioactive glasses. To that end, more than 70

bioactive glasses were reviewed in the literature, in order to collect a significant amount of information on the relation existing between their composition and their (experimentally determined) CTE. Then four different models were applied to estimate the CTE of the same glasses and the calculated values were compared to the experimental results, in order to assess the reliability of the models and identify the most suitable one for bioactive glasses. The effect of composition on the CTE value was also discussed on the basis of the available literature, with the aim of offering a guideline for the control of the CTE, which is a basic requirement to design high quality glass coatings and composite systems.

2. Literature data

The ability to bond to bone tissue was first observed for glasses belonging to the Na_2O–CaO–SiO_2–P_2O_5 system, with specific proportions of the constituent oxides [21,22]. In particular, the bioactivity of such glasses relies on (1) a relatively low content of silica (usually less than 60 mol% for melt-derived glasses), (2) a high content of network modifiers, and (3) a high CaO/P_2O_5 ratio. The most famous glass belonging to this family is the so-called 45S5 Bioglass®, which was first introduced by Prof. L.L. Hench at the end of the 1960s [21]. The name ''45S5'' means that the SiO_2, whose content is 45 wt%, is the network former, and that the CaO/P_2O_5 ratio is 5:1. Due to its extraordinary bioactivity and its ability to bond to both hard and soft tissues, this glass has been the object of a continuative research activity since it was discovered and now it is widely diffused in several clinical applications [23]. A great number of alternative bioactive glasses, based on the original 45S5 Bioglass®, have been proposed to fit special requirements, however the glass composition cannot be freely modified, since a change in composition may dramatically alter the bioactivity [24]. For example, if the Na_2O–CaO–P_2O_5–SiO_2 system is considered and the content of P_2O_5 is fixed to 6 wt% (the same amount of the standard 45S5 Bioglass®), the bonding ability is governed by the Na_2O/CaO/SiO_2 ratios, since very specialized glasses are able to bond to both hard and soft tissues, a wider group of glasses is able to bond to bone only, some glasses are rapidly degradable in aqueous media, while other are not even technically feasible by means of conventional melting techniques [3,25]. The introduction of additional oxides may have striking consequences. For example, it has been proved that the bioactivity of the 45S5 Bioglass® is not sensibly changed if 5–15 wt% B_2O_3 is introduced instead of SiO_2 or 12.5 wt% CaF_2 is used instead of CaO [22]. However, the addition of as little as 3 wt% Al_2O_3 is enough to hinder the bone-bonding ability [26]. Due to its strong effect on bioactivity, it is understandable that the composition of the greatest part of the bioactive glasses in the literature does not significantly deviate from that of the 45S5 Bioglass®.

This is a key factor, because the available data mainly refer to glasses belonging to the Na_2O–CaO–P_2O_5–SiO_2 system (with different proportions of the constituent oxides) or deriving from it with the addition of a limited range of oxides, mainly K_2O and/or MgO. Most of all, the specialized formulation of bioactive glasses may require an adjustment of the CTE estimation models in order to achieve an improved predictivity.

A survey of the literature made it possible to find out more than 70 values of the CTE for various bioactive glasses, described in some 20 papers [27–46]. They are all listed in Table 1, which also includes the corresponding glass name and composition, literature reference and (when available) CTE measurement conditions. It should be underlined that some papers report the glass composition in oxide weight percent, other in oxide molar percent. Since the most common equations to estimate the CTE of glasses work on weight fractions, all the molar-based compositions were converted to weight percents and the corresponding glass names in Table 1 were written in italics (they were grouped in the second part of the list). Sometimes the same glass is investigated in two or more papers (this is the case, for example, of 45S5 Bioglass®). The names of double items in Table 1 were highlighted with colours.

3. Estimate models for the CTE of glasses

The phenomenon of thermal expansion below the glass transition depends on the asymmetry of the amplitude of thermal vibrations in the glass structure. As a general trend, strong bonds in the glass network result in small amplitudes and hence in reduced values of the CTE. The change in the CTE caused by the introduction of an oxide in the glass composition is often proportional to the relative amount of the oxide itself. The assumption that each oxide may have a direct and predictable effect on the CTE of glasses has led to the formulation of the general additive equation [19,47]:

$$\mathrm{CTE} = \sum_{i=1}^{n} \alpha_i p_i \tag{1}$$

where α_i is a proportionality factor, p_i is the weight fraction of the corresponding oxide and n is the total number of constituent oxides in the glass.

Several models are currently available to estimate the CTE of glasses. Most of them are based on the aforementioned additive

Table 2
Proportionality factors (α_i) for various estimate models (p = wt%).

Oxide	W.S. [19,48]	E.T. [19,49]	G.D. [19]	H. [19,50]
SiO_2	2.67	0.50	0.4	1.4
B_2O_3	0.33	−6.53	$-4 + 0.1\,p$	2.0
P_2O_5	6.67	–	–	–
P_2O_5 [24]	0.35	0.24	0.59	0.36
Al_2O_3	16.67	1.40	2.0	5.0
Na_2O	33.33	41.60	$51 - 0.33\,p$	38.0
K_2O	28.33	39.00	$42 - 0.33\,p$	30.0
MgO	0.33	4.50	0.0	2.0
CaO	16.67	16.30	$7.5 + 0.35\,p$	15.0
ZnO	6.00	7.00	$7.75 - 0.25\,p$	10.0
BaO	10.00	14.00	$9.7 + 0.14\,p$	12.0
PbO	13.00	10.60	$11.5 - 0.05\,p$	7.5

Eq. (1), but they propose different values for the proportionality factors α_i, due to the different approaches applied to calculate or derive them. Table 2 lists the coefficients for the models considered in the present contribution. It should be noted that Winkelmann and Schott (W.S.) calculated their α_i values from a mathematical model [19,48]; the other models were based on empirical results and, in particular, the English and Turner (E.T.) model referred to values in the 25–90 °C range [19,49], the Gilard and Dubrul (G.D.) one to values in the 100–130 °F range [19] and the Hall (H.) model to values from 25 °C to the lower limit of the critical temperature range for the analysed glass [19,50].

These models were taken into consideration since they are relatively easy to handle and therefore they are widely diffused to predict the CTE of glasses [47]. However it should be kept in mind that the aforementioned models were developed for ''general purpose'' glasses (such as tile glazes or vitrified abrasive products), and not specifically for bioactive glasses. For this reason, the phosphorous oxide, P_2O_5, which is extremely common in the composition of bioactive glasses, is not included in the original formulation of the models, except for the W.S. one [18,48]. Candidate values for the proportionality coefficients for P_2O_5 were proposed for bioactive glasses in the Na_2O–K_2O–MgO–

Table 3
Estimates for the CTE of bioactive glasses belonging to the Bioglass® system (Na_2O–CaO–P_2O_5–SiO_2) and to the Bioglass® system with the addition of MgO and/or K_2O.

Code	SiO_2	Na_2O	CaO	P_2O_5	MgO	K_2O	Bioglass® system +	CTE exp	W.S.	E.T.	H.	G.D.	REF.
Bioglass	45	24.5	24.6	6.0				15.1	13.5	14.4	13.7	14.7	[27]
BG1	47.0	47.0	0.0	6.0				17.4	16.9	19.8	18.5	16.8	[34]
BG2	47.0	37.6	9.4	6.0				16.9	15.4	17.4	16.4	15.7	
BG3	47.0	32.9	14.1	6.0				15.2	14.6	16.2	15.3	15.2	
BG4	47.0	28.2	18.8	6.0				13.4	13.8	15.0	14.2	14.6	
BG5	47.0	23.5	23.5	6.0				12.3	13.0	13.9	13.1	14.1	
BG6	47.0	18.8	28.2	6.0				12.4	12.2	12.7	12.1	13.5	
BG7	47.0	14.1	32.9	6.0				12.0	11.5	11.5	11.0	13.0	
BG8	47.0	9.4	37.6	6.0				11.7	10.7	10.3	9.9	12.5	
BG10	75.2	18.8	0.0	6.0				11.8	8.3	8.2	8.2	8.7	
BG11	65.8	18.8	9.4	6.0				11.7	9.6	9.7	9.5	9.7	
BG12	56.4	18.8	18.8	6.0				12.2	10.9	11.2	10.8	11.3	
ICSW2	46.8	26.8	21.3	5.0				15.70	13.8	14.9	14.1	14.7	[41]
ICSW3	42.2	26.7	21.1	9.9				16.18	13.6	14.8	13.9	14.6	
ICSW4	33.3	26.3	20.8	19.5				18.88	13.2	14.6	13.7	14.4	
ICSW8	41.9	27.8	22.0	8.2				16.37	14.1	15.4	14.5	15.2	
ICSW10	38.4	28.1	22.3	11.3				16.54	14.1	15.5	14.6	15.3	
LG208	48.9	27.0	21.3	2.8				16.9	13.9	14.9	14.1	14.7	[43][a]
LG211	49.3	20.4	27.5	2.8				15.9	12.7	13.2	12.6	13.9	
LG214	49.6	13.7	33.9	2.8				13.4	11.5	11.5	11.0	13.1	
LG223	49.9	6.9	40.4	2.9				12.1	10.4	9.7	9.4	12.3	
LG224	50.2	0.0	46.9	2.9				10.8	9.2	7.9	7.7	11.4	
ICIE1	49.1	27.0	21.4	2.5	0.0		MgO	17	13.9	15.0	14.2	14.8	[42][a]
ICIE1-25Mg	49.8	27.4	16.3	2.5	3.9		MgO	15.8	13.2	14.5	13.6	13.8	
ICIE1-50Mg	50.6	27.8	11.0	2.6	7.9		MgO	16.3	12.5	14.0	13.1	13.1	
ICIE1-75Mg	51.4	28.3	5.6	2.6	12.1		MgO	16.3	11.8	13.5	12.6	12.5	
ICIE1-100Mg	52.2	28.7	0.0	2.7	16.4		MgO	16.8	11.0	13.0	12.0	12.1	
6P44-a	44.2	23.6	12.6	6	7.1	6.5	MgO, K_2O	15.6	13.0	15.0	13.6	14.5	[27]
6P44-b	44.2	17	18	6	10.2	4.6	MgO, K_2O	13.0	11.2	12.5	11.4	12.3	
6P44-c	44.2	10.3	23.4	6	13.3	2.8	MgO, K_2O	11.3	9.4	10.0	9.2	9.9	
6P50	49.8	15.5	15.6	6	8.9	4.2	MgO, K_2O	12.2	10.3	11.3	10.4	11.1	
6P53-a	52.7	17	12.6	6	7.1	4.6	MgO, K_2O	12.9	10.5	11.5	10.6	11.3	
6P53-b	52.7	10.3	18	6	10.2	2.8	MgO, K_2O	11.5	8.7	9.0	8.4	8.8	
6P55	54.5	12	15	6	8.5	4	MgO, K_2O	11.0	9.1	9.7	9.0	9.4	
6P57	56.5	11	15	6	8.5	3	MgO, K_2O	10.8	8.6	8.9	8.3	8.6	
6P61	61.1	10.3	12.6	6	7.2	2.8	MgO, K_2O	10.2	8.0	8.1	7.7	7.8	
6P64	64.1	9.8	11.1	6	6.3	2.7	MgO, K_2O	9.1	7.6	7.6	7.2	7.3	
6P68	67.7	8.3	10.1	6	5.7	2.2	MgO, K_2O	8.8	6.9	6.6	6.4	6.3	
A-3	54.5	12	15	6	8.5	4	MgO, K_2O	11.6	9.1	9.7	9.0	9.4	[35]
A-5	56.5	11	15	6	8.5	3	MgO, K_2O	8.5	8.6	8.9	8.3	8.6	
SCK	51.7		42.5			5.8	K_2O	9.5	10.1	9.4	8.8	12.0	[44]

[a] CTE values extrapolated from figure.

$CaO–P_2O_5–SiO_2$ system by Lopez-Esteban et al. [27]; such values were reported in Table 2 as well.

4. CTE calculation for bioactive glasses

The models in Table 2 were applied to estimate the CTE of the bioactive glasses in Table 1 and the calculated values were compared to the corresponding experimental ones. Unfortunately not all the glasses listed in Table 1 could be included in the calculations. For some glasses, for example, it was not clear whether the composition was expressed in weight percent or molar percent (for example, Ref. [32]; such glasses were reported in Table 1 with the same format used for glasses whose formulation was declared in weight percent). For some glasses, "compositional ranges" were given instead of exact formulations (for example, Ref. [37]). Some glasses were discarded because their composition did not match the limits and compositional intervals of models in Table 2. For example, Fredholm et al. discussed the effect of a systematic substitution of SrO for CaO in bioactive glasses, including the change in CTE [46]. However the proportionality coefficients are not available for SrO and hence these glasses could not be

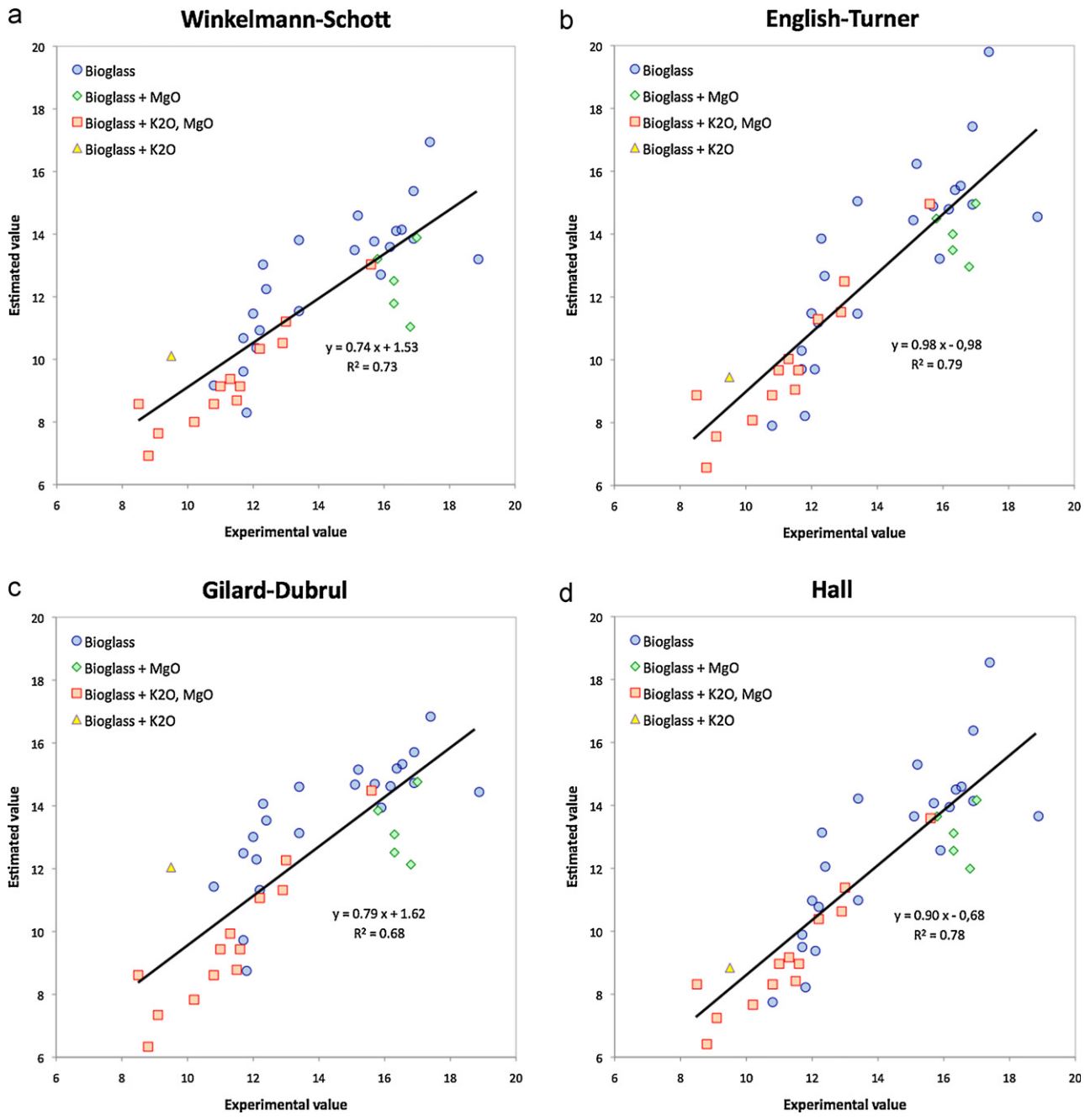

Fig. 1. Estimates for the CTE of various bioactive glasses calculated with different models: Winkelmann–Schott (a); English–Turner (b); Gilard–Dubrul (c); Hall (d). Circles are associated to glasses belonging to the "basic" Bioglass® system ($Na_2O–CaO–P_2O_5–SiO_2$); lozanges to glasses belonging to the Bioglass® system plus MgO; squares to glasses belonging to the Bioglass® system plus K_2O and MgO; triangles to glasses belonging to the Bioglass® system plus K_2O.

considered for the estimates. For the same reason, also TiO_2- and CaF_2-containing glasses were discarded. *A fortiori*, phosphate-based glasses (for example, Ref. [30]) and borate-based glasses (for example, Ref. [39]) could not be contemplated, because the CTE models in Table 2 apply to silicate-based glasses. To conclude, glasses cited in more than one paper were considered only once. It is interesting to observe that, in most cases, when a glass is mentioned in two (or more) contributions, the declared CTE value is the same. This happens, for example, with several glasses originally proposed by Lopez-Esteban et al. (6P57, 6P61, etc.) [27]. Nevertheless, some glasses recur in several papers and the corresponding CTE value is not always the same. The most striking example is represented by the 45S5 Bioglass®, whose CTE usually falls within the $14 \times 10^{-6}\ K^{-1}$ [35] to $17 \times 10^{-6}\ K^{-1}$ [39] interval, with differences depending on the measurement technique and parameters. In this case, only one CTE value was chosen, usually the most diffused one (for the 45S5 Bioglass®, $15.1 \times 10^{-6}\ K^{-1}$).

These restriction sets led to define a panel of bioactive glasses belonging to the Na_2O–K_2O–MgO–CaO–P_2O_5–SiO_2 system (i.e. the "basic" Bioglass® system, comprising Na_2O–CaO–P_2O_5–SiO_2, plus K_2O and/or MgO) that were analysed with the models listed in Table 2. As regards the P_2O_5 proportionality coefficients, the values suggested by Lopez-Esteban et al. [27] were used. The results are presented in Table 3. Moreover, for each estimate model, a graphical correlation between the calculated coefficients of thermal expansion and the experimental data was shown in Fig. 1. Linear fits were calculated and included in the graphs.

5. Results and discussion

Generally speaking, the fit is acceptable for all the analysed models, but the best results are provided by the H. model ($R^2 = 0.78$) and the E.T. one ($R^2 = 0.79$) (Fig. 1). This confirms the predictive capability of the E.T. model, which has already been observed for other glass families [47], and suggests a comparable reliability for the H. model. However, as already mentioned, the temperature range of applicability is larger from the H. model (indicatively from 25 °C to the lower limit of the critical temperature range [19,50]) than for the E.T. one (from 25 °C to 90 °C [19,49]).

Independently of the applied model, a certain data scattering can be observed. Usually the quality of predictions depends on the test conditions and the accuracy of the experimental data [18,47]. Since the experimental values used to validate the models for the Na_2O–K_2O–MgO–CaO–P_2O_5–SiO_2 system were taken from 7 different contributions (Table 3), it is likely that the scattering observable in Fig. 1 (including Fig. 1b, which refers to the E.T. model) was mainly due to the different measurement conditions applied by the Authors to determine the CTE of the glasses. Several parameters may be relevant. First of all, the amplitude of the asymmetric thermal vibrations, which are the root cause of the thermal expansion phenomenon, depends on the temperature. If L_0 is the original length of the sample at the reference temperature T_0 and L is the length of the sample at the temperature T, it is possible to define the expansivity α as [18,47]:

$$\alpha = \frac{dL}{L_0 dT} \tag{2}$$

and the CTE as [18,47]:

$$\mathrm{CTE} = \frac{\Delta L}{L_0 \Delta T} \tag{3}$$

where dL is the infinitesimal length change corresponding to the infinitesimal temperature change dT and ΔL is the length change caused by the temperature change ΔT. If $\Delta T \to 0$, $\Delta L \to dL$ and $\mathrm{CTE} \to \alpha$. Except for very few glasses (such as for pure silica), the expansivity α increases with increasing temperature, hence the CTE also increases if the temperature interval ΔT increases and/or if ΔT is fixed at higher temperatures. Most literature data refer to the intervals 20–300 °C or 100–300 °C, but this is not a standardized procedure [18,47]. In fact, in spite of the relevant effect of the temperature on the CTE, the choice of the temperature range is often discretionary and the temperature limits considered for the measurement are not always explicitly declared. Whenever available, the temperature range was indicated in Table 1. From this list, it is evident that the literature data used to validate the analytical models refer to different temperature intervals and this may contribute to the data scattering revealed in Fig. 1.

The CTE of a glass may also depend on its thermal history. For example, Schott detected relevant differences (up to 5%) between perfectly annealed and chilled glass samples [18]. In fact, a rapidly quenched (or poorly annealed) glass keeps a structure similar to that of the melt, i.e. an "open" structure, with relatively large distances between the mass particles. For this reason, when the temperature is relatively low, the density of a rapidly quenched glass is lower than that of the perfectly annealed counterpart, while its CTE is somewhat higher. Then, in a range of about 100 °C below the glass transition temperature, the thermal behaviour of the rapidly quenched glass significantly deviates from that of the annealed one. In fact, the increased mobility enables a "densification" of the glass structure, which may even exceed the thermal expansion caused by the increased amplitude of the thermal vibrations. The rapidly quenched glass and the annealed one may expand in the same way as soon as a balance is reached between these opposing phenomena [18]. The estimate models for the CTE apply to well annealed glasses [18] and, for this reason, only annealed glasses were considered in the present contribution. However it should be kept in mind that different annealing procedures may result in different CTE values and this may be an additional source of data scattering.

To conclude, the value of the CTE of a glass may be affected by the measurement technique. High precision tests should be performed with the interferometric method, however several alternative approaches are currently stated in the literature and this is a further reason of data variability [18]. Unfortunately the technique and experimental conditions used to quantify the CTE are rarely described in papers on bioactive glasses. For this

reason, in the present contribution it was not possible to select the literature data on the basis of the experimental setup.

Since the additive models are mainly of empirical nature, it is not possible to attribute an advanced physical meaning to the proportionality coefficients [18]. Nevertheless, observing the results in Table 3 and Fig. 1, some considerations may be proposed. First of all, as already mentioned, the E.T. and the H. models offer the best estimates for the CTE of bioactive glasses belonging to the Na_2O–K_2O–MgO–CaO–P_2O_5–SiO_2 system. In fact, the fit is fairly good for both of them (Figure 1). Nevertheless, some data sensibly deviates from the linear predictions. The most striking discrepancies can be observed for the glasses named BG1 in Ref. [34] and ICSW4 in Ref. [41]. The former is characterized by a very high content of Na_2O (47 wt%), which is very close to the upper limit for the applicability of the predictive models [47]. The latter contains a very high percentage of P_2O_5 (19.5 wt%), which is more than three times higher than that considered by Lopez-Esteban et al. [27]. From this point of view, it is worth noting that the proportionality coefficients proposed by Lopez-Esteban et al. [27] were calculated for bioactive glasses containing a fixed and relatively low amount of P_2O_5 (6 wt%) and therefore it is reasonable that such coefficients could be adjusted to improve the predictivity of the models on a wider compositional range.

The graphs in Fig. 1 suggest that the CTE values of the glasses added with MgO only strongly deviate from the linear fit (lozanges in Fig. 1a–d). These data for MgO-containing glasses were taken from a work by Watts et al., specifically dedicated to the influence of magnesia on the properties of bioactive glasses [42]. The Authors observed that, after a modest initial decrease, the CTE values slightly augmented when the magnesia content exceeded 20 mol%. This result was surprising, because it contradicted the decreasing trend predicted for the CTE of MgO-containing glasses by additive (Appen. in Ref. [42]) models. The Authors argued that this deviation from the expected trend was due to a change in the structural role of MgO, from a modifier oxide to an intermediate oxide, when its content was higher than 20 mol%.

As a general trend, when both MgO and K_2O are incorporated in the basic Na_2O–CaO–P_2O_5–SiO_2 system, the CTE values result relatively low (red squares in Fig. 1a–d) (for interpretation of the references to colour in this sentence, the reader is referred to the web version of the article), even if the effect of K_2O on the CTE is stronger than that of Na_2O [17,18]. Two concurrent reasons can be proposed for this tendency. First of all, MgO is usually introduced instead of CaO and the effect of MgO on the CTE is smaller than that of CaO [18]. Moreover, as already suggested for MgO-added glasses, the role of magnesia can change from modifier oxide to intermediate oxide when its percentage is high enough. Such behaviour of MgO has been reaffirmed in a recent contribution by O'Donnell focused on the prediction of the glass transition temperature of bioactive glasses from their composition [6]. The Author hypothesized that MgO can form $[MgO_4]^{2-}$ units, which would require charge balancing from other alkaline and alkaline-earth ions, including K^+, Na^+ and Ca^{2+}, thus removing them from the silicate network and promoting an increase in Q^{3+} structural units (and a corresponding decrease in Q^{2+} units) [6]. In this way, low-expansion bioactive glasses can be achieved by introducing proper amounts of appropriate oxides [18], such as MgO, which do not alter the bioactivity of the glass.

6. Conclusions

Bioactive glasses are commonly applied as coatings or used in composite systems. The possibility of matching them with a substrate or a second phase deeply relies on their CTE, which governs the eventual development of thermal residual stresses. In spite of the technological relevance of the CTE for bioactive glasses, few contributions are currently available in the literature which are specifically focused on this topic.

In the present paper, more than 70 bioactive glasses were reviewed in order to define the relation existing between their composition and their CTE value and various analytical models were compared to estimate the CTE. Unfortunately, some glasses described in the literature could not be included in the calculations, because their composition did not fall within the applicability range of the CTE models or their formulation was not unambiguously reported. For this reason, the analysis was focused on a set of 41 bioactive glasses belonging to the Na_2O–K_2O–MgO–CaO–P_2O_5–SiO_2 system (i.e. the "basic" Bioglass® system, comprising Na_2O–CaO–P_2O_5–SiO_2, plus K_2O and/or MgO). The CTE of these glasses was calculated with the models proposed by Winkelmann and Schott (W.S.), English and Turner (E.T.), Gilard and Dubrul (G.D.) and Hall (H.) and compared to the experimental outcomes. The most appropriate predictions were obtained with the E.T. model and the H. one. In both cases, the fit was fairly good ($R^2 \approx 0.79$), but some data scattering was due to the different experimental conditions applied in the original papers, since the CTE value is sensitive to the glass thermal history, as well as to the measurement temperature range and equipment. In spite of this scattering, as a general trend, the analysis of the reviewed data showed that, when both MgO and K_2O are incorporated in the basic Na_2O–CaO–P_2O_5–SiO_2 system, the CTE values result relatively low. This is mainly due to the presence of MgO, whose role in the glass structure may change from modifier oxide to intermediate oxide. In this way, it is possible to reduce the CTE of bioactive glasses and promote their adhesion to low-expansion substrates or second phases by acting on their composition, with a proper choice of the constituent oxides and their relative amounts.

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