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LETTER

Thermoluminescence in silicon substituted apatite and silicon stabilized tricalcium phosphate bioceramic

Alexis Pietak · Michael Sayer

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Silicon stabilized tricalcium phosphate (Si-TCP), with a crystal structure similar to α-TCP ($Ca_3(PO_4)_2$) is formed when a stoichiometric calcium hydroxyapatite (HA or $Ca_5(PO_4)_3OH$) precipitate is sintered in the presence of added silica (SiO_2) at temperatures between 850 and 1,000 °C [1–3]. A change in the lattice constants with silicon content of both the $P2_1/a$ Si-TCP and the $P6_3/m$ HA crystallographic unit cell suggests that Si is incorporated into both of these phases [3]. In the absence of silicon, an α-TCP phase is expected to be present only after sintering at temperatures greater than 1,200 °C [4]. Unlike undoped counterparts, Si-TCP based materials prepared by adding SiO_2 to HA are resorbable by osteoclast cells and exhibit good osteoconductive properties [2]. As Si is implicated in the biological performance of these materials, it is of the utmost importance to determine the changes induced by Si in this calcium phosphate system.

IR and NMR measurements indicate a significant loss of OH from the starting HA composition as a function of silica doping [3]. It has been suggested that when HA is sintered in the presence of SiO_2, species such as SiO_4^{4-} substitute for PO_4^{3-} with the creation of $V_{OH}^{\cdot}$ for charge compensation [5, 6]. Recently it has been proposed that SiO_2 substitution in HA without removal of phosphate from the HA mix to ensure stoichiometric production of Si-HA, results in the formation of α-TCP, according to the reaction [7]:

$$\begin{aligned}&Ca_5(PO_4)_3OH + BSiO_2\\&= CCa_5(PO_4)_{3-x}(SiO_4)_x(OH)_{1-x} + DCa_3(PO_4)_2 + EH_2O\end{aligned} \tag{1}$$

The nominal hydroxyapatite phase is significantly dehydrated as a result of the incorporation of Si and may consist of a mixture of partially dehydrated hydroxyapatite and oxyapatite. In the following it is therefore referred to as Si-apatite (Si-Ap). Si substitution occurs in α-TCP to form Si-TCP and an amorphous phase when SiO_2 in excess of the substitution limit in HA is present [7]:

$$\begin{aligned}Ca_3(PO_4)_2 + (y+DB)\,SiO_2 &\rightarrow Ca_3(P_{1-y/2}Si_{y/2}O_{4-y/4})_2\\&+ 0.1\,P_2O_5\,DSiO_{2\,(\text{amorphous})}\end{aligned} \tag{2}$$

In this letter we identify a thermoluminescence emission peak associated with a OH vacancy in HA and silicon related centers in the phase mixture of Si-TCP and Si-Ap. Thermoluminescence is shown to be a sensitive tool to detect the presence of silicon in the calcium phosphate system.

HA powders were prepared by spray drying colloidal sols, created via a basic precipitation reaction in an ammoniated aqueous mixture [1]. Silica doped sols were created by the addition of Cab-o-sperse™ fumed SiO_2 powder to the HA sol with no further adjustment of ion concentrations in the sol. The molar concentration is expressed as mol [SiO_2]:mol [$Ca_5OH(PO_4)_3$]. Some undoped HA powder and 0.1:1 mol SiO_2: mol HA powder was prepared in a plastic vessel to eliminate potential silica contamination from the glassware as a result of the highly basic reactants. All other powders were prepared in standard glassware. The phase composition of the powders as a function of Si content was determined using Rietveld X-ray diffraction, with method and results described in [3].

A. Pietak (✉) · M. Sayer
Queen's University, K7L 3N6 Kingston, Ontario, Canada
e-mail: alexis.pietak@gmail.com

Silica doped powders were calcined at 500 °C to remove remaining organics, pressed into pellets 12.5 mm in diameter and 1 mm thick, pre-sintered at 500 °C for 1 h, followed by 1 h at 1,000 °C. Undoped HA pellets were sintered for a similar thermal cycle at 10% and 55% partial pressure of H_2O. A summary of processing methods of the various samples is given in Table 1.

All samples were irradiated as ceramic pellets at room temperature. Pellets were exposed to a precise dose of 10 G Co-60 radiation using a cancer therapy 8,500-Thetatron apparatus. Thermoluminescence emission measurements were carried out using a Harshaw-Filtrol-4000 model thermoluminescent dosimeter reader. The temperature was ramped linearly at 10 °C/s from 50 °C to 260 °C. All thermoluminescence glow curves are shown normalized to their respective maxima.

Thermoluminescence in undoped HA prepared in plastic and sintered at 55% ppH_2O exhibits two peaks, as shown in Figure 1. Peak 1 is centered at 470 ± 2 K and a smaller contribution arises from Peak 2 centered at $T = 425 \pm 5$ K. Sintering HA at 10% ppH_2O leads to a shift in the peak maximum to $T = 477 \pm 2$ K and to a significant broadening of the peak. For the case of general order kinetics, thermoluminescence intensity is described by [8]:

$$I(t) = \frac{n_o s'' \exp(-E/k_b T)}{\left[(1 + ((b-1)s''/\beta))\left(\int\limits_{To}^{T} \exp(-E/kT)dT\right)^{(b/(b-1))}\right]} \tag{3}$$

Here, n_o is the number of carriers in traps at the initiation of heating. The variable s'' is the effective attempt to escape frequency. The temperature T is ramped linearly at rate $\beta = 10$ K/s, from an initial temperature $T_o = 300$ K.

Table 1 Summary of processing treatments for the various experimental samples

Sample	Treatment
HA 10% ppH_2O	Powder prepared in plastic. No SiO_2 added. Pellet sintered at 1,000 °C in dry (10% ppH_2O) air.
HA 55% ppH_2O	Powder prepared in plastic. No SiO_2 added. Pellet sintered at 1,000 °C in wet (55% ppH_2O) air.
HA glass	Powder prepared in glassware. No additional SiO_2 added. Pellet sintered at 1,000 °C in ambient air.
0.1:1–1:1 mol SiO_2: mol HA	Powder prepared in glassware. Colloidal SiO_2 introduced at stated level. Pellet sintered at 1,000 °C in ambient air.

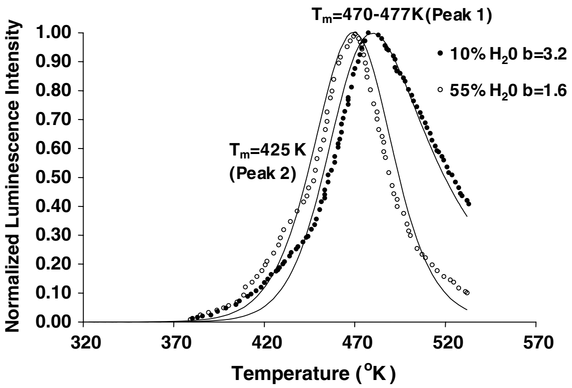

Fig. 1 Thermoluminescence emission from undoped hydroxyapatite sintered in low (10% ppH_2O) or high (55% ppH_2O) humidity with associated fits to theoretical thermoluminescence curves having the parameters shown on the diagram. A broadening of the peak indicative of a delay in the release of trapped carriers occurs with sintering in drier environments

The influence of re-trapping is described by the parameter 'b', where a value larger than 1.0 describes a recombination process in which the number of recombination centers is smaller than the number of traps [8]. In this experiment it was not possible to determine the frequency of the emitted light, and therefore, no estimates of trap depth are available.

Thermoluminescence peak 1 for undoped HA sintered at 10% and 55% partial pressures of H_2O was fit to equation (3). Estimates of the attempt to escape frequency s'' of $2–3 \times 10^{11}$ s^{-1} Hz and the activation energy E of 1.2 ± 0.1 eV were obtained based on the fit of Eq. (3) to the data of peak 1. For samples sintered at 55% ppH_2O, the luminescence decay is close to first order with $b = 1.6$, while sintering at 10% ppH_2O leads to peak broadening with $b = 3.2$. The increase in b with decreasing sintering humidity indicates an increased ratio of trapping to recombination centers.

Figure 2 shows that when the HA precipitate is sintered in the presence of SiO_2 the form of thermoluminescence curves changes significantly with the appearance of peaks 3 and 4, centered at $T = 410 \pm 5$ K and $T = 366 \pm 5$ K, respectively. The intensity of peak 1, which dominated the thermoluminescence of pure HA decreases dramatically with SiO_2 addition, while peak 4 increases with SiO_2 addition. The integrated areas for peaks 1 and 4 were calculated from the fitting of an asymmetric peak function to the experimental data and normalized to the total area of the glow curve. Figure 3 shows the relative areas of peaks 1 and 4 as a function of SiO_2 addition to the system. Figure 4 shows the relative area of peak 1 normalized to the wt% HA phase of the sample. Similar calculations were not made for peaks 2 and 3 because of the difficulty of resolving them.

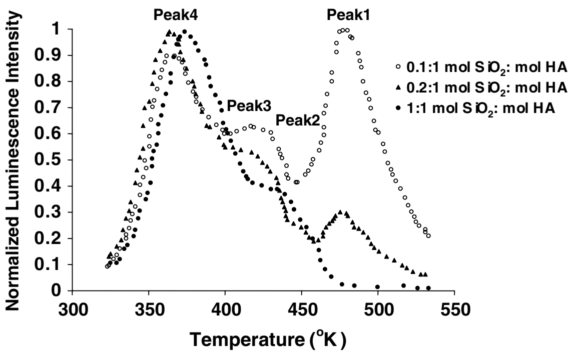

Fig. 2 Thermoluminescence emission from Si-TCP/Si-Ap phase mixtures at various doping levels of SiO_2

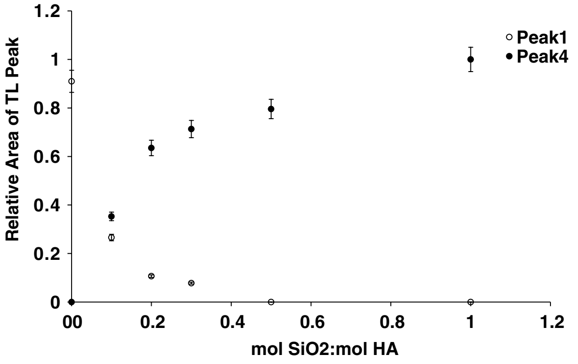

Fig. 3 Change in the area of peak 1 and peak 4 as the SiO_2 doping increases. The areas were calculated by the fitting of an asymmetric peak function

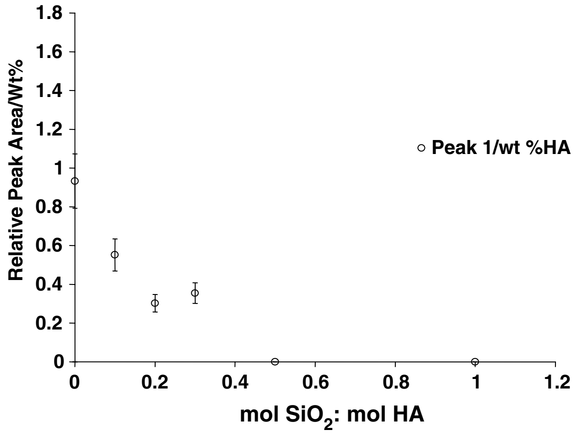

Fig. 4 Change in the area of peak 1 normalized to the weight % HA phase as the SiO_2 doping increases. The areas were calculated by the fitting of an asymmetric peak function

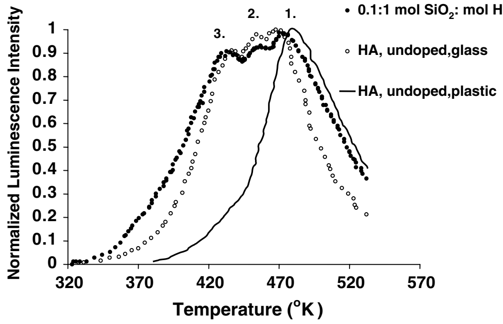

Fig. 5 Thermoluminescence emission from undoped materials prepared in glass and plastic vessels. For comparison emission is shown from a sample having composition 0.1 mol SiO_2:1 mol HA

Figure 5 shows a strong similarity between the thermoluminescence output for undoped HA prepared in a glass vessel and HA doped with 0.1:1 mol SiO_2: mol HA prepared in a plastic vessel. Both of these curves differ significantly from the output for undoped HA prepared in plastic.

It is well known that OH vacancies ($V_{OH}^{\bullet}$) are formed when the HA lattice dehydrates at high temperatures (>700 °C) [9]. The major defect center in stoichiometric HA heated above 700 °C and irradiated has been identified by previous authors using electron spin resonance (ESR), as an electron localized at $V_{OH}^{\bullet}$ to form an e-$V_{OH}^{\bullet}$ center [10, 11]. Previous ESR investigations on this Si-TCP system have revealed a number of paramagnetic trapping centers and support the existence of hydroxyl vacancies [12]. The relationship between Si addition and the intensities of the various ESR centers correlate well with the current Thermoluminescence data [12].

Thermoluminescence peak 1 is characteristic of undoped HA and is attributed to the release of electrons localized at $V_{OH}^{\bullet}$. The dependence of the kinetic order parameter *b* on sintering humidity supports the identification of the trapping site as e-$V_{OH}^{\bullet}$. For materials irradiated at $T \sim 300$ K the recombination center for electrons in the HA structure has been proposed to be a phosphate (PO_4^{2-}) radical [13]. Unlike the e-V_{OH} centers, the formation of PO_4^{2-} centers is not expected to depend on the sintering humidity. Therefore, HA sintered at low humidity will have a higher proportion of e-$V_{OH}^{\bullet}$ to humidity independent PO_4^{2-} recombination centers than HA sintered at high humidity, leading to the significant re-trapping and the broadening of peak 1 observed in dry sintered material.

The significant decrease in the integrated intensity of the e-$V_{OH}^{\bullet}$ center of peak 1 as SiO_2 is added to the system is not explained by the disappearance of HA from the system, as is shown by the normalization of peak 1 to the wt% HA of the sample in Fig. 4. Trapping of a carrier at a defect site in a crystal lattice occurs because relaxation of the lattice about the carrier decreases the free energy of the lattice [13]. If the lattice structure changes, trapping of the carrier at $V_{OH}^{\bullet}$ centers may no longer be thermodynamically favorable and sites associated with silicon may be favored.

Peaks 3 and 4 are clearly associated with the presence of silicon. As Fig. 3 shows, the relative intensity of peak 1 and peak 4 correspond well with the level of HA and Si-TCP phases in the system as a function of SiO_2 doping.

The correlation between the intensity of peak 4 and the phase fraction of Si-TCP suggests that the Si center is a property of this phase.

Thermoluminescence emission suggests excellent sensitivity to changes occurring in the Si doped CaP system when silicon is present, even in trace quantities. Thermoluminescence of HA prepared in glass and HA prepared in plastic show different glow curves. The glow curve of HA prepared in glass is nearly identical with the HA system doped with 0.1:1 mol Si:HA prepared in plastic, Fig. 5. This demonstrates that HA prepared via a basic precipitation method in a glass vessel incorporates some silica from the glassware.

In conclusion, thermoluminescence emission provides a sensitive, qualitative representation of the effects of sintering HA in the presence of SiO_2. Thermoluminescence peaks observed from the Si-TCP/Si-Ap phase mixture at $T = 410 \pm 5$ K and $T = 366 \pm 5$ K suggest one or more defect centers in the Si-TCP and Si-Ap phases are associated with Si. A strong decrease in the intensity of the thermoluminescence emission peak at $T = 470 \pm 2$ K attributed to an e-$V_{OH}^{\bullet}$ defect in undoped HA is increased support for the concept of a Si doped apatite, and hence the proposed chemical reaction model (1). Finally, the results of this study indicate that Si in calcium phosphates may exist because of addition during material preparation, or be incorporated as a result of processing strongly basic reactants in silica-based glassware.

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