

Magnetic Phase Transitions in Macro/Mesoporous Bioactive Glass by Ferric Nitrate Addition in Sol-Gel Synthesis

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Abstract

Multifunctional macro/mesoporous bioactive glasses (MMBG) with magnetic sensitivity are prepared by adding ferric nitrate in a one-pot sol-gel synthesis. Three different magnetic properties are obtained depending on the synthesis composition and calcination atmosphere. The gradual transition from paramagnetism to superparamagnetism is observed when ferric nitrate is increased from 5 up to 20 mol%. In contrast to minimal paramagnetic response to an applied magnetic field, substantial magnetizations are induced in superparamagnetic MMBG owing to the formation of iron oxide nanoparticles, which is signified by the change in color after calcination. The transition from superparamagnetism to ferromagnetism occurs when the MMBG are calcined in an argon instead of an oxygen atmosphere. This ferromagnetic hysteresis coincides with the formation of Fe-rich spheres with diameters larger than 100 nm.

Keywords: Bioactive glass, mesopore, macropore, sol-gel method, magnetic properties

I. Introduction

Porous bioactive materials have been researched for implantation in bone tissue engineering and drug delivery systems¹⁻⁴. With the advances in additive manufacturing of bioactive glasses and bioceramics^{5,6}, the incorporation of magnetic phase into porous bioactive glasses is interesting for the combination of biocompatible porous structures with magnetic sensitivity. In previous reports^{7,8}, the response to magnetic fields has been used in the hyperthermia treatment of bone cancer. Such treatment is an effective way to eliminate cancerous cell in bone with a temperature above 43 °C. When the heat is induced by the magnetic field for an appropriate period of time, it is possible to damage the cancerous cells without altering the healthy cells⁷. Macro/mesoporous bioactive glasses (MMBG) with uniform pore distribution and the high surface area have enhanced features for bone-forming bioactivity and drug delivery of MMBG compared to conventional bioactive glasses (BG). Magnetic MMBG are therefore promising candidates for multifunctional cancer therapy and bone regeneration materials.

Melt quenching and sol-gel methods have been developed to synthesize magnetic BG⁹⁻¹⁶. For the melt quenching method, the compositions of $41\text{CaO} \cdot (52-x)\text{SiO}_2 \cdot 4\text{P}_2\text{O}_5 \cdot x\text{Fe}_2\text{O}_3 \cdot 3\text{Na}_2\text{O}$ ($2 \leq x \leq 10$ mol % Fe_2O_3)

were studied by Singh *et al.*¹³. With an increase in molar concentration of iron oxide (Fe_2O_3), the area under the hysteresis loop of this glass-ceramic system was increased and the coercivity was reduced. Leventouri *et al.* similarly found that the rise in iron oxide enhanced the magnetization and hysteresis of magnetic bioceramics¹⁶. The drawback of the melt quenching method was that the processing temperature was raised above the glass transition temperature of materials. As a consequence, the glass-ceramic phase was formed with the reduction in the bioactivity¹⁷⁻¹⁹. It must also be taken into consideration that the apatite-forming ability and cell attachment tend to decrease when the magnetic phase in BG²⁰ is increased. An alternative is the sol-gel method widely used to prepare conventional BG. The solution chemistry allows the easy mixing of chemicals and thus ensures homogenization and uniformity. Low-temperature hydrolysis and condensation processes promote bioactivity by preventing potential crystallization and phase separation. In addition, the sol-gel also gives rise to MMBG with high porosity and surface area suitable for tissue scaffolds^{17,18,21}.

In this work, successive evolutions of paramagnetism-superparamagnetism-ferromagnetism in MMBG from one-pot sol-gel synthesis are demonstrated. Unlike mixing iron oxides with BG, either iron oxide or other Fe-based phases of varying sizes can be obtained by adding iron compounds in the sol-gel reaction. It follows that the

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magnetic sensitivity of MMBG may be tuned by varying process parameters in the sol-gel synthesis. The effect of calcination atmosphere is also observed.

II. Experimental

Three sets of MMBG were synthesized using the one-pot sol-gel process summarized in Fig. 1 with reagent compositions shown in Table 1. The compositions of Si-Ca-Na-P were respectively obtained from tetraethyl orthosilicate (TEOS, $\text{C}_8\text{H}_{20}\text{O}_4\text{Si}$), calcium nitrate tetrahydrate (CNT, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), sodium nitrate (NaNO_3) and triethyl phosphate (TEP, $\text{C}_6\text{H}_{15}\text{O}_4\text{P}$). Ferric chloride (FeCl_3) and ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were selected as iron compounds to incorporate magnetic phase into MMBG. Polymethyl methacrylate (PMMA) colloidal crystals were used as the template to generate macropores and P123 block copolymers were employed as the structure-directing agent for mesoporous structures. To obtain the homogeneous gel and allow slow interactions, the reagents were gradually added drop by drop and gently mixed. After immersion of PMMA, the gels were aged, dried and finally calcined at 600°C . In this work, the thermal decomposition of iron compounds occurred during the calcination process instead of the reduction process commonly used to obtain magnetic iron oxides in reducing atmosphere.

In this first set of samples, magnetic MMBG samples prepared with FeCl_3 (sample 80S5Fe.C) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (sample 80S5Fe.N) were compared and a controlled MMBG sample referred to as 80S0Fe was also prepared without any iron compound. In the second set of samples, the $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was further investigated with the increase to 10 and 15 mol% (samples 70S15Fe, 65S15Fe, 60S15Fe, 60S10Fe). The catalyst was changed from HCl to HNO_3 to avoid the by-product from Cl ions

or molecules. Moreover, the ageing and drying temperatures were lowered to 45°C to prevent MMBG from collapsing. The composition of magnetic phase in MMBG is raised in the third set by changing the $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ to 20 and 30 mol%. Whereas the first two sets were calcined in oxygen, samples in the third set from the same synthesis received heat treatment in the furnace separately filled with either argon (samples 60S20Fe_Ar, 50S30Fe_Ar) or oxygen gas (samples 60S20Fe_O₂, 50S30Fe_O₂) in order to compare the effect of the calcination atmosphere. Phases and magnetic properties were respectively characterized by means of x-ray diffractometry (XRD) and vibrating sample magnetometry (VSM). In addition, the third set of samples was also characterized by means of Fourier transform infrared (FT-IR), synchrotron x-ray absorption near edge structure (XANES), energy-dispersive x-ray (EDX) spectroscopy and field emission scanning electron microscope (FESEM).

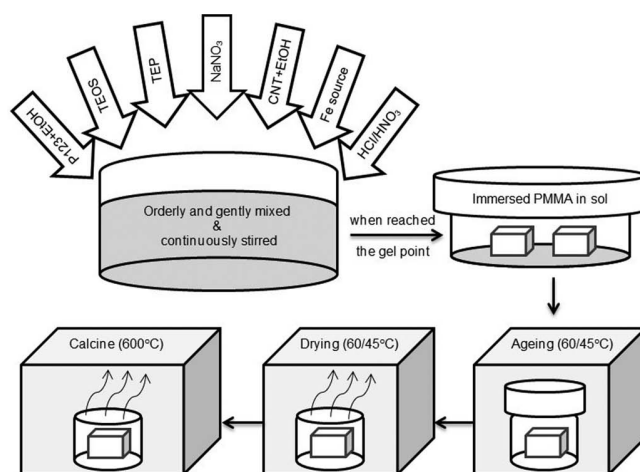


Fig. 1: Diagram of synthesis procedure for magnetic MMBG.

Table 1: Composition of reagents in the sol-gel synthesis.

Sample codes	Composition Si-Ca-Na-P-Fe (mol %)	P123 (g)	TEOS (ml)	TEP (ml)	NaNO_3 (ml)	CNT (g)	* FeCl_3 or $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (g)	†(0.5M)HCl or (1M) HNO_3 (ml)	EtOH (ml)
80S0Fe	80–10–5–5–0	0.667	1.79	0.15	1.00	0.235	–	1.00†	2.50
80S5Fe.C	80–5–5–5–5	0.667	1.79	0.15	1.00	0.118	0.080*	1.00†	2.50
80S5Fe.N	80–5–5–5–5	0.666	1.79	0.15	1.00	0.118	0.202	1.00†	2.50
70S15Fe	70–5–5–5–15	0.586	1.57	0.15	1.00	0.119	0.627	1.00	2.50
65S15Fe	65–10–5–5–15	0.543	1.46	0.15	1.00	0.237	0.607	1.00	2.50
60S15Fe	60–15–5–5–15	0.501	1.34	0.15	1.00	0.356	0.607	1.00	2.50
60S10Fe	60–20–5–5–10	0.503	1.34	0.15	1.00	0.473	0.404	1.00	2.50
60S20Fe_O ₂	60–10–5–5–20	0.506	1.34	0.15	1.00	0.236	0.808	1.00	2.50
60S20Fe_Ar	60–10–5–5–20	0.506	1.34	0.15	1.00	0.236	0.808	1.00	2.50
50S30Fe_O ₂	50–10–5–5–30	0.417	1.12	0.15	1.00	0.236	1.212	1.00	2.50
50S30Fe_Ar	50–10–5–5–30	0.417	1.12	0.15	1.00	0.236	1.212	1.00	2.50

III. Results and Discussion

(1) Phases of MMBG

All dried gels look homogeneous and the magnetic MMBG samples prepared with iron compounds are yellow. When the $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ is increased to 10–20 mol%, the colors of the samples become darker. All MMBG glitter slightly after calcination owing to reflections from their porous surfaces and turn brownish purple on account of the reduction of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ into other iron oxide phases. Since magnetite (Fe_3O_4) and hematite ($\alpha\text{-Fe}_2\text{O}_3$) are respectively black and red, the color observed after calcination is closest to the brown color of maghemite ($\gamma\text{-Fe}_2\text{O}_3$). While the distribution in pore size also influences the colors of MMBG, the amount of iron oxides can still be roughly compared based on the differences in color shade.

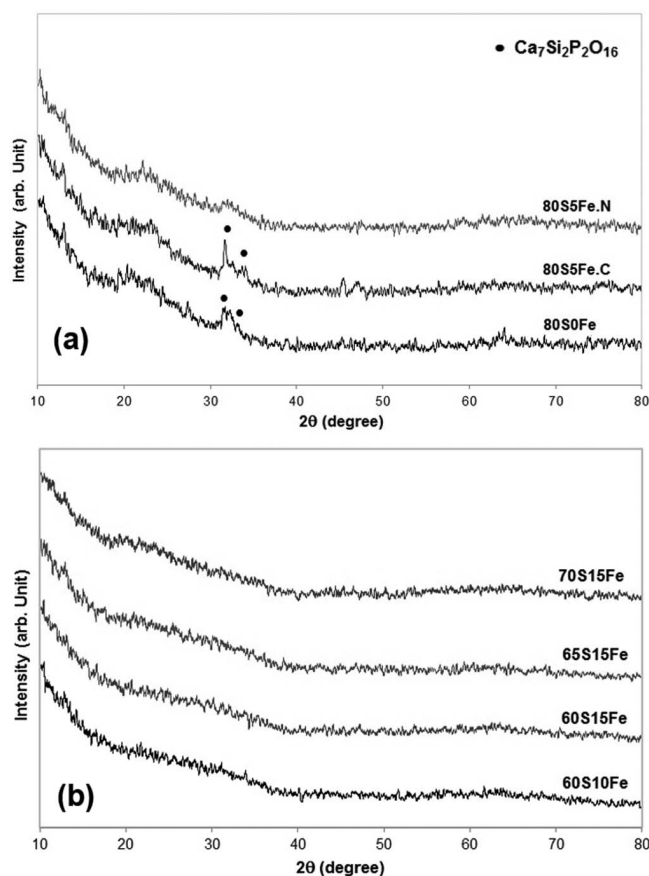


Fig. 2: XRD patterns of (a) MMBG (80S0Fe) and magnetic MMBG synthesized with two different Fe sources (80S5Fe.C and 80S5Fe.N) and (b) magnetic MMBG synthesized with varying composition of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.

In Fig. 2, XRD spectra are used to confirm the crystalline phases in magnetic MMBG. Whereas no diffraction peak is revealed in the case of a sample synthesized with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (80S5Fe.N), two other samples in Fig. 2(a) (80S0Fe and 80S5Fe.C) exhibit the peaks at around 31.57 and 33.39 degrees, corresponding to the nagelschmidtite ($\text{Ca}_7\text{Si}_2\text{P}_2\text{O}_{16}$) phase (JCPDS 011–0676). This bioceramic material is under investigation for applications in bone and periodontal tissue regenerations^{22,23}. When $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ is increased to

10 and 15 mol%, XRD spectra of all samples in Fig. 2(b) do not show any characteristic peak of $\text{Ca}_7\text{Si}_2\text{P}_2\text{O}_{16}$. Therefore, it can be concluded that the use of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in the sol-gel synthesis inhibits the crystalline $\text{Ca}_7\text{Si}_2\text{P}_2\text{O}_{16}$ phase. Interestingly, the diffraction peaks of iron oxides are not observed in all samples even after $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ is increased in Fig. 2(b).

(2) Effects of synthesis conditions

Magnetic properties are compared by plotting magnetization against an applied magnetic field (M-H plot) in Fig. 3 with the highly magnified response at low fields as insets. In Fig. 3(a), the controlled MMBG sample synthesized without any iron compound (80S0Fe) is exclusively diamagnetic with the magnetization induced in the direction opposite to the applied magnetic field. By contrast, paramagnetic characteristics are observed in samples synthesized with 5 mol % FeCl_3 (80S5Fe.C) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (80S5Fe.N). Their magnetizations are rather small and directly proportional to the applied magnetic field up to 1.5 kOe in both directions.

When $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in the synthesis is increased to 10 and 15 mol%, the superparamagnetic characteristics typically manifested by single-domain magnetic nanoparticles are observed in Fig. 3(b) at the expense of paramagnetism. The magnetization is only proportional to the applied magnetic field in the low-field regime. The rate is then continually reduced at high fields. When the magnetic MMBG are demagnetized, their coercivity values are close to zero and the M-H plots are virtually free of hysteresis. Whereas ferromagnetic particles generated heat in the hysteresis loss mechanism, superparamagnetic particles can also be used in hyperthermia treatment based on their response to alternating magnetic fields. The paramagnetic-to-superparamagnetic phase transition in Fig. 3 signifies the formation of iron oxide nanoparticles in the synthesis with 10–15 mol% $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. In the case of 5 mol% $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, only paramagnetic Fe ions are likely present in the synthesized MMBG. This conclusion is well supported by the color change previously discussed. Since its diffraction peaks are not observed in all samples, the iron oxides exist in either amorphous state²⁴ or nanocrystalline maghemite phase which cannot be detected with XRD.

(3) Effects of calcination conditions

Interestingly, the transition from superparamagnetic to ferromagnetic characteristics is observed when the samples are calcined in an argon instead of in an oxygen atmosphere. For both 20 and 30 %mole $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Fig. 3(c) shows that samples calcined in oxygen have superparamagnetic characteristics similar to those shown in Fig. 3(b) whereas samples 50S30Fe_Ar and 60S20Fe_Ar in Fig. 3(d) have hysteresis. The coercive fields around 100 Oe were observed in the insets. Such a change in magnetic properties suggests that the argon atmosphere enhances Fe-rich clusters beyond the single-domain regime.

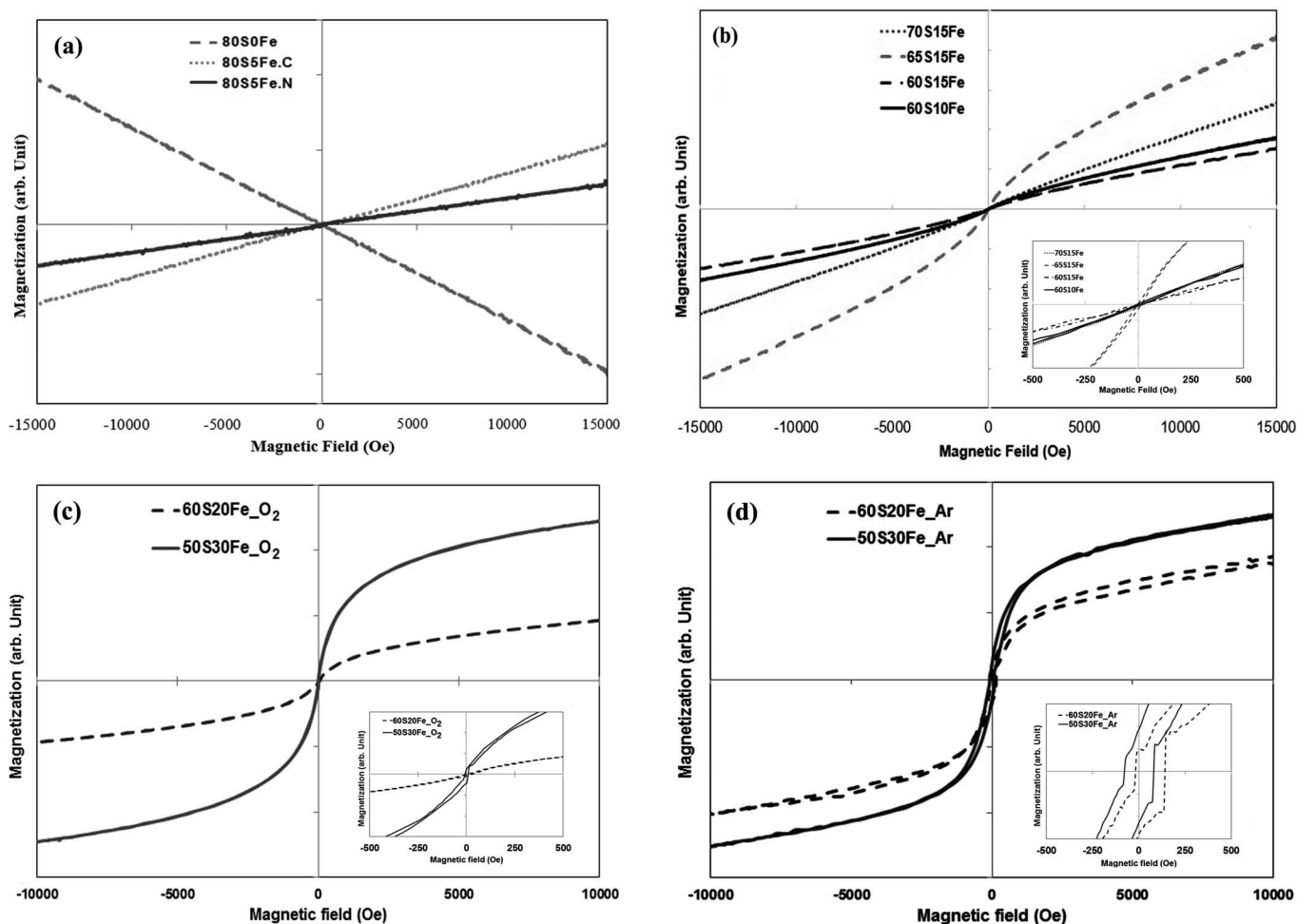


Fig. 3: M-H plots of (a) MMBG (80S0Fe) and magnetic MMBG synthesized with two different iron compounds (80S5Fe.C and 80S5Fe.N), (b) magnetic MMBG synthesized with varying composition of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, (c) magnetic MMBG calcined in oxygen and (d) magnetic MMBG calcined in argon.

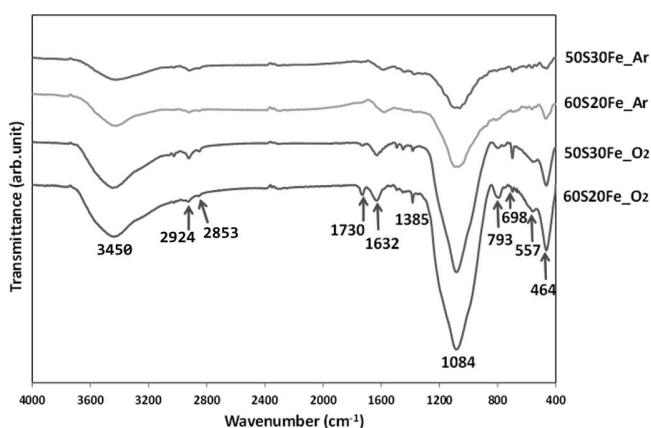


Fig. 4: Comparison of FTIR of magnetic MMBG calcined in either oxygen or argon atmosphere.

Other characterization techniques are used to confirm the effect of the calcination atmosphere. From the FTIR spectra in Fig. 4, the peaks around at 3450 and 1632 cm^{-1} correspond to residual water and those around 2924 and 2853 cm^{-1} correspond to the methanediyl group. In addition, the peak at 1730 and 1385 cm^{-1} is assigned to carbonyl and carbonate, respectively²⁵. The characteristic peaks of Si-O-Si (1084 and 464 cm^{-1}) and P-O (557 cm^{-1}) vibrations are shifted to lower wavenumbers compared to those

of typical MMBG without magnetic phase. Whereas each peak remains at an identical position for both calcination atmospheres, its intensity is greatly reduced in the case of argon. This is likely due to the disruption of Si-O-Si and P-O vibrations by the formation of large magnetic clusters. The vibration bands at 698 cm^{-1} assigned to iron oxides are prominent only in the case of sample 50S30Fe_O₂. The effect of calcination atmosphere agrees well with the XANES spectrum of sample 60S20Fe_O₂ in Fig. 5 which resembles the maghemite reference. When the samples are calcined in argon, the peak of 60S20Fe_Ar is shifted to a lower wave number and the intensity of pre-edge is substantially decreased as a result of some conversions of Fe^{3+} in maghemite into Fe-rich phase.

As shown by insets in FESEM in Fig. 6, the calcination in oxygen gives rise to an ordered porous structure with some collapsed walls. By contrast, the surface of MMBG calcined in argon is covered by a lot of spheres larger than 100 nm in diameter. This distinct feature was further investigated with EDX. The elemental compositions in Fig. 6 exhibit a large variation from one point to another. The sphere exhibits an increase in Fe at the expense of Si, Ca, Na and P. FESEM and EDX results provide the link to the ferromagnetism previously shown in Fig. 3(d). The collective magnetic property in the sample calcined in argon at-

mosphere is dominated by the contribution from these Fe-rich microspheres which are much larger than the superparamagnetic regime (order of 10 nm).

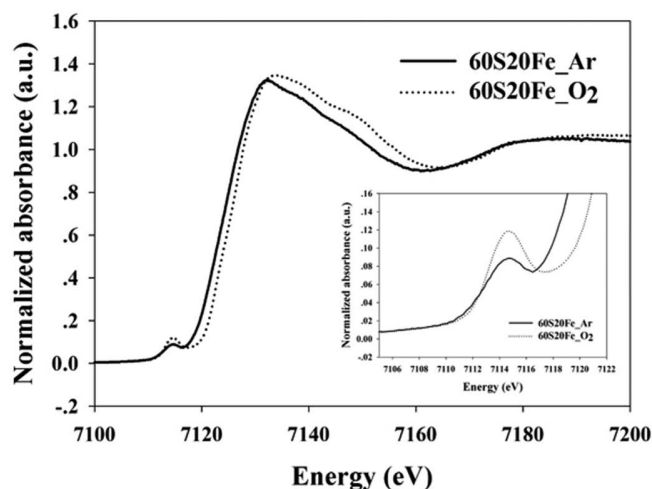


Fig. 5: Comparison of XANES spectra of magnetic MMBG calcined in either oxygen (60S20Fe_O₂) or argon (60S20Fe_Ar) atmosphere.

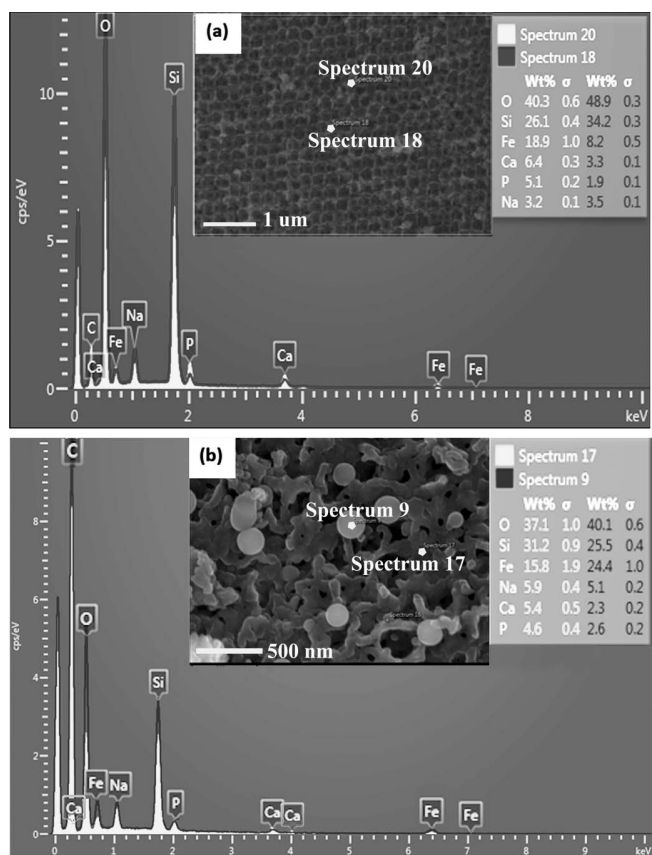


Fig. 6: EDX spectra of magnetic MMBG calcined in (a) oxygen (60S20Fe_O₂) and (b) argon (60S20Fe_Ar) atmosphere with FE-SEM images shown as insets.

IV. Conclusions

Magnetic MMBG were successfully synthesized by the one-pot sol-gel method and the diamagnetic-superparamagnetic-ferromagnetic transitions were demonstrated. The evolution from paramagnetic to superparamagnetic phase was demonstrated by increasing Fe(NO₃)₃·9H₂O from 5 to 20 mol%. Based on the changes in colors and

magnetic sensitivity, it was suggested that superparamagnetic maghemite nanoparticles were formed during calcination in oxygen when the MMBG was synthesized with higher amounts of Fe(NO₃)₃·9H₂O. No crystalline phase in these magnetic MMBG was confirmed by XRD but the Ca₇Si₂P₂O₁₆ phase was detected when Fe(NO₃)₃·9H₂O was replaced with FeCl₃ in the synthesis. The transition from superparamagnetic to ferromagnetic phase occurred when oxygen gas was replaced with argon in the calcination process. This ferromagnetic hysteresis was linked to the formation of large Fe-rich spheres beyond the single-domain regime.

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