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Synthetic magnetic opals

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Abstract. We present studies of novel nanocomposites of BiNi *impregnated* into the structure of opals as well as inverse opals. Atomic force microscopy and high resolution elemental analyses show a highly ordered structure and uniform distribution of the BiNi filler in the matrix. These BiNi-based nanocomposites are found to exhibit distinct ferromagnetic-like ordering with transition temperature of about 675 K. As far as we know there exists no report in literature on any BiNi compound which is magnetic.

Keywords. Nanocomposites; BiNi impregnated opals; atomic force microscopy; ferromagnetism.

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1. Introduction

Recently, ordered nanostructured materials have gained tremendous interest because of their unusual properties. In microelectronics, nanotechnology has already made a quick impact through their quantum characteristics. Synthetic opals are a new class of ordered templates [1] which have gained importance in recent years as photonic crystals for the visible and near-infrared region of the electromagnetic spectrum. The silica opals have modest photonic band-gap properties due to their material characteristics but the synthesis of a guest material within the inter-sphere cavity network of ordered arrays of opals can lead to extraordinary enhancement of these properties [2]. By dissolving the silica spheres it is possible to create ordered arrays of any chosen elements for basic studies and thus tailor many technologically interesting nanostructured electronic materials [3].

In the present work we show that BiNi infiltrated into the opals is ferromagnetic with a transition temperature around 675 K. As far as we know there is no report in literature on any BiNi compound which is magnetic. A systematic study of the structural and magnetic properties of BiNi impregnated both into the periodic opal as well as the replica structures is presented.

2. Experimental

Monodispersed silica sphere nanoparticles were synthesized as colloids by the TEOS (tetraethoxysilane) route. The average diameter could be controlled in the range 160–300 nm. The SiO_2 nanoparticles were then assembled into fcc lattices by sedimentation of the colloidal solution in glass cylinders over a period of 6–10 months [3]. Finally, in order to produce a mechanically robust opal structure, the solid precipitate was sintered first at 110–120° C for 2 days and then at 750° C for 4 h.

The prepared templates were infiltrated with BiNi alloy from the melt at an elevated temperature under pressure. The porous matrix was put in a stainless steel capsule; the capsule was tightly filled with BiNi powder and sealed. The infiltration procedure included heating the capsule to a temperature slightly above the melting point of the filler, subjecting it to a pressure of 1–2 kbar and then cooling it to room temperature under pressure. The isostatic compression of the melt under mild conditions excludes any possible distortions of the fragile matrices. However, we notice that the composition of the alloy tends to change as it penetrates the network of interconnected submicron channels in the matrices.

The surface topography of the samples was investigated in a Joel scanning electron microscope (SEM). Detailed dimensional analysis of silica spheres and the consequence of impregnation of BiNi on the opals were carried out by atomic force microscopy using the Digital Instruments Nanoscope III. Gold-coated Si_3N_4 cantilevers were utilized and all the images were obtained in a contact mode. The elemental analyses and the distribution of a specific element were carried out by mapping over the sample surface using energy dispersive spectroscopy (EDS) combined with the Jeol scanning electron microscope. A SQUID magnetometer was used to study the magnetic properties of these impregnated as well as pristine opals.

3. Results and discussion

3.1 *Physical characterization*

Figure 1a shows the scanning electron microscopic observation of pristine opals. As seen in the figure, the spheres settled into an fcc (face centered cubic) structure. The layer-by-layer dense packed planes are found to grow along the (111) direction. Energy dispersive spectroscopic analyses of these materials shows the presence of only Si and O. The atomic force microscope (AFM) images investigating the silica spheres in the opals are presented in figures 1b and 2a. The AFM line profile analysis shown in figures 2b–2c illustrates the typical diameter of the SiO_2 spheres to be 200 nm with a pore size of 100 nm.

In order to make the opals magnetic, nanoparticles of BiNi were impregnated into the pristine opal. Nickel when impregnated into the opals could also remain magnetic. However, we find that the observed magnetic transition temperature for the BiNi compound does not correspond to that of pure Ni. Also, we find the BiNi alloy to be nonmagnetic at concentrations greater than 70% Bi. These observations suggest that we are probably observing the manifestations of the magnetic properties of a BiNi compound rather than of pure nickel. A high pressure necessary for metal infiltration into the opal, is found to be dependent on the minimum radius of the interconnects between nearest voids in the opals. We find that the smaller the radius, the higher is the pressure which must be applied for

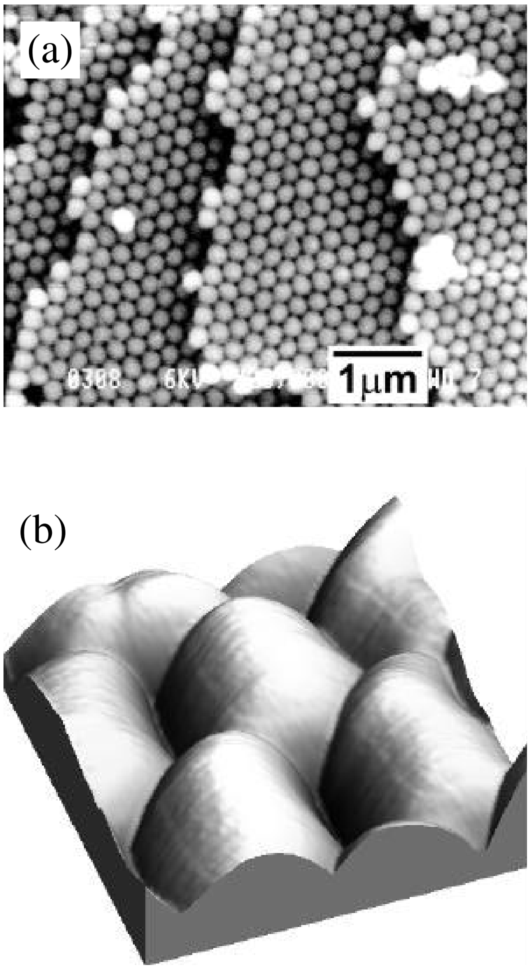

Figure 1. Arranged silica spheres in a synthetic opal observed by (**a**) scanning electron microscope and (**b**) atomic force microscope (420 nm $\times$ 420 nm scan).

infiltration [3]. So by controlling this radius, the material can be made to impregnate only into the opals rather than fill the voids between them. Local elemental analysis has been carried out on opals after impregnation by means of the EDS technique. Such an analyses indicates the presence of Bi and Ni (see figure 3). However, local elemental mapping shows that only partial impregnation of BiNi into the opal (see figure 4) has been achieved. The presence of bright spots observed in the elemental maps indicates the distribution of the particular element being detected as shown in figure 3. The observed distortion and local structural disorder from the spherical geometry of the silica spheres noticeable in the AFM images (see figure 5) is also a signature of partial impregnation. In the case of magnetic opals the sample was cut along (110) axis and hence, as is obvious from the AFM

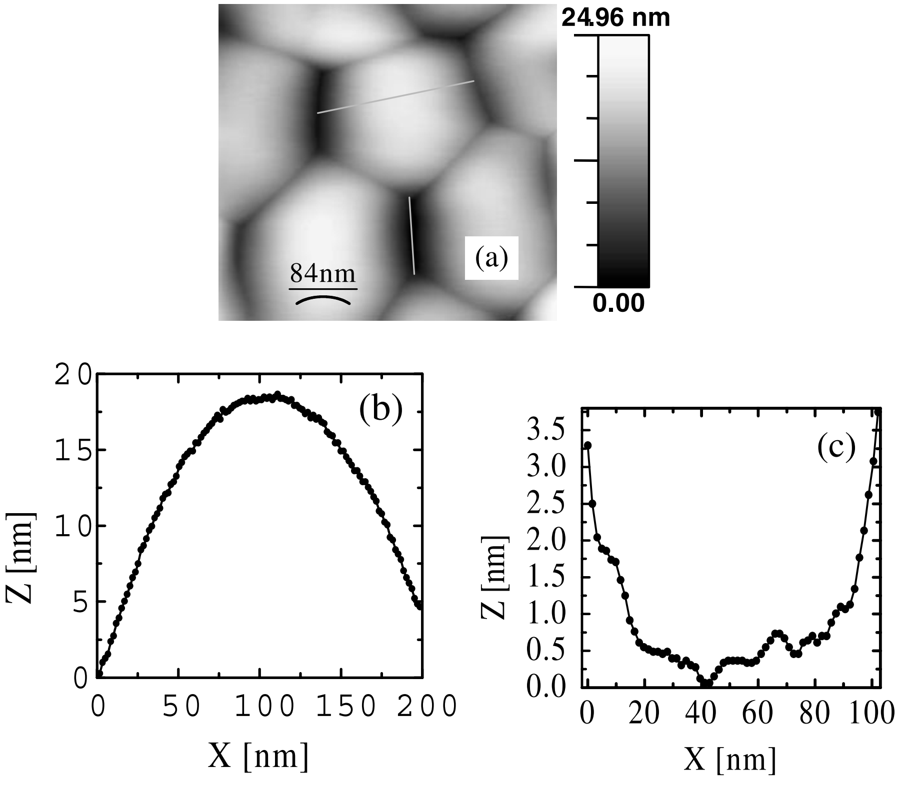

Figure 2. A 420 nm × 420 nm image of the opal obtained by AFM (**a**) topographic image; (**b**) line profile of an individual particle; (**c**) line profile of a pore between the SiO_2 spheres.

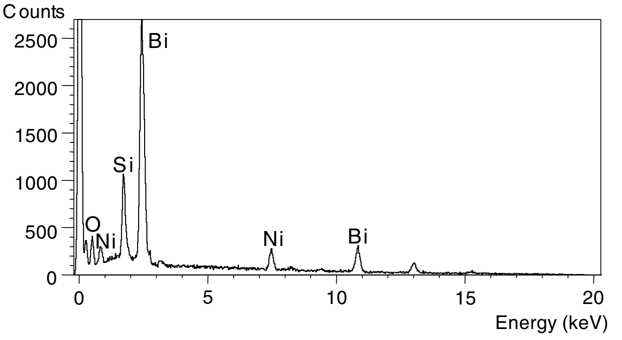

Figure 3. Elemental analysis of magnetic opal: EDS spectrum.

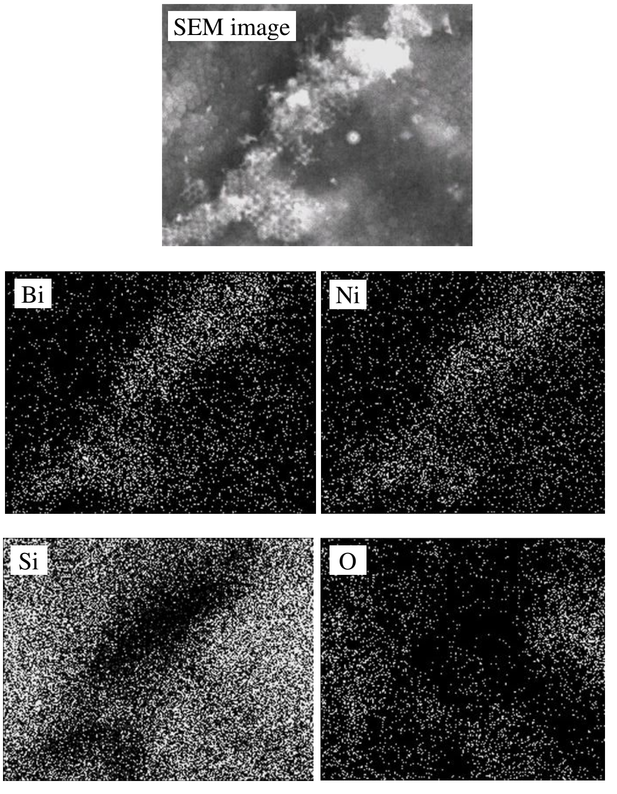

Figure 4. SEM and EDS local elemental mapping of the magnetic opal.

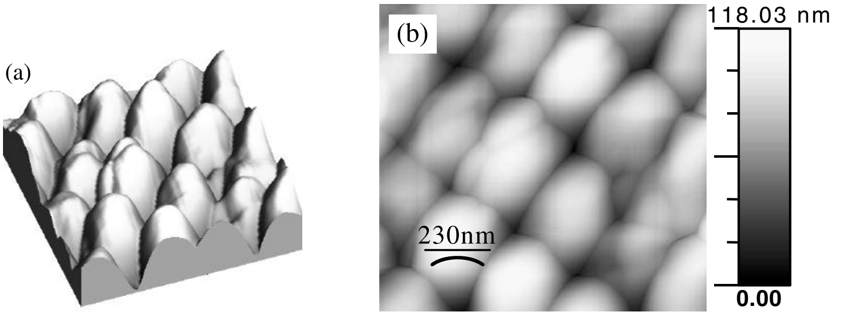

Figure 5. AFM topographic image of the magnetic opal impregnated with NiBi (1.25 μm $\times$ 1.25 μm area): (**a**) 3D view, (**b**) 2D top view.

data, the cell shapes are rectangular when compared to that of the pristine opals for which we observe hexagonal cells. It is also seen from the AFM images that the pristine opal and replica samples are cut along (111), whereas impregnated opal samples are cut along (110).

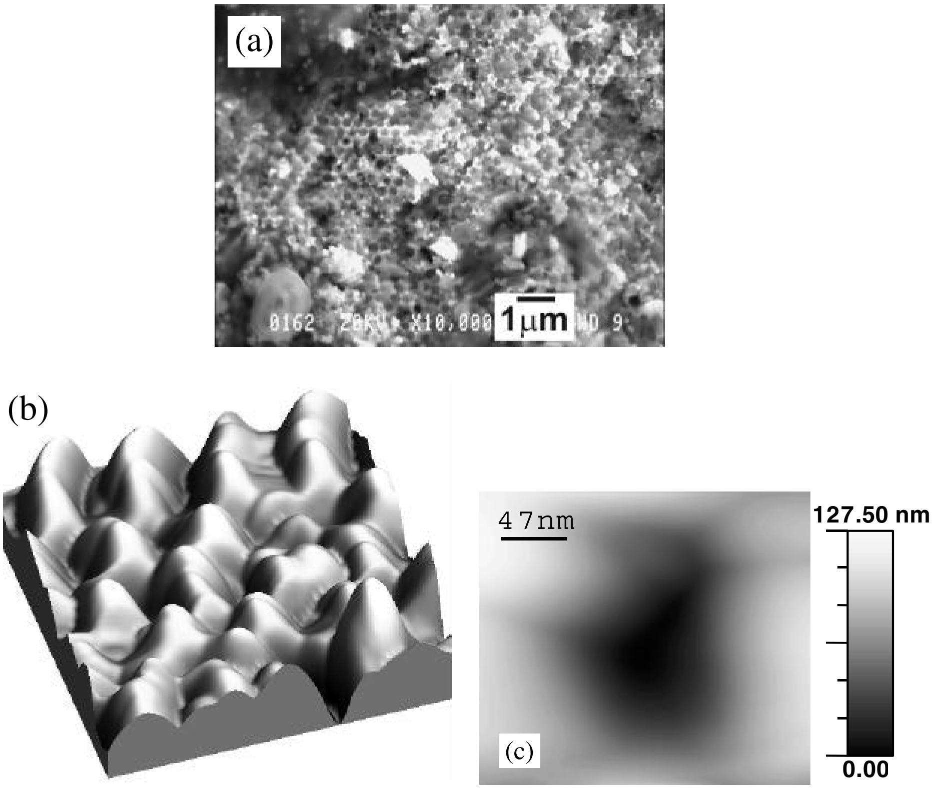

Figure 6. Opal replica: (**a**) SEM image, (**b**) AFM image 3D view (1.2 μm $\times$ 1.2 μm); (**c**) zoomed image of a vacant site formed after the removal of a silica sphere.

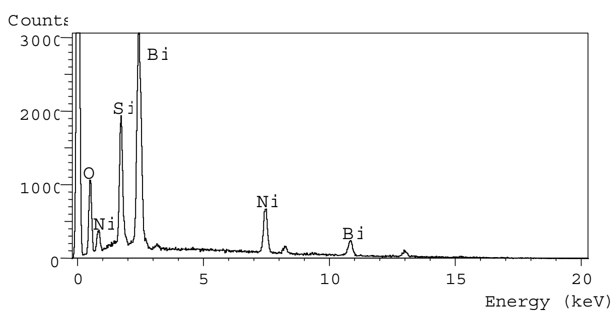

Figure 7. Elemental analysis of the opal replica: EDS spectrum.

The silica spheres in a virgin opal were dissolved in order to obtain an inverse opal structure, the so-called replica [4]. An opal replica was used to obtain a percolative network of BiNi nanoparticles by filling them in the octahedral and tetrahedral voids of fcc structured opal, after dissolving the silica spheres. Figure 6 shows the SEM and AFM images of the replica structure at various length scales. The AFM imaging data shows that typical diameter of a vacant site after removal was 230 nm, which is of the same order of magnitude as the diameter of a silica sphere.

The elemental distribution density observed for Ni (see figure 7) is found to be much smaller in the magnetic opals than is the case of the replica, which indicates that only a partial impregnation of opals with BiNi has been achieved in both these samples.

3.2 *Magnetic characterization*

Magnetic properties of the pristine opal, the replica, and the impregnated opal were studied using a SQUID magnetometer MPMS2 by quantum design. As expected, for the pristine opals, a negative susceptibility of 0.2 emu g^{-1} Oe^{-1} is observed at room temperature (figure 8b), indicating a diamagnetic property. In contrast, for the impregnated opals and the replica we observe the magnetic characteristics of an ordered state with a typical hysteresis and an approach to saturation behavior over the temperature range 5 K to 300 K. Further-

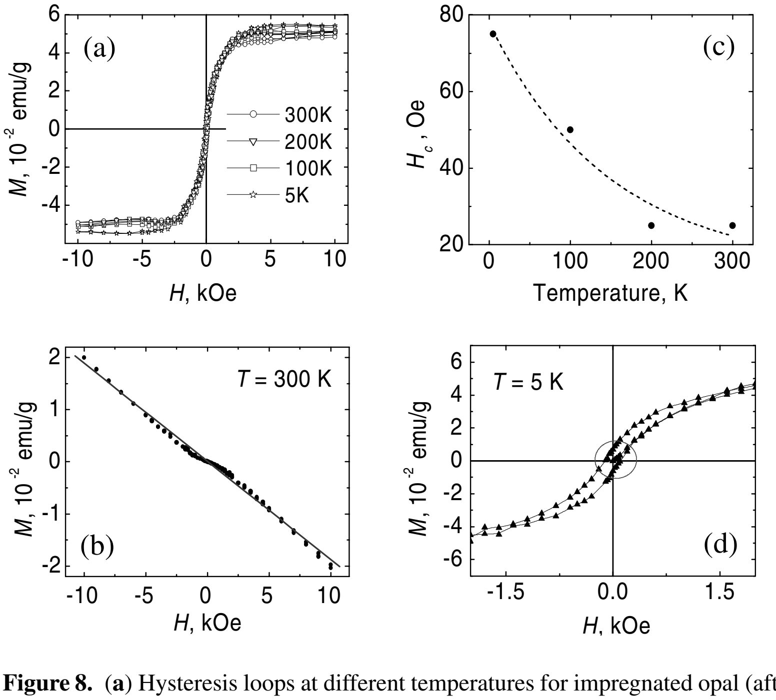

Figure 8. (**a**) Hysteresis loops at different temperatures for impregnated opal (after accounting for the diamagnetic background from the opal matrix); (**b**) room temperature hysteresis loop for the diamagnetic opal matrix; (**c**) temperature dependence of coercivity for impregnated opal; (**d**) enlarged hysteresis loop at 5 K for impregnated opal.

more, the temperature dependence of the magnetization, figure 8a, for impregnated opal over the range 50–300 K is found to fit into a $T^{3/2}$ functional form as expected for Bloch waves in a typical ferromagnetically ordered material (see figure 9). From a thermogravimetric study in a low external magnetic field we find the magnetic transition temperature to be around 675 K, which is much higher than that known for pure Ni. We are not aware of any suitable BiNi compound with the above magnetic properties. Therefore, we may assume that perhaps the observed magnetic properties arise from finely distributed Ni particles alone in the matrix. Under such an assumption, table 1 shows the estimated percentage of nickel in the impregnated opal, as well as the replica respectively. These estimates have been obtained by comparing the observed saturation magnetization with that known [5] for pure nickel, 57.50 emu/gm. The values of Ni concentration of 0.092% obtained from the room temperature data for the impregnated opal, as compared to 6.43% for the replica again suggests that only a partial impregnation of BiNi has been achieved both in the opals and the replica. At this time we have no explanation as to why more Ni can be impregnated into the replica than in the opals; perhaps it is because of the open replica structure. More detailed understanding of the appropriate BiNi compound and its magnetic properties are needed before carrying out any further quantitative analyses of the magnetic properties of BiNi and their properties when infiltrated into the opals and the replica.

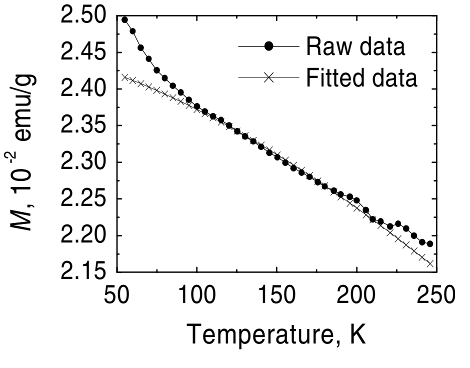

Figure 9. Temperature dependence of magnetization for impregnated opal in field $H = 2$ kOe. Both raw and fitted data are shown. The extrapolated marked line shows an $M(T)$ data fit to the Bloch function: $M(T) = M_0(1 - H \times T^{3/2})$.

Table 1. Comparison of measured properties for opals.

	Saturation magnetization at 5 K (emu/g)	Saturation magnetization at 300 K (emu/g)	% of Ni at 5 K	% of Ni at 300 K
Opal virgin	–	–	–	–
Opal impregnated	0.059	0.050	0.102	0.092
Opal replica	3.81	3.52	6.63	6.43

4. Conclusion

We have successfully achieved impregnation of magnetic nanoparticles of BiNi into opals as well as their replica as confirmed by AFM, SEM, EDS and XRD studies. Elemental analyses of the replica indicate Ni content up to 20.35% while in contrast the opal structure is found to contain only 1.32% of Ni content in the sample. Diamagnetic pristine virgin opal as well as the replica are found to become ferromagnetic-like after impregnation with BiNi.

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