Relieving geometrical frustration through doping in the Dy$_{1-x}$Ca$_x$BaCo$_4$O$_7$ swedenborgites

Soumendra Nath Panja$^1$, Jitender Kumar$^1$, Shanu Dengre$^1$ and Sunil Nair$^{1,2}$

$^1$ Department of Physics, Indian Institute of Science Education and Research, Dr. Homi Bhabha Road, Pune, Maharashtra-411008, India
$^2$ Centre for Energy Science, Indian Institute of Science Education and Research, Dr. Homi Bhabha Road, Pune, Maharashtra-411008, India

E-mail: sunil@iiserpune.ac.in

Received 13 July 2016, revised 10 August 2016
Accepted for publication 26 August 2016
Published 26 September 2016

Abstract
The geometrically frustrated antiferromagnet DyBaCo$_4$O$_7$ is investigated through a combination of x-ray diffraction, magnetization and dielectric measurements. Systematic doping in the series Dy$_{1-x}$Ca$_x$BaCo$_4$O$_7$ causes a lifting of the geometrical frustration resulting in a structural transition from a trigonal $P31c$ to an orthorhombic $Pbn2_1$ symmetry at $x = 0.4$. This structural transition can also be accessed as a function of temperature, and all our orthorhombic specimens exhibit this transition at elevated temperatures. The temperature at which this structural transition occurs is observed to scale linearly with the mean ionic radius of the $R$ site ion. However, CaBaCo$_4$O$_7$ which has an equal number of Co$^{2+}$ and Co$^{3+}$ ions clearly violates this quasilinear relationship, indicating that charge ordering could also play a critical role in stabilizing the orthorhombic distortion in this system. Using thermoremanent magnetization measurements to circumvent the problem of the large paramagnetic background arising from Dy$^{3+}$ ions, we chart out the phase diagram of the Dy$_{1-x}$Ca$_x$BaCo$_4$O$_7$ series.

Keywords: geometrically frustrated magnets, multiferroics, phase transitions

(Some figures may appear in colour only in the online journal)

1. Introduction
Magnetic ions in geometrically frustrated lattices are of great experimental and theoretical interest, and materials in which this is realized exhibit a rich diversity in their magnetic ground states [1, 2]. In strongly correlated oxides, this frustration is typically a consequence of specific structural motifs, with edge sharing tetrahedra, triangular lattices, and kagome lattices or their variants being popular candidates. The inherent competition between the propensity of the system to order magnetically and the magnetic frustration manifests itself in complex magnetic and structural phase transitions as a function of temperature or other control parameters. This is widespread in the transition metal oxides, and a number of material classes like the pyrochlores [3], spinels [4, 5], jarosites [6], and the double perovskites [7] are reported to exhibit such phase transitions.

A valuable addition in this class of geometrically frustrated magnets has been the swedenborgites of the form $R$Ba$_2$M$_4$O$_7$, where $R = Y$, a trivalent rare earth, or Ca, and $M = $ Co or Fe [8–12]. Structurally related to the spinels, the swedenborgites are characterized by the fact that the magnetic ion is solely tetrahedrally co-ordinated, thus differentiating them from most oxide families—where magnetic ions are either octahedrally co-ordinated or exhibit a combination of octahedrally and tetrahedrally coordinated environments. The structure can be broadly described as a stack of triangular and kagome sublattices alternating along the crystallographic $c$ axis, with subtle variations within the sublattices being dictated by the nature of the $R$ site ion [13]. A defining feature of the cobalt based
swedenborgites is the observation of a temperature driven phase transition from a high-symmetry Hexagonal (P6\textit{3}mc) or trigonal (P3\textit{1}c) phase to a low-symmetry orthorhombic (typically Pbn\textit{2}1 or Cmc\textit{2}1) phase with decreasing temperature [14]. This structural phase transition relieves the geometrical frustration dictated by the lattice, and magnetic order is then stabilized within the low-symmetry phase. Among the $R^{3+}$BaCo$_4$O$_7$ systems which have been reported, it has been suggested that the temperature at which this structural phase transition occurs scales linearly with the ionic radii of the trivalent $R$ site ion [10, 11].

The magnetism is critically influenced by both the ionic radius of the $R$ site ion, and its valency. For instance, most members of the $R^{3+}$BaCo$_4$O$_7$ series exhibit low temperature antiferromagnetic order [10, 12], whereas for $R = Y^{3+}$, the stabilization of a glassy state along with short range magnetic correlations in both the triangular and kagome sublattices have been suggested [15]. The only cobalt based swedenborgite with a divalent $R$ site ion is CaBaCo$_4$O$_7$, where the lifting of the geometric frustration by the stabilization of an orthorhombic distortion is reported to drive it to a ferromagnetic pyroelectric state with a significant magnetoelastic coupling [16, 17]. It remains to be investigated whether this system with equal Co$^{2+}$ and Co$^{3+}$ ions also undergo a temperature driven transition to a high-symmetry structure, like the $R^{3+}$BaCo$_4$O$_7$ systems where the Co$^{2+}$:Co$^{3+}$ ratio is 3 : 1. The magnetism and structure of these materials is also reported to be strongly influenced by doping in the $R$ site, and heterovalent substitution in the Ca site of CaBaCo$_4$O$_7$ is reported to weaken the orthorhombic distortion, and also give rise to an admixture of a cluster/spin glass phase along with a weak ferromagnetic contribution [18].

Here, we report on the structure and magnetism of the hitherto unexplored DyBaCo$_4$O$_7$ system, and also the series Dy$_{1-x}$Ca$_x$BaCo$_4$O$_7$, where the ratio of Co$^{2+}$:Co$^{3+}$ smoothly varies from 3 to 1. Using a combination of temperature dependent x-ray diffraction and magnetization measurements, we investigate the evolution of the crystallographic structure, as well as the magnetic transitions, both as a function of temperature and of doping. We establish that DyBaCo$_4$O$_7$ stabilizes in a high-symmetry phase at room temperature. Using thermoremanent magnetization measurements to circumvent the problem of the large Dy$^{3+}$ paramagnetic background, we also trace the phase diagram of the Dy$_{1-x}$Ca$_x$BaCo$_4$O$_7$ solid solution.

2. Experiment

Polycrystalline specimens of the series Dy$_{1-x}$Ca$_x$BaCo$_4$O$_7$ ($x = 0$ to 1) were synthesized by the standard solid state reaction technique. Stoichiometric amounts of high purity Dy$_2$O$_3$, CaCO$_3$, BaCO$_3$, and CoO$_2$ were thoroughly ground using a mortar and pestle to get homogeneous mixtures, which were then fired in air at 900 °C for 24h, followed by a treatment at 1000 °C for 48h. These powders were then cold pressed and heat treated in air for 12h at temperatures varying from 1100 °C to 1050 °C. Slow cooling was observed to introduce traces of a brownmillerite phase, and hence all samples were
furnace quenched to room temperatures. The temperature dependent x-ray powder diffraction patterns were measured using a Bruker D8 Advance diffractometer with Cu K$_\alpha$ source under the continuous scanning mode. Structural details were analyzed by the Rietveld method using the Fullproof refinement program [19]. Elemental compositions were confirmed by using an energy dispersive x-ray spectrometer (Ziess Ultra Plus). Magnetization measurements were performed using a quantum design (MPMS-XL) SQUID magnetometer. Temperature dependent dielectric measurements were performed in the standard parallel plate geometry, using a NOVOCONTROL (Alpha-A) high performance frequency analyzer. Measurements were done using an excitation ac signal of 1 V at frequencies varying from 1 kHz to 6.5 MHz.

3. Result and discussions

3.1. Structural investigations

Room temperature x-ray diffraction patterns for the solid solution Dy$_{1-x}$Ca$_x$BaCo$_4$O$_7$ are shown in figure 1(a).

All the specimens were seen to be single phase, with no traces of either the starting materials, or other spurious phases. Rietveld refinement could be performed for all these patterns, with the typical goodness of fit ($R_{wp}/R_e$) being $<0.16$. Representative fits for the two end members DyBaCo$_4$O$_7$ (DBCO), and CaBaCo$_4$O$_7$ (CBCO) are shown in figures 1(b) and (c) respectively. Prior experimental reports have suggested that DBCO crystallizes in the high-symmetry $P6_3mc$ phase, whereas the other members of the $R$BaCo$_4$O$_7$ series (with $R =$ Ho, Er, Tm, Yb and Lu) prefer the closely related $P3_1c$ phase [20]. However, our analysis indicates that the DyBaCo$_4$O$_7$ system also crystallizes in the trigonal $P3_1c$ phase. CBCO on the other hand crystallizes in the $Pbn2_1$ space group (table 1), as has been reported in literature [21]. Since the ambient temperature structure of CBCO is orthorhombically distorted, one would expect to see a $P3_1c \rightarrow Pbn2_1$ transition as one traverses across the Dy$_{1-x}$Ca$_x$BaCo$_4$O$_7$ series. Our diffraction patterns indicate that this transition happens at $x > 0.4$, as is shown in figure 1(d), where the evolution of additional Bragg peaks corresponding to the (132), (202), (041) and (221) planes of the orthorhombic phase can be clearly seen. The differences in these structures are clearly depicted in figure 2, where a view along the crystallographic $c$ axis is shown for both the end members of this series. DBCO has two inequivalent sites for the magnetic Co ion, with one of them forming the kagome sublattice, and the other constituting the intervening triangular layers. The ratio of the tetrahedra in

![Figure 2](image1.png)

Figure 2. The crystal structure of the trigonal DyBaCo$_4$O$_7$ (left) and the orthorhombic CaBaCo$_4$O$_7$ (right) as viewed along the crystallographic $c$ axis. The orthorhombic distortion affects the arrangement of tetrahedra in the kagome layer, thus relieving the geometrical frustration.

![Figure 3](image2.png)

Figure 3. The variation of the lattice parameters $a$–$c$, across the Dy$_{1-x}$Ca$_x$BaCo$_4$O$_7$ series. For all the orthorhombically distorted members of the series, the lattice parameter $b$ is replaced by the reduced lattice parameter $b/\sqrt{3}$. The shaded region corresponds to the specimens crystallizing in the high-symmetry $P3_1c$ space group. The right axis of the lower panel exhibits the variation of the orthorhombic distortion ($D = (b/\sqrt{3} - a/a)$ for all the specimens crystallizing in the $Pbn2_1$ space group. 

J. Phys.: Condens. Matter 28 (2016) 486001
the kagome and the triangular layers is 3 : 1, and it has been suggested that Co$^{2+}$ occupies the kagome sublattice, with the Co$^{3+}$ making up the triangular lattice. In the orthorhombically distorted CBCO on the other hand, Co has four inequivalent crystallographic positions, with the kagome layer now being made up of three corrugated tetrahedra. This relieves the geometrical frustration, and is also thought to be responsible for the stabilization of a ferrimagnetic ground state.

Figure 3 summarizes the evolution of structural parameters across the Dy$_{1-x}$Ca$_x$BaCo$_4$O$_7$ series. The lattice parameters are seen to vary systematically across the series with the possible exception of the $x = 0.1$ specimen. The lower panel of figure 3 depicts the evolution of the $c/a$ ratio as a function of doping, where the crossover from P31c to Pbn2$_1$ symmetry is seen in the form of a discontinuity at a critical value of the doping of $x = 0.4$. Within an orthorhombic structure, the extent of distortion can be quantified using the parameter $D = (b/\sqrt{3} - a)/a$, which corresponds to an expansion along the [1 1 0]$_H$ direction and a contraction along the [1 1 0]$_H$ direction within the hexagonal symmetry. This is also depicted in the lower panel of figure 3 for all the orthorhombic members of the Dy$_{1-x}$Ca$_x$BaCo$_4$O$_7$ series. Not surprisingly, this distortion is the largest for the end member CBCO, and we obtain $D = 1.14\%$, which is similar to the previously reported value of 1.05% [21]. This distortion decreases monotonically with increasing Dy content, and falls to a value of $D = 0.47\%$ for the Dy$_{0.5}$Ca$_{0.5}$BaCo$_4$O$_7$ system. This is comparable to that observed in other members of the $R^{3+}$Ba$_{M}$O$_{47}$ family. For instance, the values of $D$ in the Yb [22], Tm [23] and Ho [24] systems have been calculated to be 0.67%, 0.53% and 0.44% respectively at different temperatures.

A temperature-driven change in the geometry of the BaO$_{12}$ polyhedra has been suggested to be a critical component (and possibly even the driving force) of a temperature-driven...
P31c → Pbn21 transition in some of the $R^3^+\text{BaCo}_4\text{O}_7$ systems [22]. This was inferred from the fact that $\text{Ba}^{2+}$, which occupies an anticubooctahedral site, appears to be underbonded, with structural refinement models indicating a number of bonds with unphysical bond lengths. This manifests itself in the distortion of the anticubooctahedron, resulting in an equal number of small (and large) $\text{Ba}–\text{O}$ bond lengths, such that the average $\text{Ba}–\text{O}$ bond length is invariant. An earlier report on the closely related $\text{YbBaCo}_4\text{O}_7$ has indicated that the $P31c$ symmetry is associated with three long and three short bonds, with the other six bonds being close to 3.14 Å. The structural transition from a $P31c$ to a $Pbn21$ symmetry as a function of temperature is associated with a change in this ratio from 3 : 3 : 6 to 6 : 6 : 0, with the low-symmetry structure being characterized by an equal number of large and short bonds [22]. Our analysis of room temperature diffraction data shows that the scenario is similar in the $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ series, where this structural transition is observed as a function of doping. Though the average $\text{Ba}–\text{O}$ bondlength of 3.14 ± 0.02 Å is invariant across the whole series, the specimens which crystallize in the high-symmetry phase at room temperature ($x = 0$, to $x = 0.4$) have six bond lengths with an average value of 3.15 ± 0.02 Å, and three long and short bonds each, with average lengths of 3.45 ± 0.02 Å and 2.85 ± 0.02 Å respectively. For samples with $x > 0.4$ which crystallize in the

**Figure 5.** The variation of the high-symmetry to low-symmetry structural transition temperature as a function of mean $R$ site ionic radius for all cobalt based swedenborgites reported to date. The mean ionic radii for members of the $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ series have been calculated using the formula $r_R = (1 - x)r_{\text{Dy}} + xr_{\text{Ca}}$. As is evident, a quasilinear relationship between this transition temperature and $r_R$ is seen for all members of this family, except $\text{CaBaCo}_4\text{O}_7$.

**Figure 6.** (a) Exhibits the magnetization of the $\text{DyBaCo}_4\text{O}_7$ system measured using the zero field cooled (ZFC) and field cooled (FC) protocols at a field of 100 Oe. The inset shows the ac susceptibility measurement of the same system at varying frequencies. (b) depicts the ZFC curves of all members of the $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ series as measured at 100 Oe. (c) shows the temperature dependence of the thermoremanent magnetization ($\text{M}_{\text{TRM}}$) as measured for all members of the $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ series. All the measurements are normalized with $\text{M}_{\text{TRM}}(300\text{ K})$ for the sake of clarity. The onset of the magnetic transitions is clearly evidenced by a sharp upturn in $\text{M}_{\text{TRM}}(T)$. 
low-symmetry $Pbn_2$ space group, the $BaO_{12}$ polyhedra is characterized by six long and short bonds each, with average lengths of $3.50 \pm 0.02 \, \text{Å}$ and $2.78 \pm 0.02 \, \text{Å}$ respectively. Thus, the underbonding of $Ba^{2+}$, which possibly drives this structural transition, is clearly endemic to all members of the swedenborgite family. A temperature-driven transition from the low-symmetry $Pbn_2$ to a high-symmetry $P31c$ or $P6_3mc$ phase would be expected in all our orthorhombically distorted specimens. Interestingly, in spite of a large number of experimental reports on $CaBaCo_4O_7$, the presence of such a phase transition remains to be verified. We have performed high temperature diffraction measurements on CBCO to explore this phase transition temperature, and observe a $Pbn_2 \rightarrow P31c$ transition in this system with the largest orthorhombic distortion. This is shown in figure 4(a), where a narrow region between $33.8^\circ$ and $34.5^\circ$ is expanded for the sake of clarity, depicting the transformation from the orthorhombic $Pbn_2$ to a trigonal $P31c$ symmetry. A similar structural transition is also present in all our doped orthorhombic specimens, and figure 4(b) depicts the structural transition in the $Dy_0.4Ca_0.6BaCo_4O_7$ sample. It has previously been suggested that the temperature of this structural transition scales linearly with the ionic radius of the $R$ site ion [10, 11]. We evaluate this relationship using the data at our disposal, as is shown in figure 5, where the transition temperature is plotted as a function of the mean ionic radius of the $R$ site ion. Our high temperature diffraction data for selected doped members of the $Dy_{1-x}Ca_xBaCo_4O_7$ family indicate that this quasi-linear relationship is satisfied for samples with different ionic radii as well as with varying $Co^{2+}$:$Co^{3+}$ ratios. However, the behavior of the end member $CaBaCo_4O_7$ is clearly anomalous, with the structural transition temperature being far in excess of that expected solely on the basis of its $R$ site ionic radius. For instance, though the difference in the mean ionic radii between $CaBaCo_4O_7$ and $Dy_0.1Ca_0.9BaCo_4O_7$ is only $0.88\%$, the structural transition temperature in the former is larger by a factor of $1.48$. It has been recognized that CBCO exhibits charge ordering, with the $Co^{2+}$ and $Co^{3+}$ ions exclusively occupying the kagome and triangular layers respectively [21]. Considering the fact that tetrahedral coordination of $Co^{3+}$ is rare, the possibility of a metal to ligand charge transfer analogous to that observed in layered cuprates has also been suggested [25]. Our data indicates that these factors could also play a crucial role in stabilizing the large structural distortion observed in this system, thus necessitating temperatures of the order of $1073 \, \text{K}$ to stabilize the high-symmetry $P31c$ phase.

3.2. Magnetic and dielectric investigations

Preferential occupation of the kagome and triangular layers by $Co^{2+}$ and $Co^{3+}$ ions, coupled with a large structural distortion, is thought to be responsible for the ferrimagnetic ground state in CBCO, and the magnetic structure is reported to comprise ferromagnetic zig-zag chains of $Co^{2+}$ coupled anti-ferromagnetically with the $Co^{3+}$ sublattice [21]. However, the magnetic behavior of the DBCO remains to be reported to date. Our magnetic measurements reveal that DBCO exhibits a magnetic transition at $76 \, \text{K}$, which appears to be antiferromagnetic in nature, as is shown in figure 6(a). This is in broad agreement with the earlier reports on related $R^{3+}Ba_{3}O_{7}$ systems. Measurements of the ac susceptibility show that this peak in the magnetic susceptibility is frequency independent (inset of figure 6(a)), thus ruling out the possibility of a glassy phase. As is clearly evident from the data, magnetic measurements are plagued by the presence of the large $Dy^{3+}$ paramagnetic moment, and no order is seen within the $Dy^{3+}$ sublattice down to the lowest measured temperatures. Due to this large paramagnetic background, the transition within the $Co$ sublattice is barely discernible. This problem is accentuated in the other members of the $Dy_{1-x}Ca_xBaCo_4O_7$ series as is shown in figure 6(b), and conventional Zero Field cooled measurements are unable to pick up the onset of magnetic ordering in these specimens owing to the large $Dy^{3+}$ paramagnetic moment. To circumvent this problem, we have employed the relatively underutilized technique of thermo-remanent magnetisation (TRM) in an attempt to identity the magnetic ordering temperatures in the $Dy_{1-x}Ca_xBaCo_4O_7$ series. Used extensively in the investigation of spin glasses [26], the protocol used in our TRM measurements is as follows: (i) A dc field ($H_{ap}$) is applied at room temperature, and the system is cooled to a temperature $(5 \, \text{K})$ below the transition temperature (ii) The field is reduced to zero, and the remnant magnetization $M_{TRM}(T)$ is measured on warming at a constant rate. As has been demonstrated in the case of spin glasses, $M_{TRM}(T)$ is seen to be zero in the paramagnetic region, and the magnetic transition temperature is clearly identified in the form of an upturn in the magnetization [27]. This measurement protocol has also found limited utility in the investigation of antiferromagnets, where it has been used to infer on the domain dynamics of diluted magnets [28] and on more exotic phenomena like piezomagnetism [29]. Temperature dependent $M_{TRM}$ measurements performed after a field cool of $100 \, \text{Oe}$ are shown in figure 6(c).
As is evident, TRM measurements are relatively insensitive to the Dy$^{3+}$ paramagnetic background, and allow us to clearly identify magnetic transitions in all the members of the Dy$_{1-\delta}$Ca$_{\delta}$BaCo$_4$O$_7$ series. Our $M_{\text{TRM}}(T)$ measurements indicate that the antiferromagnetic $T_N$ varies smoothly among the intermediate compositions. Interestingly, the only exception to this rule is the ferrimagnetic CaBaCo$_4$O$_7$, where long range order sets in at a temperature ($T_C$) lower than that observed for the $x = 0.9$ member of the Dy$_{1-\delta}$Ca$_{\delta}$BaCo$_4$O$_7$ series. We wish to emphasize that in systems with multiple magnetic sublattices, identifying the onset of magnetic order in one of the sublattices can be non-trivial. Our observations show that in such cases, TRM measurements can be far more effective than conventional FC or ZFC measurement protocols in the identification of magnetic transitions.

The magnetic transition in CBCO is also known to be characterized by a sharp peak in the real part of the dielectric permittivity ($\varepsilon'$), indicating a large coupling of the spin and charge degrees of freedom. The main panel of figure 7 shows the temperature dependence of ($\varepsilon'$) as measured for all the orthorhombic members of the Dy$_{1-\delta}$Ca$_{\delta}$BaCo$_4$O$_7$ series. Interestingly, with Dy doping, this feature in the dielectric permittivity is seen to weaken considerably, and the onset of the magnetic transition in the orthorhombic transition is barely discernible. This is in spite of the fact that the magnitude of $\varepsilon'$ does not change appreciably with doping, and reaffirms the fact that the charge ordered CBCO with its large magnetoelastic coupling behaves differently from the doped members of the Dy$_{1-\delta}$Ca$_{\delta}$BaCo$_4$O$_7$ series. In contrast to CaBaCo$_4$O$_7$, the DyBaCo$_4$O$_7$ does not exhibit any signatures of long or short range electrical ordering at the magnetic ordering temperature as is shown in the inset of figure 7. Interestingly, the dielectric permittivity of DyBaCo$_4$O$_7$ exhibits a high dielectric constant of the order of several thousand near room temperature. A frequency-dispersive sharp drop (typically below 200K) and an almost T and $\omega$ insensitive plateau in the higher temperature regime observed in DyBaCo$_4$O$_7$ resembles the behavior of colossal dielectric constant (CDC) materials [30, 31]. The origin of the CDC may be due to electrical heterogeneous states originating from the semi-conducting grains and insulating grain boundaries as is known to happen in many strongly correlated oxide materials [32, 33]. The results of our structural, magnetic and dielectric measurements are summarized in figure 8, which shows the phase diagram of the Dy$_{1-\delta}$Ca$_{\delta}$BaCo$_4$O$_7$ series.

4. Conclusions

In summary, we have charted out the phase diagram of swedenborgites of the form Dy$_{1-\delta}$Ca$_{\delta}$BaCo$_4$O$_7$ system using x-ray diffraction, magnetization, and dielectric measurements. The DyBaCo$_4$O$_7$ system is seen to crystallize in the trigonal P31c phase, and on traversing the Dy$_{1-\delta}$Ca$_{\delta}$BaCo$_4$O$_7$ series, a structural transition from the high-symmetry trigonal $P31c \rightarrow$ low-symmetry $Pbn2_1$ phase is observed at $x = 0.4$. All the orthorhombic members of this series undergo a transition to the high-symmetry $P31c$ phase at elevated temperatures. The temperature at which this transition occurs is seen to scale linearly with the mean ionic radius of the R site ion. The orthorhombically distorted CaBaCo$_4$O$_7$, which has an equal number of Co$^{3+}$ and Co$^{2+}$ ions, clearly violates this rule, indicating that the charge ordering scenario also possibly plays a role in stabilizing the structural distortion in this compound. The large paramagnetic background of Dy$^{3+}$ masks the magnetic transitions occurring within the Co sublattice, and we demonstrate the utility of temperature dependent thermo-remanent magnetization measurements in identifying the phase transition temperatures in such systems.

Acknowledgments

The authors acknowledge Nilesh Dumbre for technical assistance in high temperature x-ray measurements. SN acknowledges DST India for support through grant no. SB/S2/CMP-048/2013.

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