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Ba_{0.9}Ca_{0.1}TiO₃: microwave-assisted hydrothermal synthesis and piezoelectric properties

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ABSTRACT

This communication reports the microwave-assisted hydrothermal synthesis of the $x = 0.1$ member of the solid solution Ba_{1-x}Ca_xTiO₃ (BCT) materials, its structural and microstructural characterisation and the piezoelectric properties. Using this novel – ‘fast chemistry’ – synthetic procedure, this material can be obtained in much shorter periods of time in comparison with conventional solid-state methodologies: just a few minutes instead of days. Under microwave irradiation in aqueous basic solutions, the material produced is a polycrystalline and nanosized powder which was processed as a ceramic disc in order to measure piezoelectric properties. A maximum d_{33} value of 118 pC/N is obtained for this sample with a poling electric field of 1.5 KV mm⁻¹, a value similar to those reported for conventionally made BCT materials.

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Introduction

Among all ferro-piezoelectric ceramic materials, the so-called PZT (PbTi_{1-x}Zr_xO₃), featuring the perovskite structure, is the most widely studied and used because of its outstanding properties. Nevertheless, due to the toxicity of lead and, on the grounds of environmental concerns, many countries have legislated against using it and this has promoted intense research in ‘lead-free piezoelectrics’ looking for alternative, environment-friendly materials, most of them oxides [1]. A classic ferro-piezoelectric oxide material is barium titanate (BaTiO₃), also known as BT and, if calcium partially replaces barium, the perovskite structure is maintained, the formula becomes Ba_{1-x}Ca_xTiO₃ ($0 < x < 0.2$) and it is shortly referred as BCT. This solid solution has been known since 1955 when it was prepared at very high temperatures by the ceramic method [2]. As it is well known, BT shows a very interesting polymorphism with different phase transitions, rhombohedral-, orthorhombic- tetragonal-cubic at moderate-low temperatures, the cubic polymorph being formed at 120°C. Partially introducing calcium in the structure stabilises the tetragonal, non-centrosymmetric structure at lower temperatures, and BCT becomes piezoelectric at room temperature. The synthesis of BCT has been reported by several methods [2–4] and, in spite of the fact that the microwave-assisted hydrothermal synthesis of BT has already been reported [5–10], as far as we know, a similar methodology has never been used for the synthesis of BCT and this is the main goal of our work. It is worth recalling that different synthesis methods using microwaves as the source of heat

have attracted much attention due to the much shorter times needed (thus, a ‘fast chemistry’ procedure), and, due to the consequent energy saving and if the synthesis is performed in hydrothermal conditions in the absence of organic solvents, the method can be tagged as ‘eco-friendly’ or a ‘green-chemistry’. The thermal and non-thermal effects of microwaves on the synthesis are still under discussion, but it is well established that they promote dipole rotation (water molecules) which produces heat, and ion conduction which increases diffusion [11, 12] allowing much faster synthesis than in conventional hydrothermal/solvothermal methods. Besides the short time of synthesis, another advantages of this methodology are the low temperature if compared with the ceramic procedure (below 250°C since Teflon containers are used), the beneficial effects of autogenous pressure (the autoclaves are sealed) and also the fact that most of the times, the materials obtained are nanometre-sized powders which can be conveniently processed to form high-quality, well-sintered ceramics. Therefore, all these referred advantages have contributed to the popularisation of microwave-assisted synthesis. In this context, we have shown that many perovskite materials can be prepared using microwaves as the source of heat (either working in the solid state or using hydrothermal conditions) [13] and one of the aims of this work is to show, for the first time, how this solid solution can be readily prepared using microwaves as the source of heat in hydrothermal conditions together with a preliminary structural and electrical characterisation of the $x = 0.1$ material.

Experimental

Synthesis

For an experiment planned to yield 3 g of BCT, the stoichiometric amounts of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ba}(\text{NO}_3)_2$ (ARG purity) were dissolved in the minimum amount of water and, separately, 50 mL of 12 M NaOH solution was prepared to which the stoichiometric amount of titanium isopropoxide was mixed dropwise, forming a white titanium dioxide gel. The nitrate solution and the gel were mixed and the mixture was stirred and gently heated for 1 h. For the microwave synthesis, a commercial Milestone ETHOS 1 apparatus, operating at 2.45 GHz and equipped with a stirring motor, was used. This equipment allows fully automated operation of the most important reaction parameters (pressure, power-temperature and time) [7]. The reaction was carried out in a 100 mL Teflon pressure vessel in which the above-described mixture was transferred and the maximum values for pressure and temperature were set to 100 bars and 250°C, respectively. The optimised heating programme used was as follows: a heating slope to 220°C for 15 min, then 30 min at 220°C followed by switching off the microwave set-up. Finally, the product was recovered, washed with deionised water several times to remove the excess NaOH, filtered and air-dried in an oven at 80°C. The dry powder is milled in a mortar and pressed into pellets.

To improve the purity and the density of the samples, thermal treatments at different temperatures have been carried out (from 500 to 1350°C for 1 h) to perform the structural determination. Ball milling for 20 hours led to the elimination of powder aggregates and to a better homogeneity in powder particle sizes, allowing us to obtain dense ceramics by sintering at 1100°C for 3 h for electrical characterisation. Ceramic density was determined by Archimedes' method in water. In order to perform the piezoelectric

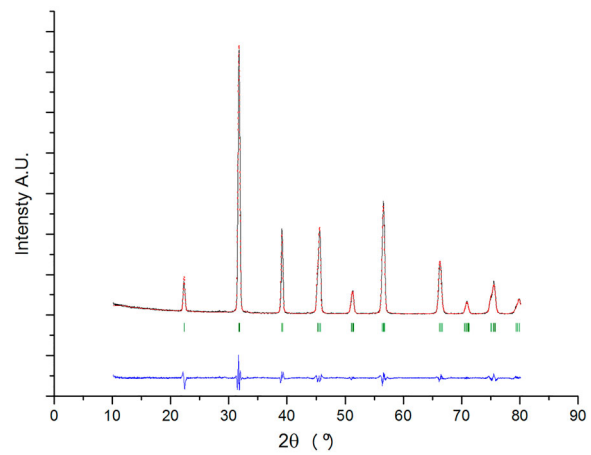


Figure 2. LeBail refinement of $\text{Ba}_{0.9}\text{Ca}_{0.1}\text{TiO}_3$ treated at 1100°C.

characterisation of the sample, thin discs of 0.9-mm thickness and diameter of 12.8 mm were prepared, and silver paint electrodes attached to the major faces of the sample by firing at 400°C for 30 min. Ceramic discs were poled successively under electric fields up to 3.3 KV mm^{-1} at 50°C in silicone oil to determine the saturation poling conditions.

Structural and microstructural characterisation

The structural characterisation of the samples has been carried out by means of X-ray diffraction using Cu K α radiation (X'Pert-MPD diffractometer) and, in the case of the 1100°C, used for piezoelectric measurements, the Le Bail method was used for profile fitting and calculating cell parameters. Powder morphologies and chemical composition were examined by scanning electron microscopy (JEOL JMS 6400 microscope fitted with a EDS analyser) and the microstructural analysis of selected samples was performed by transmission electron microscopy (JEM 3000F microscope) operating at 300 KV.

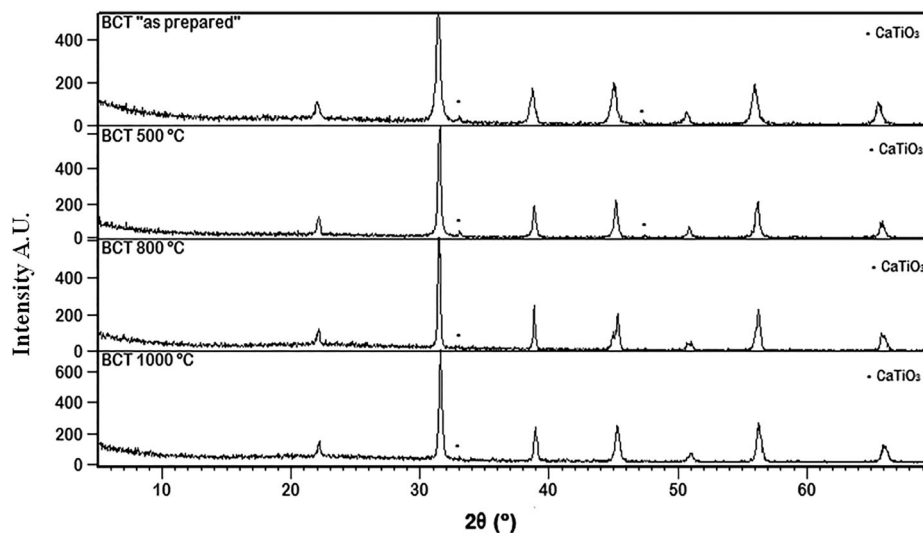


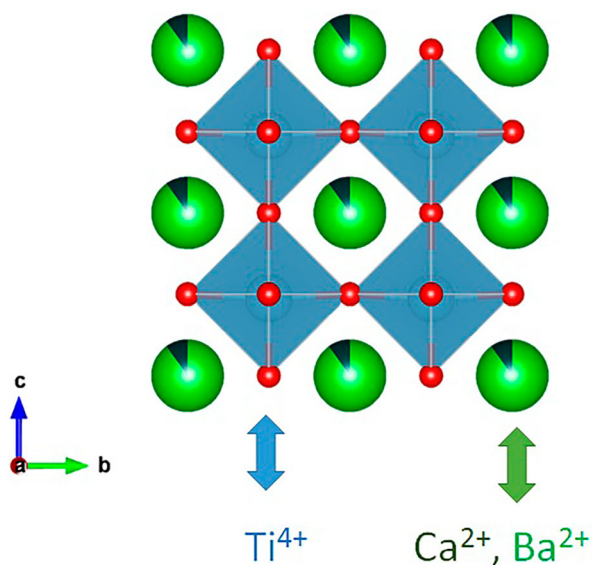
Figure 1. X-ray diffraction patterns of $\text{Ba}_{0.9}\text{Ca}_{0.1}\text{TiO}_3$ 'as prepared' in microwave-hydrothermal conditions and further calcined at different temperatures.

Table 1. Structural parameters of BCT ($x = 0.1$).

Space group	$P4mm$
$a =$	3,9758(0) Å
$b =$	3,9958(0) Å
$c =$	4,0054(1) Å
$c/a =$	1,0074

Piezoelectric measurements

The piezoelectric parameter d_{33} was measured with a d_{33} Berlincourt piezometer. Piezoelectric, elastic and dielectric complex material coefficients were obtained from complex impedance measurements ($|Z|$, Θ) at the resonance modes of thickness-poled discs (Figure 1) at an HP4192A LF Precision Impedance Analyzer. The d_{31} and g_{31} piezoelectric coefficients, and the electrochemical coupling factors k_p and k_{31} , and corresponding frequency numbers, N_p and N_{31} , together with Poisson's ratio, σ , elastic stiffness $c_{11p}^{E,D}$ and compliances $s_{11}^{E,D}$ and $s_{12}^{E,D}$ and dielectric permittivity, ϵ_{33}^T , at the resonance frequency, were calculated by an automatic

**Figure 3.** Structure of $\text{Ba}_{0.9}\text{Ca}_{0.1}\text{TiO}_3$.

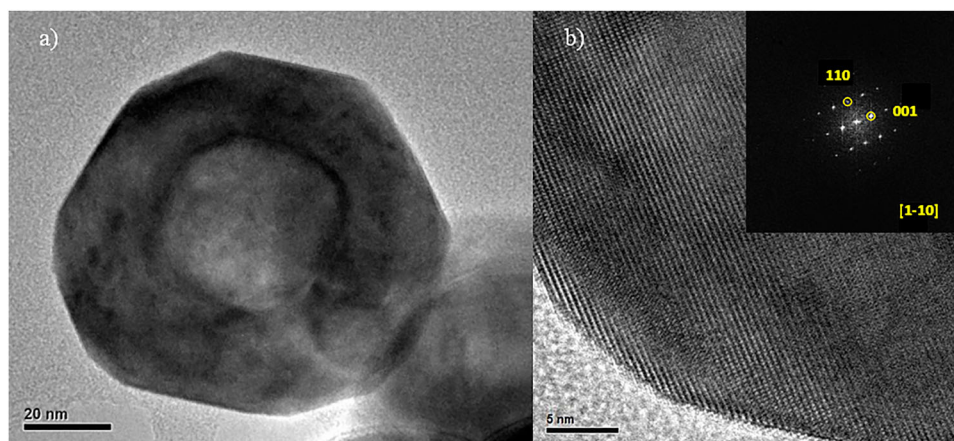
iterative analysis of the complex impedance spectra at the radial mode [14]. The e_{33} and h_{33} piezoelectric coefficients, k_t , N_t , together with the elastic stiffness $c_{33}^{E,D}$ and dielectric permittivity, ϵ_{33}^S , at the resonance frequency, were calculated by the automatic iterative analysis at the thickness mode [15]. All coefficients were calculated in the complex form, thus taking into account piezoelectric, elastic and dielectric losses.

Results and discussion

It can be observed, from the X-ray diffraction patterns corresponding to the as-prepared samples, (Figure 2) that there is some degree of phase segregation, the desired product $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ being obtained together with a small amount of CaTiO_3 ($\leq 2\%$). In order to get pure samples, thermal treatments were further performed in air at different temperatures for quite short times (1 h) and, as evidenced in this figure, starting at 800°C , CaTiO_3 begins to be reabsorbed. This is because the 'as prepared' materials are nanometric (particle size ≈ 25 nm calculated with the Debye-Scherrer formula) and therefore, are very reactive.

The LeBail method applied to the XRD data corresponding to the $x = 0.1$ sample, after being treated at 1100°C (Figure 2), confirms the tetragonal structure and allows the calculation of the cell parameters and hence, the c/a ratio (Table 1). This also confirms that the Ti position is slightly offset with regard to the centre of the octahedron along the c -axis (Figure 3), as it is well known to happen in BT. On the other hand, TEM images (Figure 4) do confirm the nanometric size of the particles (~ 60 nm) in agreement with XRD, even after the thermal treatment.

The samples were sintered at different temperatures (Figure 5) in order to carry out the study and measurement of piezoelectrical properties. However, the density obtained at 1200°C was only 70%, due to the formation of polyhedral crystals and, at 1350°C , a superficial melting of the particles was observed.

**Figure 4.** (a) TEM image of a $\text{Ba}_{0.9}\text{Ca}_{0.1}\text{TiO}_3$ nanoparticle ($\varnothing \approx 60$ nm), (b) corresponding HRTEM image and electron diffraction pattern.

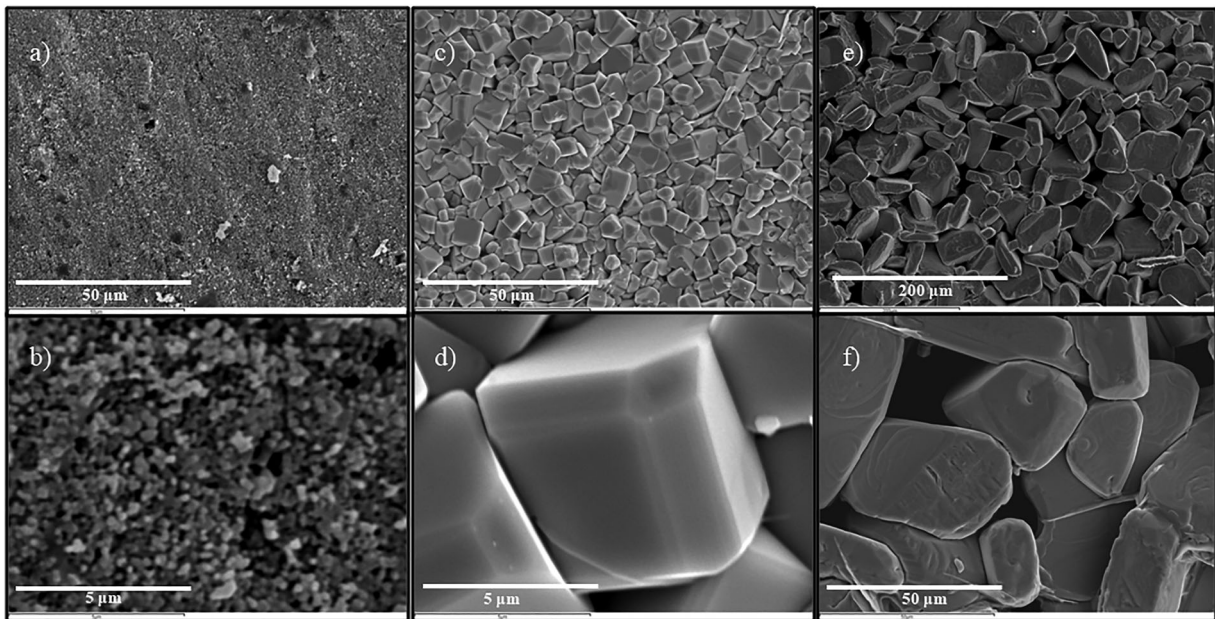


Figure 5. SEM images of BCT sintered at different temperatures: (a), (b) 1000°C; (c), (d) 1200°C; (e), (f) 1350°C.

Therefore, as explained in section 2.1., other more effective strategies for sintering were carried out for the electrical characterisation

The sample was characterised by the resonance method when poled to saturation and Figure 6 shows that the best poling conditions correspond to an electric field of 1.2 kV mm^{-1} , for which $d_{33} = 118 \text{ pC/N}$. Although the sample can stand higher poling fields, up to 3.3 kV mm^{-1} , without suffering electric breakdown, the piezoelectric d_{33} coefficient decreases, which most probably indicates a mechanical damage of the sample [16]. Figure 7 shows an uncoupled radial resonance and, as expected, a thickness resonance with a certain coupling to other undesired resonances. Both resonances present narrow peaks that indicate low mechanical, dielectric and piezoelectric losses and the calculated coefficients from these two electromechanical resonances of the disc are shown in Table 2.

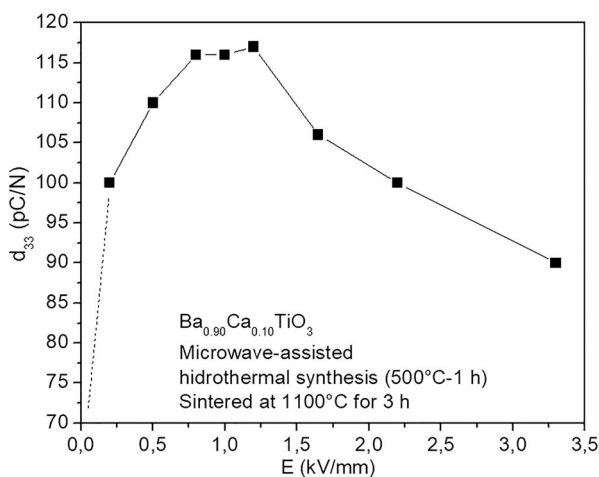


Figure 6. Piezoelectric charge coefficient of a thin ceramic disc as a function of the poling electric field.

In order to evaluate these results, it is worth to recall that coefficients as high as $d_{33} = 350 \text{ pC/N}$ and $k_p = 36\%$ were reported for pure BT ceramics prepared by

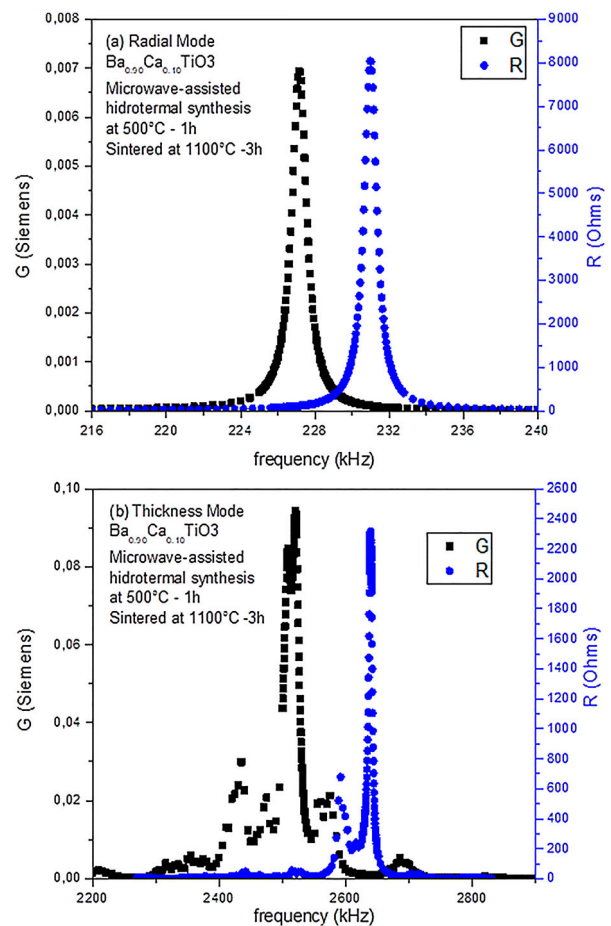


Figure 7. Complex impedance, represented as Resistance (R , real part of the complex impedance, Z^*) and conductance (G , real part of admittance, $Y^* = 1/Z^*$) peaks for the extensional: (a) radial and (b) thickness modes of resonance of a thin ceramic disc, thickness poled to saturation.

Table 2. Results of the piezoelectric, elastic and dielectric characterisation from the complex impedance spectra of thin discs sintered at 1100°C – 3 h at the extensional radial and thickness modes.

Radial mode		Thickness mode	
Density (g cm^{-3})	4.7		
N_p (kHz.mm)	2808	N_t (kHz.mm)	2294
k_p (%)	19	k_t (%)	42
k_{31} (%)	12	–	–
Poisson's ratio: σ	0.273	–	–
c_{11p}^E (10^{10} N.m $^{-2}$)	8.86 + 0.038i	c_{33}^E (10^{10} N.m $^{-2}$)	9.59 + 0.15i
s_{11}^E (10^{-12} m 2 .N $^{-1}$)	12.18-0.05i	–	–
s_{12}^E (10^{-12} m 2 .N $^{-1}$)	–3.32 + 0.01i	–	–
d_{31} (10^{-12} C.N $^{-1}$)	–29.67 + 0.49i	e_{33} (C.m $^{-2}$)	9.21-0.18i
ϵ_{33}^T	599.7 – 7.0i	ϵ_{33}^S	467.9 – 0.16i
s_{66}^E (10^{-12} m 2 .N $^{-1}$)	31.02 – 0.13i	–	–
c_{11p}^D (10^{10} N.m $^{-2}$)	9.08 + 0.35i	c_{33}^D (10^{10} N.m $^{-2}$)	11.60 + 0.08i
s_{11}^D (10^{-12} m 2 .N $^{-1}$)	12.02-0.05i	–	–
s_{12}^D (10^{-12} m 2 .N $^{-1}$)	–3.49 + 0.02i	–	–
g_{31} (10^{-3} m.V.N $^{-1}$)	–5.59 + 0.03i	h_{33} (10^8 V m $^{-1}$)	21.84 – 0.31i

hydrothermal synthesis and a MW sintering process of 8 h with a peak temperature of 1300–1320°C, having a density of 5.83 g cm $^{-3}$ and $\epsilon_{33}^T = 4200$ at 1 kHz [17]. Current expected values for pure BT ceramics are $d_{33} = 190$ pC/N and $k_p = 36\%$ with a density of 5.7 g cm $^{-3}$ [18].

Regarding BCT ceramics, there are controversial results in the literature on whether or not the transition temperature increases with Ca-doping [19,20] when Ca $^{2+}$ ions replace Ba $^{2+}$ ions, opposite to the earlier results [19]. Also the effect is different when Ca $^{2+}$ ions replace Ti $^{4+}$ ions [20]. Consequently, it is not clear if the room temperature permittivity increases or decreases [20–23] for these compositions, i.e. if the doped ceramic is more or less polarisable than the pure BT and, therefore, more or less piezoelectrically active, respectively.

Conclusions

To summarise these results, considering the above-mentioned controversy and the mild conventional sintering conditions used here, the material coefficients found in this work are within the expected values and validate the synthesis route here developed to prepare lead-free piezoelectric ceramics. Work is in progress to enhance sintering and densification of this ceramics with the aim of an improvement of the piezoelectric properties.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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