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# Preparation and properties of artificial bone with lead-free piezoelectric materials

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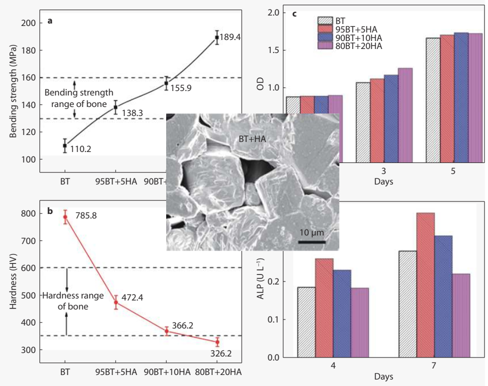
**In order to fabricate the artificial bone with high bioactive property, lead-free barium titanate ($BaTiO_3$, BT) piezoelectric material added hydroxyapatite (HA) composites were prepared in this study. Compared with the pure HA materials, the introduction of BT can increase the electrical properties of the samples while ensuring good biological properties. The electrical properties, such as piezoelectric constant $d_{33}$, hysteresis loop and dielectric spectrum were measured, respectively. The bending strength, Vickers hardness, cytotoxicity and osteogenic property of the BT/HA composites were also discussed. It is revealed that the non-toxic sample with 95 wt% BT and 5 wt% HA (95BT+5HA) has the best osteoinductivity, the piezoelectric constant $d_{33}$ of which is 79.2 pC $N^{-1}$. The bending strength and Vickers hardness of the 95BT+5HA sample are 138.3 MPa and 472.4, respectively, realizing the desired mechanical properties of human bones. Comprehensive analyses of various properties show that the 95BT+5HA composite can meet the requirements of artificial bone, and is expected to be a promising generation of substitute bone materials.**




Bone is an important organ of human body, which plays a vital role in human physiological health.[1] However, there are 3 million cases of bone defects every year due to the aging of the population and various accidental injuries.[2]. The demand for bone is clinically second only to that for blood. Autogenous bone graft, allogeneic bone graft and artificial bone graft are commonly used to treat bone defects, and autogenous bone graft is most widely accepted for the treatment of bone defects. Whereas, the autogenous bone transplantation has some problems, such as insufficient donors, secondary damage to patients, etc.[3] Allogeneic bone transplantation can easily lead to infection, immune rejection and other risks. Therefore, the demand for artificial bone increases dramatically.[4] Artificial bone has the advantages of adjustable components and customizable structures. Moreover, it may also have excellent biological activity, cytocompatibility, osteoinductive capacity, and non-toxic nature.[5] With the development of materials, artificial bone materials can be degraded spontaneously and has the adjustable degradation rate.[5] Webster et al. successfully prepared submicron materials which had similar properties to the human bones, and then were used to prepare artificial bones. It was found that the as-prepared artificial bones possessed great mechanical properties.[6] In order to explore the histocompatibility of degradable artificial bone composite materials, Cen et al. used L-polylactic acid and tricalcium phosphate as raw materials to print a composite scaffold using 3D printing technology, and observed its growth after inoculation with cells. The results showed that the cells grew well and the scaffold had excellent biological properties.[7]

At present, the materials used for the preparation of artificial bone mainly include polymer, metal and bioceramics. Polymer materials have poor biocompatibility and bioactivity, and could not achieve great mechanical properties compared to human bone.[8] Because of its excellent mechanical properties and biological inertia, metal materials are widely used, among which titanium alloy is mainly used for the preparation of human knee and human bone plate.[9] However, metal materials for artificial bone also have many problems. For example, its mechanical properties do not match those of human bone, and it does not have self-degradability. In most cases, the patients even need a second operation, which increases the patient's suffering and medical expenses.[10] Compared with metal materials and polymer materials, ceramic materials have more excellent mechanical and biological properties. Hu et al. prepared bio-scaffolds based on hydroxyapatite materials based on 3D printing technology. The experimental results revealed that the scaffolds prepared by inorganic ceramic materials were rich in pores and had excellent properties which are suitable for cell adhesion and growth.[11] After thousands of years of evolution, natural bone

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tissue has achieved perfect coordination in composition, structure, function and performance. Researchers found that the composition of hydroxyapatite (HA) is similar to that of human bone, and the porous bone scaffolds based on HA are used in the field of bone repairs.[12] Scalera applied HA to prepare the porous-internal and dense-external ceramic structures which have both excellent mechanical and biological properties.[13] Kim et al. enhanced the mechanical properties of HA by adding sodium borosilicate, and found that the composite after adding sodium borosilicate has better mechanical properties than the pure HA.[14]

In order to further improve the performance of ceramic based artificial bone, the bionic performance in function should be noted. The bionic bone not only lies in the shape similarity of composition and structure, but also in the similarity of function. However, the research on the bionic composition and structure are preferred, and the bionic performance in function is less understood.[15] Fukada and Yasuda proposed that bones had piezoelectric properties.[16] They found that the strain could produce potential changes in the bone when the external force is applied. Bassett also confirmed that bones had piezoelectric effect.[17] Damask found that a force of $10^7$ N $m^{-2}$ to bone could produce a current of 10 Mvd. The change of potential can cause the reaction of cells and extracellular environment, and finally lead to the growth of bone tissue.[18] Nowadays, it has become a common understanding that human bone has piezoelectric properties, and human bone tissue is a typical piezoelectric material. The piezoelectric effect of bone tissue is similar to that of piezoelectric material, but the excitation mode is different. Piezoelectric material is deformed by pressure, which makes the electric axis of the material deflect, thus generating electric charge.[19] In the case of bone, the piezoelectric effect is produced by the deflection of the electric axis of bone tissue through the interaction of various organic components. It is found that negative charge can promote the proliferation and differentiation of osteoblasts, accelerate calcium deposition and promote bone healing.[20] Also, when human bone is deformed by force, electrical charge will be generated inside the bone. Especially, when it is periodically deformed, regular electron flow can be generated. The piezoelectric signal will affect the differentiation behavior of bone cells and regulate their function.

In this paper, an effective approach of adding piezoelectric BT powder to HA was proposed to ensure both electrical and biological performance. Ceramic composites with different BT/HA contents were prepared. The BT/HA contents were modified, the effect of which on electrical properties and biological properties of BT/HA bioceramics were explored in detail.

## Materials and methods

### Materials preparation

Barium titanate (99.99%, Aladdin, China) and hydroxyapatite (99.99%, Shanghai Hualan Chemical Technology Co., Ltd, China) were used as raw materials, and the powders with the proportions of 100 wt% BT (abbreviated as 100BT), 95 wt% BT+5 wt% HA (95BT+5HA), 90 wt% BT+10 wt% HA (90BT+10HA), 80 wt% BT+20 wt% HA (80BT+20HA) were weighed, respectively, and mixed by ball-milling with water for 24 h. After that, the mixed powders were dried at 80 °C for 24 h and then pressed into disks with dimensions of 10 mm in diameter and 2 mm in thickness with the pressure of 10 MPa. Meanwhile, the standard samples with length × width × height of 25 mm × 2 mm × 1.5 mm were prepared. The green bodies were sintered in a muffle furnace at 1250 °C for 2 h to obtain BT/HA ceramics. Finally, both sides of the disk samples were painted with silver and dried in an oven at 150 °C for 2 h. The samples were placed in an oil bath at 85 °C and poled for 30 minutes with a DC voltage of 1.5 kV $mm^{-1}$.[21]

### Structure and electrical properties characterization

Phase structure of the sintered BT/HA bioceramics was characterized by X-ray diffraction (XRD, D8 ADVANCE A25, Bruker, Germany). The morphology and microstructure of the ceramic samples were observed by scanning electron microscopy (SEM, Zeiss Merlin, Germany). The porosity of the samples was measured using the Archimedes method.[22] The shrinkage of the samples was calculated based on the sample size. The piezoelectric constant $d_{33}$ was measured by a quasi-static $d_{33}$ (ZJ-6, The Institute of Acoustics of the Chinese Academy of Sciences, China).[23] Ferroelectric analyzer (Synerce, Radiant, Italy) was used to obtain the hysteresis loop. The dielectric properties of the samples with the frequencies of 100 Hz, 1000 Hz and 10000 Hz was characterized with a temperature range of -50 °C~300 °C by dielectric spectrometer (HCWP-S, Centre Testing International, China). Standard samples with length × width × height of 25 × 2 × 1.5 mm were prepared, and the bending strength of the samples was tested by electronic universal testing machine (AG-IC20KN, Shimadzu, Japan) with the span of 20 mm and the loading rate of 0.2 mm $min^{-1}$. The hardness value (HV) of the samples was recorded by a Digitalized Micro Hardness Tester (TuKon2500B, Wilson, America).

### Biological properties characterization

The mouse embryonic osteoblast precursor cells were used to evaluate the cytotoxicity of samples.[24–26] The samples were immersed in the cell culture medium for 24 h and the extraction solution was prepared at the ratio of 10 g $L^{-1}$. The mouse embryonic osteoblast precursor cells were cultured in the extracts of composite samples for 1, 3 and 5 days. Afterward, the absorbance value (OD) at 450 nm was detected via CCK-8 by microplate. The mouse embryonic osteoblast precursor cells were used to analyze alkaline phosphatase activity (ALP) of the specimens.[27–29] The specimens were immersed in the cell culture medium which contains 10 % fetal bovine serum for 24 h. The cells were inoculated on the samples and put into a $CO_2$ incubator at 37 °C. The activity of alkaline phosphatase (ALP) was detected after 4 and 7 days of co-culture procedure.

## Results and discussion

### Materials structure

XRD patterns of sintered BT/HA ceramics are shown in Fig. 1. All the BT/HA samples with various proportions ranging from 100BT to 80BT+20HA show the matched patterns with those of $BaTiO_3$ structure, as indexed by PDF#74-1957. Meanwhile,

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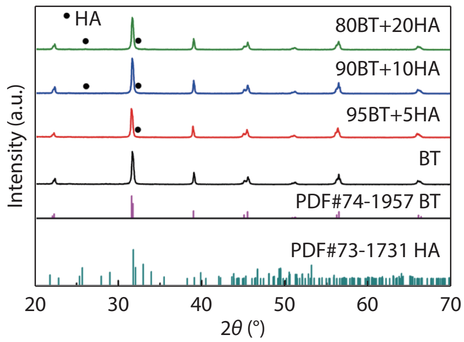

**Fig. 1** XRD patterns of BT/HA composites.

the HA phase which provides biological properties can also be indexed by PDF#73-1731. As is known, the lead-free BT phase possesses great piezoelectric properties, which would be beneficial to the biological properties enhancement of HA based materials.[30–32] Thus, it is highly expected that the BT/HA ceramics would have great biological performance.

According to the SEM images shown in Fig. 2, uniform grains and defined grain boundaries can be observed. The difference in grain size of 100BT is relatively small, and other 95BT+5HA, 90BT+10HA, 80BT+20HA samples also present similar results. There is no excessive growth of the crystal grains, which has a positive effect on ensuring the performance stability of biomaterials. It should be noted that the pores in the ceramics increase with the increase of HA content, which can be attributed to the fact that the organic matter and adsorbed water in HA will volatilize during the high temperature sintering. Meanwhile, HA is dispersed in BT, and there is no direct reaction between HA and BT during the sintering process. Therefore, the combination between HA and BT is a physical combination, which hinders the densification process of BT, leading to an increase of pores. On the basis of certain ceramic strength, pores would be beneficial to cell proliferation.[33]

It can be seen from Fig. 3a that porosity increases with the increase of HA in the BT/HA composites. It is also confirmed in Fig. 2 that the BT/HA composites seem to have a lower density, and the grains are separated compared with pure BT ceramics. The shrinkage rate of sintered samples of BT, 95BT+5HA, 90BT+10HA and 80BT+20HA is shown in Fig. 3b. The shrinkage increases with the increase of HA. Due to the fact that the densities of BT and HA are 6.08 g cm$^{-3}$ and 3.16 g cm$^{-3}$, respectively, and the sintering shrinkage rates of these

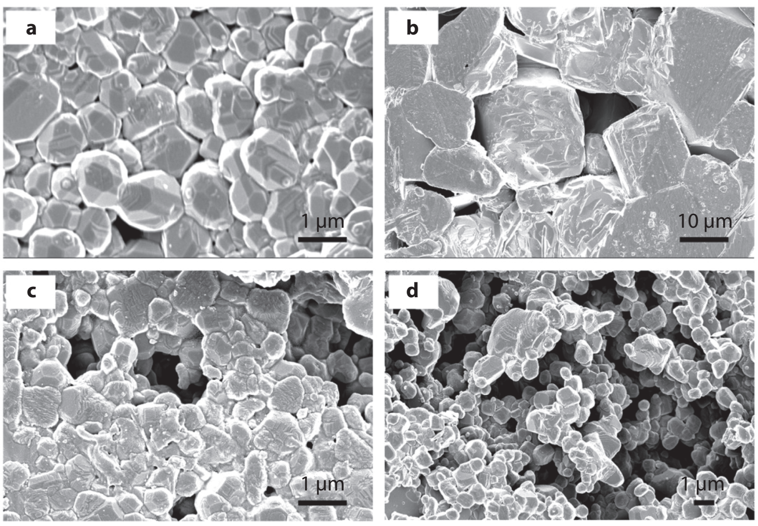

**Fig. 2** SEM morphology of **a** 100BT, **b** 95BT+5HA, **c** 90BT+10HA, and **d** 80BT+20HA samples, respectively.

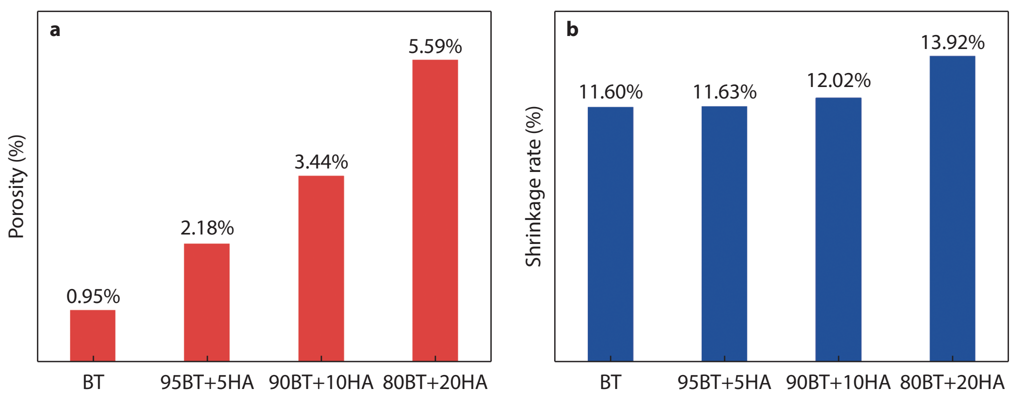

**Fig. 3** Comparisons of **a** porosity and **b** shrinkage rate of BT/HA composites.

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two are quite different.[34] During the sintering process, the densification of pure BT ceramics would be greatly different from that of BT/HA composites. In this study, HA is the less phase in the composite material and dispersed in BT, and these two materials do not react chemically, and the combination between particles is simple mechanical bite or van der Waals force, etc.[35]. In addition, the HA phase contains a large amount of adsorbed water, water of crystallization and organic matter composition, which will volatilize under high temperature environment. As a result, the shrinkage rate of BT/HA composites is relatively large, the porosity increases simultaneously, which is consistent with the results shown in the SEM images.

## Electrical performance

It is clear that $d_{33}$ decreases with the increase of HA as shown in Table 1. When the mass fraction of HA reaches 20 %, $d_{33}$ is close to 0 due to the fact that HA has no piezoelectric properties. Besides, the densities of BT and HA are 6.08 g/cm$^3$ and 3.16 g cm$^{-3}$, respectively, the volume fraction of HA in the sample reaches 40 % when HA reaches 20 %. HA is uniformly dispersed between BT, making BT a discontinuous phase. Therefore, the piezoelectric performance of the samples gradually deteriorates with the increase of HA.[36]

**Table 1.** $d_{33}$ of BT/HA composites with different BT/HA ratios.

| | BT | 95BT+5HA | 90BT+10HA | 80BT+20HA |
|---|---|---|---|---|
| | 115 | 80 | 35 | 2 |
| | 117 | 79 | 34 | 1 |
| $d_{33}$ | 116 | 79 | 35 | 2 |
| | 116 | 80 | 33 | 2 |
| | 115 | 78 | 35 | 1 |

It can be seen in Fig. 4 that when the content of HA is 20 wt%, the hysteresis loop presents almost a straight line and the sample almost has no ferroelectricity, which is consistent with the result of $d_{33}$ measured in Table 1.[37] Also, the coercive field increases with the increasing HA except for 80BT+20HA sample. Due to the increase of porosity, more electric fields are concentrated in the region of low dielectric constant, which requires a larger applied electric field to polarize the piezoelectric phase.[38] Besides, the addition of HA makes the ferroelectric phase discontinuous, which will hinder the domain orientation. The remanent polarization increases firstly and then decreases. The remanent polarization of 95BT+5HA sample is the largest and the ferroelectricity is the best. In addition, the porosity of 95BT+5HA is higher than that of BT, which would offer the space for cell proliferation. Thus, the 95BT+5HA composite is considered as the appropriate candidate for further artificial bone study in this work.

As the frequency increases, the dielectric constant decreases in Fig. 5a, which shows a typical ferroelectric behavior.[39] The Curie temperature decreases while increasing HA as shown in Fig. 5b, and the Curie temperature of 95BT+5HA is 148 °C. As is known, Curie temperature is the transition point between tetragonal phase and cubic phase, and it ensures piezoelectric properties at service temperatures without being depolarized. Tetragonal phase is the premise of piezoelectric properties of the composites, so it is particularly important to make the Curie temperature of the composites higher than the service temperature range.[40] The service temperature range of artificial bone is −30 °C~50 °C, so the samples of 95BT+5HA would maintain certain piezoelectricity in the service temperature range.

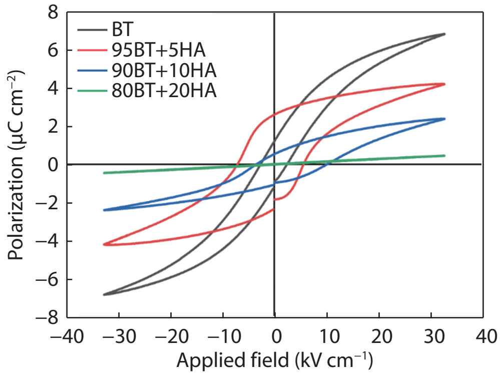


**Fig. 4** Hysteresis loops of BT/HA composites.

## Mechanical properties

As is known, the bending strength of human femur is around 130 MPa to 160 MPa.[41–43] HA is a kind of rigid particles, which can strengthen the BT matrix.[44] It is shown in Fig. 6a that the bending strength increases with the increase of HA. The 95BT+5HA and 90BT+10HA composites both fulfill the bending strength requirements of human femur. The hardness decreases with the increase of HA in Fig. 6b. Because the hardness of HA is lower than that of BT.[45] HA is dispersed in BT, which results in the decrease of hardness. The Vickers hardness of human bones ranges from 350 to 600.[46] The samples with low hardness could not be used as human bones due to the loading-bearing demand. On the other hand, when the hardness is too high, the stress shielding effect will appear. Therefore, when the content of HA is 5 wt% and 10 wt%, the hardness of BT/HA composites can be considered.

## Biological properties

It is shown in Fig. 7a that the OD value of pure BT sample increases with the prolongation of induction time, indicating that pure BT material is non-toxic.[47] The OD value of BT/HA composite increases with both of the prolongation of incubation time and the increased HA. Thus, the BT/HA composite has no cytotoxicity, and the addition of HA is more conducive to cell growth and proliferation.[48] In Fig. 7b, it can be seen that the alkaline phosphatase activity of cells increases with the prolongation of culture time. At the same time, the alkaline phosphatase activity of 95BT+5HA sample is the highest, indicating that the samples of 95BT+5HA have the best osteoinductivity.[49] Due to that the polarized ceramic surface is charged, the negative surface will absorb the positive charged ions in the culture medium to form a positive charged layer.[50] Because the protein molecules and cells are negatively charged, they would be attracted and enriched by the positive surface. The protein layer on the surface of the material will induce the production of bone like apatite on the surface of the biomaterial, and then promote the proliferation and differentiation of bone cells. When the content of BT decreases, the piezoelectric effect and the osteoinductivity deteriorate.[51] On the other hand, the osteoinductivity of the material enhances with the increase of HA, resulting in

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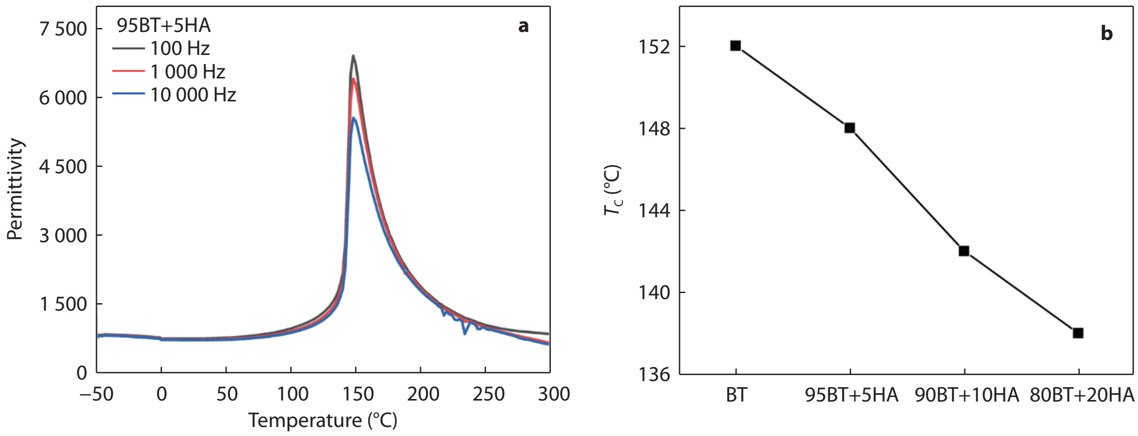


**Fig. 5** **a** Dielectric properties and **b** Curie temperatures of BT/HA composites.

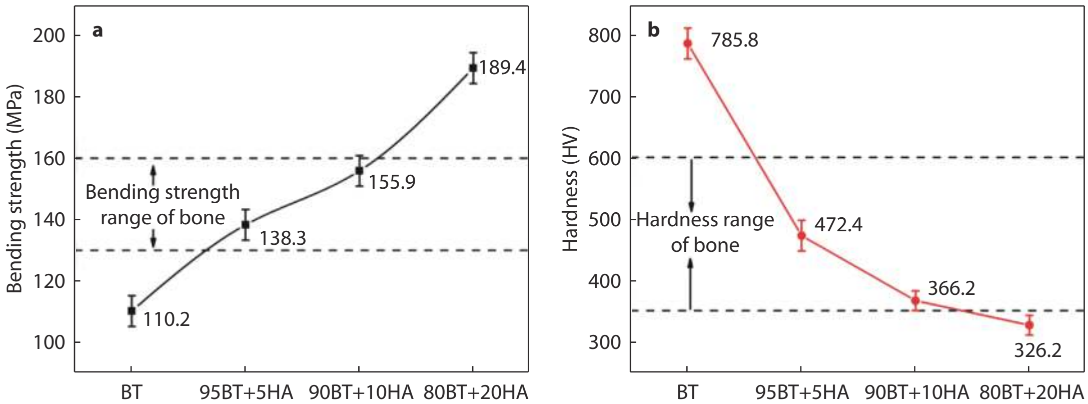


**Fig. 6** Comparisons of **a** bending strength and **b** hardness of BT/HA composites.

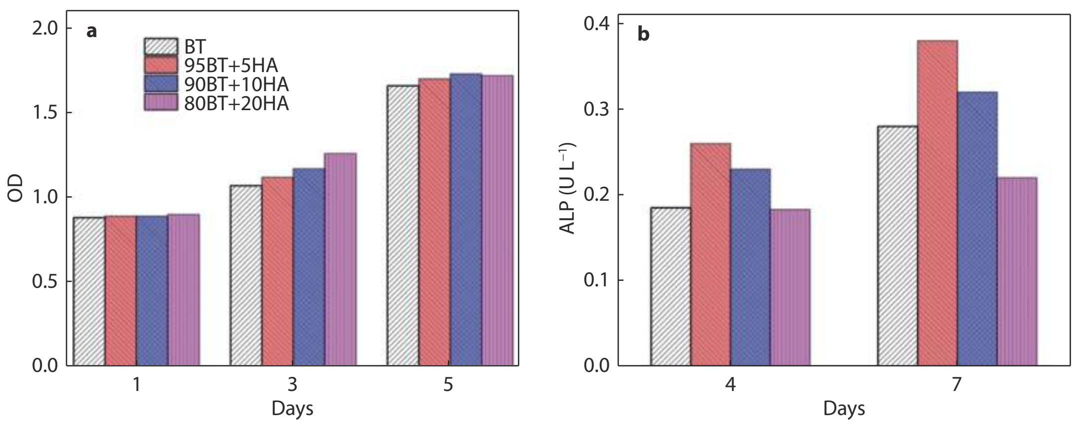


**Fig. 7** Comparisons of **a** cytotoxicity and **b** ALP results of BT/HA composites.

the highest alkaline phosphatase activity of 95BT+5HA.

## Conclusions

In order to obtain artificial bone materials with good piezoelectric effect, ceramic samples with different BT/HA contents were prepared. The results reveal that the samples consisting 95BT+5HA possess the best performance, the $d_{33}$ and $T_C$ of which are 79.2 pC $N^{-1}$ and 148 °C, respectively. The bending strength is 138.3 MPa and the Vickers hardness is 472.4. The mechanical properties fully meet the requirements of human femur. CCK-8 kit is used to detect the toxicity of the composites. It is found that the cells grow well on the composites, and the composites are non-toxic to cells. In addition, the samples with 95BT+5HA also have the best osteoinductivity. In conclusion, 95BT+5HA is the most suitable material for artificial bone in this work. In the future, this kind of bone material with piezoelectricity can be used as 3D printing consumables, achieving personalized customized human bone with 3D printing technology, so as to solve the problem of artificial bone defect in clinical trials.

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## CONFLICT OF INTEREST

The authors declare no conflicts of interest.

## AUTHOR CONTRIBUTIONS

RW: synthesis, performance measurement, writing. FG: writing. SY: performance measurement. YZ: performance measurement. LC: methodology, writing.

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