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Comment on “Hole-pinned defect-dipoles induced colossal permittivity in Bi doped SrTiO₃ ceramics with Sr deficiency”

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Abstract

With this contribution, as a comment to the publication in Journal of Materials Science & Technology 44 (2020) 54, reporting giant dielectric response, structural characterization and numerical simulations in Sr_{1-1.5x}Bi_xTiO₃ ceramics, we show that the reported results are rather contradicting and not well analysed, while the suggested mechanism for the giant permittivity response is not valid or doubtful and has to be reconsidered. Moreover, many details and data are missing making impossible not only to call the obtained results very suitable for practical application but even to reproduce them.

Key words: SrTiO₃ ceramics, Doped dielectrics, Perovskite structure, Giant permittivity

In a view of the current interest to the giant or colossal permittivity materials [1], a work on Sr_{1-1.5x}Bi_xTiO₃ ceramics, possessing the dielectric permittivity of about 14000 and losses below 0.05 around room temperature and 10 kHz frequency for $x = 0.05$, have been recently published by Qiao et al. [2]. Using structural analysis and numerical simulations, the authors of Ref. 2 have suggested that Bi_{Sr} - V_{Sr} - Bi_{Sr} defect complex aligned along [100] crystallographic direction is responsible for such performance. Particularly, they have observed that X-ray diffraction (XRD) lines shift to lower 2θ angles with increasing Bi content x , thus, indicating an increase in the lattice parameter. At the same time, (200) reflection line has been presented by Qiao et al. [2] to shift with a lower rate comparing to (111) and (110) ones. As a result, they have claimed that when Bi_{Sr} and V_{Sr} form the

$\text{Bi}_{\text{Sr}} - \text{V}_{\text{Sr}} - \text{Bi}_{\text{Sr}}$ configuration in [100] direction, the increase of the lattice spacing caused by a larger size of V_{Sr} comparing to that of Sr^{2+} is partially neutralized by [100] aligned aggregation of Bi^{3+} with an ionic radius smaller than that of Sr^{2+} , referring to our works on rare earth (RE) doped strontium titanate [1,3].

The referred articles of us indeed estimated the size of V_{Sr} in the $\text{Sr}_{1-1.5x}\text{RE}_x\text{TiO}_3$ systems to be of about 154 pm [3] that is larger than 144 pm of Sr^{2+} ionic size for the coordination number of 12 [4]. However, we have also wrote in Ref. 3 and clearly demonstrated in Ref. 5 that for the coordination number of 12, characteristic for A-site ions of the cubic perovskite ABO_3 structure of strontium titanate, Bi^{3+} ions have to be at least not smaller than Sr^{2+} ones. Here, Fig. 1 also shows that the data from Ref. 4 plotted as ionic radius versus coordination number can be linearly fitted with R^2 values close or even equal to 1, while their extrapolation for Bi^{3+} to the coordination number of 12 yields the ionic radius of 145 pm. Therefore, Bi^{3+} ions should be considered as those of similar size with Sr^{2+} , thus being not able to significantly affect the lattice parameter in contrast to the claim by Qiao et al. [2], who have compared the Bi^{3+} ionic size of 117 pm for the coordination number of 8 with 144 pm of Sr^{2+} for the coordination number of 12. Moreover, if that comparison would be correct, the lattice parameter/spacing has to decrease due to 2.7 times larger difference between the Bi^{3+} and Sr^{2+} ionic size in regard to that between the V_{Sr} and Sr^{2+} and twice larger content of Bi^{3+} comparing to that of V_{Sr} , but the spacing increase has been observed instead by Qiao et al. [2] according to their Fig. 7.

Moreover, the conclusion on the peculiar (100) spacing done by Qiao et al. [2] looks to be also incorrect, taking into account that they studied cubic perovskite structure polycrystalline material without preferential orientation according to their XRD data. Therefore, one cannot relate the [100] direction with the lattice parameter a and orthogonal directions with the lattice parameters b and c , as the authors of Ref. 2 have done in their Figs. 8 and 9 based on the structural analysis presented in their Fig. 7. Just average lattice parameter can thus be obtained, which values have been not, however, indicated by Qiao et al. [2]. Instead, they have shown in their Table 1 and Fig. 9(a) the simulated lattice parameters reaching 1180.92 pm for undoped SrTiO_3 , although according to SrTiO_3 PDF card #35-0734 it should be just 390.5 pm. As a result, there is a serious doubt in the correctness of the structural analysis done by the authors of Ref. 2 in their Fig. 7. This doubt is supported by several additional arguments. First, presenting the 2θ peak separations, Qiao et al. [2] have not shown the associated error bar. Most probably the variations found by them is within that error bar but it is hard to judge since the authors of Ref. 2 even have not presented the step and rate of their XRD experiment. Second, they have shown the separation variations only for the doped ceramics, excluding for some reason the case of $x=0$. However, if one takes these data e.g. from SrTiO_3 PDF card #35-0734 the resulting plots will look as presented in Fig. 2, showing that the

monotonous behaviour is destroyed, particularly in the cases of $2\theta_{(200)}-2\theta_{(111)}$ and $2\theta_{(111)}-2\theta_{(110)}$. Therefore, the conclusion on the specific behaviour for the (200) spacing done by Qiao et al. [2] is thus completely disabled raising again the question about the error bar. In addition, it is unclear why the authors of Ref. 2 have used (200) but not (100) line position to compare with those of (110) and (111) and discuss further the spacing behaviour in [100] direction. Third, even for the doped ceramics only, showing the monotonous variations of 2θ peak separations, the dielectric permittivity variation is not monotonous, revealing the highest values for $x=5\%$ with further decrease for $x=10\%$. This contradiction between the dielectric response, structural properties and proposed model is also evident, but not explained by Qiao et al. [2].

Furthermore, Qiao et al. [2] have concluded that no internal barrier layer capacitance (IBLC) effect is observed in their ceramics based on their impedance spectroscopy analysis. However, single R-C equivalent circuit model fitting presented by the authors of Ref. 2 in their Fig. 5, besides being not normalized and not properly plotted, show evident deviations between the data and the fitting lines. As a result, this conclusion by Qiao et al. [2] is also not supported by their data. In addition, to judge about the correctness of the fit as well as about grain and grain boundary contributions to the electrical response the authors of Ref. 2 had to present the R and C fitting parameters, but they have not done so.

Finally, besides the incomplete description and incorrect analysis of the results, Qiao et al. [2] have not reviewed the results already published on $\text{Sr}_{1-1.5x}\text{Bi}_x\text{TiO}_3$, citing instead at least 11 papers published by some of the authors of Ref. 2. However, this system is very well studied since its discovery by Skanavi in 1957 [6] with particularly deep investigations done by Ang and Yu as one can find e.g. in Refs. 7-9. Moreover, Ang and Yu reported the room temperature giant permittivity of ~ 30000 observed for SrTiO_3 ceramics doped with 5.3% of Bi and annealed in Ar-H_2 already 14 years ago [7]. On the other hand, annealing in O_2 have been shown to suppress the room temperature permittivity below 1000 [7,8]. This conclusion by Ang and Yu, clearly indicating the primary role of the oxygen vacancies in the giant dielectric permittivity of SrTiO_3 -based materials [7,8] was further confirmed by us for Y-doped SrTiO_3 ceramics [1]. The role of the strontium vacancies thus cannot be the major one in contrast to the statement by Qiao et al. [2]. These vacancies can just help to form the defect dipoles and provide the way for the oxygen to leave the lattice at reducing atmosphere and high temperature conditions as was suggested by Lu et al. for La-doped SrTiO_3 [10] and confirmed by us for Nb-doped SrTiO_3 [11]. Indeed, $\text{Sr}_{1-1.5x}\text{Bi}_x\text{TiO}_3$ ceramics prepared by Qiao et al. [2] have been sintered at a temperature at least 120°C higher than that used by Ang and Yu [8] that should result in the higher oxygen vacancy content and higher density in the former ceramics comparing to the latter ones. In its turn, the higher density and mainly higher oxygen vacancy content, if not lowered by slow cooling rate, have to result in the higher

permittivity. However, neither cooling rate nor density values of $\text{Sr}_{1-1.5x}\text{Bi}_x\text{TiO}_3$ ceramics obtained by Qiao et al. [2] have been reported by them, making impossible to reproduce and explicitly explain their results.

In conclusion, doping effects in dielectrics are certainly of high scientific and technological interest, and the publication by Qiao et al. [2] represents undoubtedly a valuable contribution to this topic. However, there are also some unsolved discrepancies between the used ionic radius values, structural analysis and dielectric response variations with Bi content, incomplete description of the results, their error bars and experimental conditions as well as often-incorrect analysis of the impedance spectroscopy and structural data as shown above. Moreover, we have clearly shown that the model proposed the authors of the Ref. 2, which do not involve the oxygen vacancies as a major component, is oversimplified, being not supported by the results and contradicting to the literature reports and additional analysis. As a result, just the $\text{Bi}_{\text{Sr}}\text{-V}_{\text{Sr}}\text{-Bi}_{\text{Sr}}$ like defect complex aligned along [100] crystallographic direction cannot be a new way to achieve high performance colossal permittivity materials in ABO_3 perovskite ceramics as stated by Qiao et al. [2].

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Figure list

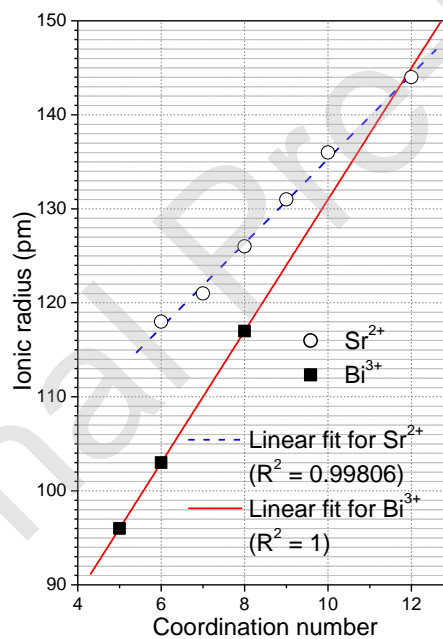


Fig. 1. Ionic radii of Sr²⁺ and Bi³⁺ versus coordination number following Ref. 4 and their linear fits with R² close or even equal to 1.

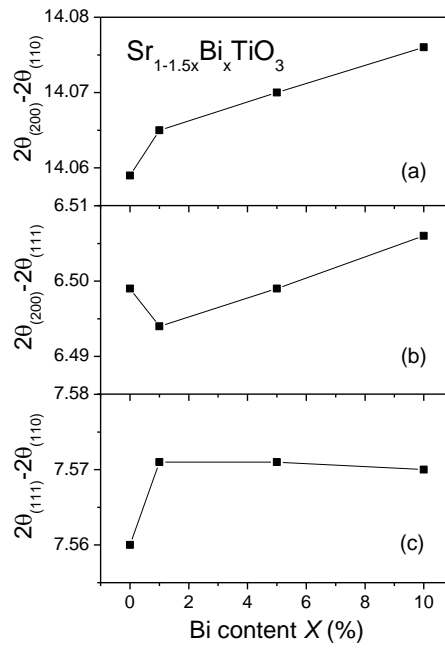


Fig. 2. $2\theta_{(200)}-2\theta_{(110)}$, $2\theta_{(200)}-2\theta_{(111)}$ and $2\theta_{(111)}-2\theta_{(110)}$ XRD peak separation as a function of Bi content x in $\text{Sr}_{1-1.5x}\text{Bi}_x\text{TiO}_3$ ceramics following data from Ref. 2 and PDF#35-0734.