

## Effect of LiSbO<sub>3</sub> on dielectric and piezoelectric properties of KNN ceramics

R. R. Wang<sup>a,\*</sup>, Y. L. Li<sup>b</sup>, Y. Tian<sup>b</sup>, Z. Q. Li<sup>c</sup>

<sup>a</sup>Marine Engineering Department, Tianjin Maritime College, Tianjin 300350, China

<sup>b</sup>College of Materials Science and Engineering, North China University of Science and Technology, Tangshan 063210, China

<sup>c</sup>Chemical College, Shijiazhuang University, Shijiazhuang 050035, China

K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, Li<sub>2</sub>CO<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub> and Nb<sub>2</sub>O<sub>5</sub> were used as the starting materials, the (K<sub>0.5</sub>Na<sub>0.5</sub>)NbO<sub>3-x</sub> mol% LiSbO<sub>3</sub> (x=0.00, 0.01, 0.02, 0.03, 0.04 and 0.05) ceramics are prepared using solid state synthesis method, and the effects of LiSbO<sub>3</sub> content on dielectric and piezoelectric properties of (K<sub>0.5</sub>Na<sub>0.5</sub>)NbO<sub>3</sub> ceramics are investigated. The results show that the crystal structure for (Na<sub>0.5</sub>K<sub>0.5</sub>)NbO<sub>3</sub> ceramics with different LiSbO<sub>3</sub> content is all perovskite structure, and the new phase structure of KNN ceramics can't be obtained when the LiSbO<sub>3</sub> content is 0.00 ≤ x ≤ 0.05. The appropriate amount of LiSbO<sub>3</sub> doped KNN ceramics can refine the grain size and increase the density of the ceramics. When x = 0.04, the relative dielectric constant reaches 980, the dielectric loss is 0.055, and the combined effect of Li<sup>+</sup> and Sb<sup>5+</sup> makes the KNN ceramics have better dielectric properties. Due to the more easily the domain wall rotates at the grain boundary, the (K<sub>0.5</sub>Na<sub>0.5</sub>)NbO<sub>3</sub> ceramics doped with 4 mol% LiSbO<sub>3</sub> shows excellent piezoelectric properties in the system of study, and the piezoelectric constant *d*<sub>33</sub> increases sharply to the maximum value of 126 pC/N.

(Received October 19, 2021; Accepted January 26, 2022)

**Keywords:** Ceramics, Doping, Dielectric properties, Piezoelectric

### 1. Introduction

With the social progress and the rapid development of science and technology, the performance of ceramic materials is more and more demanding, and new ceramic materials come into being [1-3]. As one of the functional ceramic materials, piezoelectric ceramics can realize the mutual conversion between mechanical energy and electrical energy, and its typical applications include underwater transducer, ceramic transformer, piezoelectric motor, imaging equipment [4,5], etc., and many equipments in the ship involve the application of such devices. At present, lead-based piezoelectric ceramics Pb(Zr, Ti)O<sub>3</sub>(PZT) are widely used in the field of application, and lead element accounts for a large proportion (about 70%) in PZT-based piezoelectric ceramics, in addition, improper disposal of these lead-based devices will have a huge negative impact on groundwater and farmland, endangering human beings and the ecological environment [6-8]. In recent years, the need for sustainable development of human society has been increasing and the awareness of environmental protection has been gradually enhanced. Many countries have legislated to ban the use of electronic materials containing lead, the research on lead-free piezoelectric ceramics meeting the environmental requirements and practical applications has become a hot topic for researchers [9,10].

In recent years, lead-free piezoelectric ceramics have become a research hotspot of functional ceramics, especially (K<sub>0.5</sub>Na<sub>0.5</sub>)NbO<sub>3</sub> (KNN)-based lead-free piezoelectric ceramics, which is a binary system, it is a completely solid solution of anti-ferroelectrics NaNbO<sub>3</sub> and ferroelectrics KNbO<sub>3</sub>. In 2004, Saito [11] et, al studied a kind of textured KNN ceramics containing Li, Ta and Sb, and its piezoelectric coefficient *d*<sub>33</sub> can reach 416 PC / N, which makes KNN based ceramics become a kind of hot material in the field of lead-free piezoelectric materials.

\* Corresponding author: lylll2004@aliyun.com  
<https://doi.org/10.15251/DJNB.2022.171.121>

KNN ceramics have the greatest advantage of high Curie temperature, at the same time with outstanding piezoelectric and electromechanical properties. However, KNN ceramic system also has its own defects: poor preparation technology, alkali metal elements of K and Na tend to volatile at high temperature. In order to overcome the shortcomings of KNN ceramics, researchers have improved the properties of KNN ceramics by doping modification and preparation process [12,13].

$\text{Li}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Bi}^{3+}$ , which have similar ionic radius and electronegativity to K and Na, can be used to replace A sites.  $\text{Zr}^{4+}$ ,  $\text{Hf}^{5+}$  and  $\text{Ta}^{5+}$ , which have similar ionic radius and electronegativity with  $\text{Nb}^{5+}$ , can be used to replace B sites. Some  $\text{ABO}_3$  perovskite structures (such as  $\text{CaZrO}_3$ , etc.) allow simultaneous substitution of A and B sites [14]. After doping substitution, due to the difference of ion radius and electronegativity, the lattice of KNN will be distorted to some extent, so that a certain small stress will be generated inside the crystal cell of KNN. The substitution of ions can not only lead to stress in the crystal cell, but also change the phase transition temperature. Therefore, the phase boundary structure of KNN ceramics can be adjusted and the piezoelectric properties of KNN ceramics can be tailored.

$\text{Sb}^{5+}$  can partially replace the B site  $\text{Nb}^{5+}$  in  $\text{ABO}_3$  perovskite structure. In addition, as a soft doping element,  $\text{Sb}^{5+}$  can reduce the coercivity field and cause the tripartite orthogonal phase transition to move to room temperature, and the orthogonal tetradral phase transition to room temperature, resulting in relaxation ferroelectric. In this paper,  $\text{LiSbO}_3$  is used as dopant to improve the piezoelectric properties, and the effects of  $\text{LiSbO}_3$  content on the crystal structure, microstructure, dielectric properties and piezoelectric properties of KNN base ceramics were studied.

## 2. Experimental

The general formula of the ceramics was  $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ -x mol%  $\text{LiSbO}_3$  (x=0.00, 0.01, 0.02, 0.03, 0.04 and 0.05). The samples were obtained by the two-stage method to guarantee access to a pure phase of perovskite. Reagent-grade oxide powders,  $\text{K}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{Sb}_2\text{O}_3$  and  $\text{Nb}_2\text{O}_5$ , were used as the starting materials. Firstly, a powder of  $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ , was obtained by sintering  $\text{K}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{Nb}_2\text{O}_5$ , at  $850^\circ\text{C}$  for 4 h. Secondly, the above precursor with  $\text{Li}_2\text{CO}_3$  and  $\text{Sb}_2\text{O}_3$  was weighed, and mixed through a polyethylene jar and agate balls milling media. The mixture was then dried at  $120^\circ\text{C}$ , granulated (with polyvinyl alcohol as binder), pressed into the desired form ( $\Phi \times d = 12.00 \times 2.00 \text{ mm}^2$ ) at 10 Mpa, and then sintered at  $1140^\circ\text{C}$  for 3 h in the air. The sintered samples were cleaned using an ultrasonic bath, then dried. Both sides of the specimens for dielectric property measurements were screened electrode paste composing mainly of AgO, some fluxes and binders, then fired at  $650^\circ\text{C}$  for 10 min.

The crystal phase of the specimen was determined by X-ray diffraction (XRD, Model RIGAKU D/MAX 2500V/PC, Japan) with a  $2\theta$  range from  $10^\circ$  to  $70^\circ$ . The surface micrographs of the samples were examined by field emission scanning electron microscopy (SEM, Hitachi s4800). Room-temperature dielectric constant and dielectric loss were measured by a LCR meter (WK4225, China). The temperature dependence of dielectric constant ( $\epsilon$ ) and dielectric loss ( $\tan\delta$ ) was measured using a capacitance apparatus (WK4225, China) at 1 kHz range over  $25^\circ\text{C}$  to  $500^\circ\text{C}$ . The piezoelectric coefficient  $d_{33}$  of the specimen was measured by a quasi-static piezo- $d_{33}$  meter (ZJ-4 A, China).

## 3. Results and discussions

The XRD patterns of KNN ceramics doped with different content of  $\text{LiSbO}_3$  sintered at  $1140^\circ\text{C}$  for 3 h are shown in Fig. 1. As can be seen from Fig. 1(a), all KNN samples with different  $\text{LiSbO}_3$  components form a single orthogonal phase perovskite, and no second phase diffraction peak is observed, which indicates that there is no impurity in the ceramics.

Fig. 1(b) is a local magnification of the diffraction angle range from  $44^\circ$  to  $49^\circ$ . The phase structure can be judged by observing the intensity of diffraction peak, that is, the former diffraction peak is high and the latter diffraction peak is low, the sample presents the orthogonal phase structure, while the former diffraction peak is low and the latter diffraction peak is high, the sample is tetragonal phase structure. Obviously, from Fig. 1(b), it can be found that the KNN ceramics with different content of  $\text{LiSbO}_3$  exhibit an orthogonal phase. With the increase of doping amount, the ratio of the diffraction peak strength before and after decreases gradually, and the KNN ceramics at room temperature have a trend of phase transition, the results show that the new phase structure of KNN ceramics can not be obtained when the  $\text{LiSbO}_3$  content is  $0.00 \leq x \leq 0.05$ .

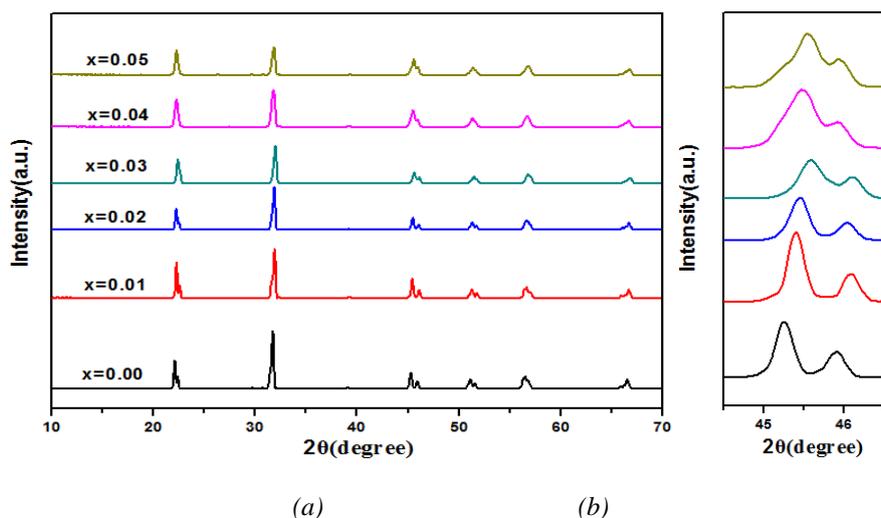


Fig. 1. XRD patterns of  $\text{KNN-xLiSbO}_3$  ceramics.

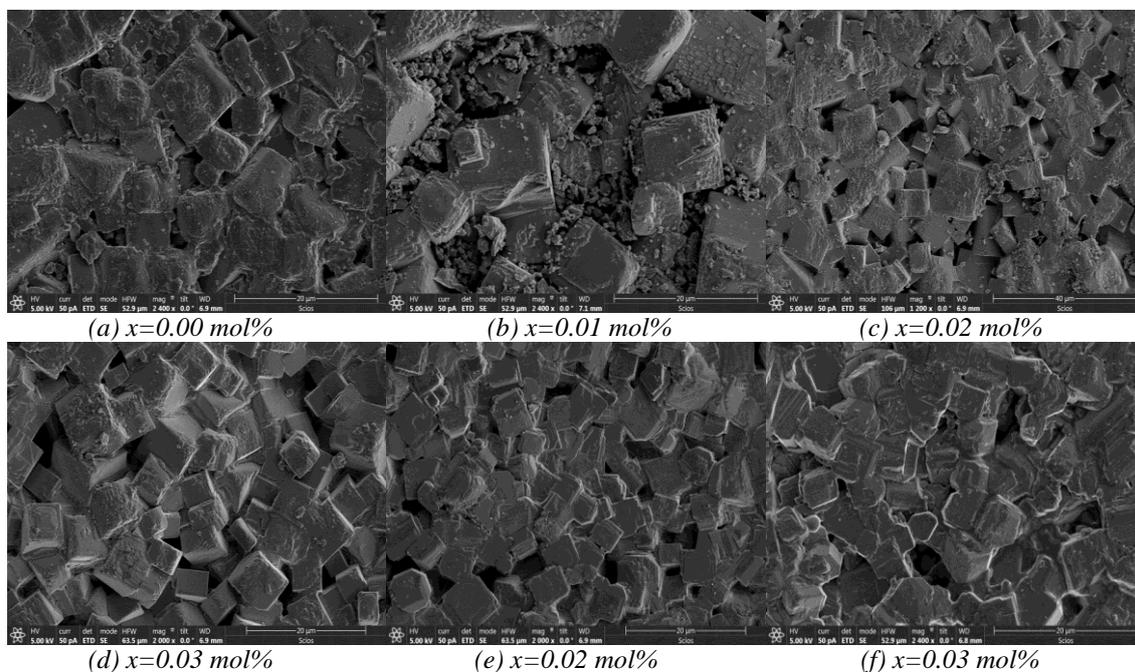


Fig. 2. SEM images of  $\text{KNN-xLiSbO}_3$  ceramics.

The SEM images patterns of KNN ceramics doped with different content of  $\text{LiSbO}_3$  sintered at  $1140^\circ\text{C}$  for 3 h are shown in Fig. 2. As can be seen from Fig. 2, in the pure KNN

ceramics, the ceramic grains are surrounded by relatively clear outline, but the size varies, and generally the large grains are surrounded by the small grains. When  $x = 0.05$ , the crystal grain becomes fuzzy, which indicates that the excess liquid phase in the sintering process of KNN ceramics changes into glass phase, the normal development of grains is hindered. The bulk density of ceramic samples was measured by Archimedes' principle method. The bulk density of ceramic samples were  $3.91 \text{ g/cm}^3$ ,  $4.02 \text{ g/cm}^3$ ,  $4.08 \text{ g/cm}^3$ ,  $4.23 \text{ g/cm}^3$  and  $4.30 \text{ g/cm}^3$ , respectively. Obviously, the bulk density of the samples increases with the increase of  $\text{LiSbO}_3$  doping amount. Therefore, appropriate amount of  $\text{LiSbO}_3$  doped KNN ceramics can refine the grain size and increase the density of the ceramics.

At Room temperature and at 1 kHz, the dielectric constant-doping amount and dielectric loss-doping amount of the samples are shown in Fig. 3. As can be seen from Fig. 3, the effect of  $\text{LiSbO}_3$  dopant content on dielectric constant and dielectric loss of KNN ceramics at room temperature is significant. With the increase of the content of  $\text{LiSbO}_3$ , the dielectric constant of KNN ceramics at room temperature first increases and then decreases, but the dielectric constant of KNN ceramics increases compared with that of pure KNN ceramics at room temperature, and the dielectric loss of KNN ceramics increases at first and then decreases. With the increasing of the  $\text{LiSbO}_3$  content, the grains tend to be homogenized, and the substitution of  $\text{Li}^+$  and  $\text{Sb}^{5+}$  for the ions at the A and B positions of the Perovskite structure lead to the lattice shrinkage and the increase of the density of the ceramics, thus increasing the dielectric constant. When  $x = 0.04$ , the relative dielectric constant reaches 980, the dielectric loss is 0.055, and the combined effect of  $\text{Li}^+$  and  $\text{Sb}^{5+}$  makes the KNN ceramics have better dielectric properties.

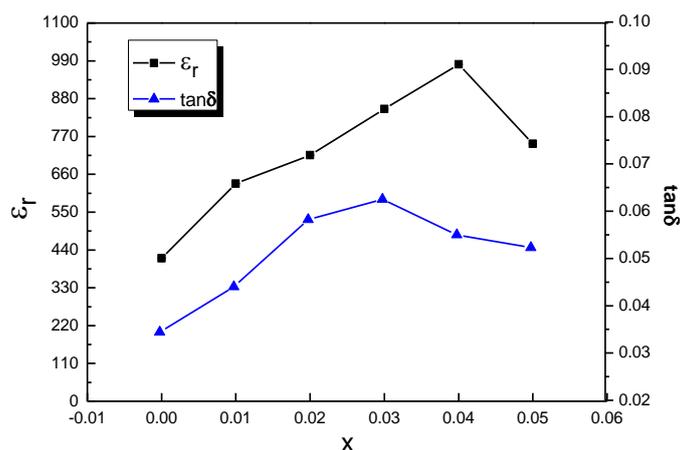


Fig. 3. Dielectric properties of  $\text{KNN-xLiSbO}_3$  ceramics.

The dependence of dielectric constant and dielectric loss on temperature for the  $\text{LiSbO}_3$  doped samples is shown in Fig. 4. As can be seen from Fig. 4, the samples with different doping have two abnormal dielectric peaks, which correspond to the phase structure transition of orthogonal-tetragonal phase and tetragonal-cubic phase, respectively, the orthogonal-tetragonal phase transition temperature ( $T_{o-t}$ ) of pure KNN ceramics is  $225 \text{ }^\circ\text{C}$ , and the tetragonal-cubic phase transition temperature ( $T_C$ ) is  $420 \text{ }^\circ\text{C}$ .  $T_C$  is called Curie temperature. With the addition of  $\text{LiSbO}_3$ , the transformation temperature of tetragonal-cubic phase decreased gradually from  $420 \text{ }^\circ\text{C}$  to  $300 \text{ }^\circ\text{C}$ , which was due to the decrease of the stability of KNN ceramics with the addition of  $\text{LiSbO}_3$ , and the transition temperature of orthogonal-tetragonal phase gradually moved to room temperature. When  $x = 0.04$ , the dielectric peak of pure KNN ceramics is 5029, which shows excellent dielectric properties.

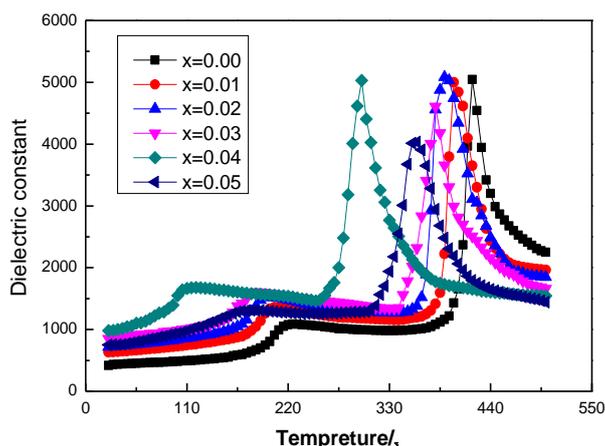


Fig. 4. The dependence of dielectric constant of KNN-xLiSbO<sub>3</sub> ceramics.

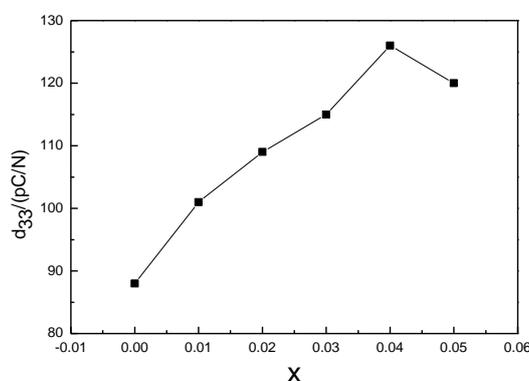


Fig. 5. Relationship between the LiSbO<sub>3</sub> doping amount and  $d_{33}$ .

Fig. 5 shows the relationship between the piezoelectric constant  $d_{33}$  and the LiSbO<sub>3</sub> doping amount. With the increase of LiSbO<sub>3</sub> content, the piezoelectric constant  $d_{33}$  increases first and then decreases. When  $x = 0.04$ , the piezoelectric constant  $d_{33}$  increases sharply to the maximum value of 126 pC/N. The addition of Li<sup>+</sup> and Sb<sup>5+</sup> leads to lattice distortion and spontaneous polarization in ceramics. Much research show that the high-voltage electric properties tend to appear on the side of tetragonal phase, that is, near the quasi-isotype phase boundary (MPB). At this point, the domain wall is more active, and the domain wall is easier to move and rotate. In addition, the higher the density, the more easily the domain wall rotates at the grain boundary, hence the ceramics doped with 4 mol% LiSbO<sub>3</sub> shows excellent piezoelectric properties.

#### 4. Conclusions

(K<sub>0.5</sub>Na<sub>0.5</sub>)NbO<sub>3</sub>-x mol% LiSbO<sub>3</sub> ceramics were prepared by a solid phase reaction method using K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, Li<sub>2</sub>CO<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub> and Nb<sub>2</sub>O<sub>5</sub> as raw materials, and the influence of LiSbO<sub>3</sub> content on piezoelectric and dielectric properties were investigated. The crystal structure for KNN based ceramics with different LiSbO<sub>3</sub> content presents the orthogonal phase structure, and the new phase structure of KNN ceramics can't be obtained when the LiSbO<sub>3</sub> content is  $0.00 \leq x \leq 0.05$ . Owing to the substitution of Sb<sup>5+</sup> for the ions at the B positions, thus increasing the dielectric constant, and when  $x = 0.04$ , the relative dielectric constant reaches 980. Due to the more easily the domain wall rotates at the grain boundary, KNN based ceramics doped with 4 mol% LiSbO<sub>3</sub> shows excellent piezoelectric properties in the system of study, and the piezoelectric constant  $d_{33}$  increases sharply to the maximum value of 126 pC/N.

### Acknowledgements

This work is supported by the Science and Technology Support Project of Hebei Province, China (Grant No. 15211111).

### References

- [1] H. J. Lee, H. Y. Park, Y. G. Jung et al, *Ceramics International* 47, 3867 (2021); <https://doi.org/10.1016/j.ceramint.2020.09.247>
- [2] Z. L. Fu, Y. F. Liu, B. Zhang, et al. *Journal of the American Ceramic Society* 103, 6586 (2020).
- [3] H. L. Ferrand, *Journal of the European Ceramic Society* 41, 24 (2021); <https://doi.org/10.1016/j.jeurceramsoc.2020.08.030>
- [4] P. Kour, S. K. Sinha, *Digest Journal of Nanomaterials and Biostructures* 7, 1327 (2012).
- [5] M. Z. Sun, J. Du, C. Chen et al, *Ceramics International* 46, 17351 (2020).
- [6] S. C. Lee, L. Wang, M. H. Lee et al, *Ferroelectrics* 401, 81(2010); <https://doi.org/10.1080/00150191003676595>
- [7] B.S. Kim, J. H. Ji, J. H. Koh, *Ceramics International* 47, 6683 (2021); <https://doi.org/10.1016/j.ceramint.2020.11.008>
- [8] D. White, X. Zhao, X. Tan, *Journal of Materials Science* 43, 5258 (2008).
- [9] T. N. Nguyen, H. C. Thong, Z. X. Zhu et al, *Journal of Materials Research* 36, 996 (2021); <https://doi.org/10.1557/s43578-020-00016-1>
- [10] L. Qiao, G. Li, F. Li, *Ceramics International* 46, 5641 (2020); <https://doi.org/10.1016/j.ceramint.2019.11.009>
- [11] Y. Saito, H. Takao, T. Tani et al, *Nature* 432, 84 (2004); <https://doi.org/10.1038/nature03028>
- [12] D. Q. Xiao, J. G. Zhu, *Ferroelectrics* 404, 10 (2010); <https://doi.org/10.1080/00150193.2010.481983>
- [13] T. A. Duong, F. Erkinov, M. Aripova et al, *Ceramics International* 47, 4925 (2021); <https://doi.org/10.1016/j.ceramint.2020.10.066>
- [14] T. Yan, F. Han, S. Ren et al, *Materials Research Bulletin* 99, 403 (2018).