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# 铌酸钾钠基无铅压电陶瓷性能研究现状及展望

赵静波[1]，屈绍波[1]，杜洪亮[2]，郑艳菊[3]，莫卫东[1]，杨　鸣[1]
(1.空军工程大学　理学院，陕西　西安　710051;2.西北工业大学　凝固技术国家重点实验室，陕西　西安　710072;3.河北大学　化学与环境学院，河北　保定　071000)

**摘　要**:伴随着科学技术的发展和人类环保意识的增强,压电陶瓷无铅化已经成为必然趋势,而铌酸钾钠KNN($K_xNa_{(1-x)}NbO_3$)基陶瓷以其优异的压电性能和较高的居里温度倍受关注。文中着重从新的组元、离子取代改性、烧结助剂和温度稳定性4个方面总结和分析了近年来KNN基无铅压电陶瓷研究状况,认为进一步提高KNN基陶瓷的电性能,解决温度稳定性问题并深入探索其微观机制应该成为未来的研究热点。提出了把弛豫机制引入KNN基陶瓷中,造成弥散相变,这样既提高了温度稳定性,又保持了较高的介电和压电性能;同时提出要探索纳米微畴对KNN基无铅压电陶瓷电性能的影响;最后对KNN基陶瓷下一阶段的工作进行了展望。

**关键词**:铌酸钾钠(KNN);无铅压电陶瓷;压电性能;纳米微畴
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压电材料作为一种高新技术材料,自19世纪80年代居里兄弟在石英晶体上发现压电效应以来,就引起了迅速的研究和发展,并广泛应用于信息、导航和生物技术领域。1952年,东京工业大学高木研究室对锆酸铅($PbZrO_3$)、钛酸铅($PbTiO_3$)固溶体($PbZr_xTi_{1-x}O_3$)进行了研究,引起了世界范围内锆钛酸铅(PZT)陶瓷研究蓬勃发展的新局面,此后半个多世纪以来,锆钛酸铅固溶体一直占据压电陶瓷的主导地位。但是锆钛酸铅(PZT)陶瓷中氧化铅的含量超过原料总质量的60%以上,氧化铅是一种易挥发的有毒物质,在生产、使用及废弃处理过程中都会给人类和生态环境造成严重污染。

近年来,有关无铅压电陶瓷研究的体系主要有($Bi_{1/2}Na_{1/2}$)$TiO_3$系[1-3]、$BaTiO_3$[4]系、$Bi_4Ti_3O_{12}$[5-6]铋层状结构和铌酸钠钾($K_xNa_{1-x}NbO_3$)[7]系,其中($Bi_{1/2}Na_{1/2}$)$TiO_3$基陶瓷具有烧结温度低、介电常数低和频率常数大等高频应用的优点,但是其退极化温度太低限制了它的应用,压电常数$d_{33}$高达231 pC/N的$Bi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}TiO_3$,退极化温度只有130 ℃[8]。$BaTiO_3$基陶瓷居里温度低(120 ℃)、工作温度范围窄限制了它的应用。铋层状结构陶瓷具有高居里温度和高温电阻率高等特点使它在高温高频领域得到了应用,但是由于结构上受到较大的二维限制,使得它矫顽场很高,极化困难,压电活性低,限制了它在常温和低温领域的应用,纯的$CaBi_4Ti_4O_{15}$的压电常数$d_{33}$只有6 pC/N。而相对来说,KNN基无铅压电陶瓷以其相对优越的压电性能和较高的居里温度倍受关注,特别是2004年,Yasuyoshi Salto等人[9]采用反应模板生长法制备出了压电常数$d_{33}$高达416 pC/N的$NaNbO_3$基陶瓷,用传统电子陶瓷工艺研制的KNN - $LiSbO_3$ - $LiTaO_3$的$d_{33}$高达300 pC/N,其性能完全可以与PZT陶瓷相比较,显示出无铅压电材料巨大的应用前景。

## 1　KNN陶瓷研究现状

众所周知,PZT陶瓷具有优异的压电性能,而KNN陶瓷与PZT陶瓷相比至少有3个共同特征:①它们同

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**作者简介**:赵静波(1980-),男,山西长治人,博士生,主要从事电子材料及应用研究;E-mail:chjzjb@163.com
屈绍波(1965-),男,安徽阜阳人,教授,博士生导师,博士(后),主要从事电子材料及应用研究.

属钙钛矿结构,都可以用公式 $A^{12}B^{6}O_3^{6}$ 型表示，上标为配位数,钙钛矿结构铁电体的自发极化主要来源于 B 位离子偏离八面体中心的运动,由于钙钛矿结构的特点，具有钙钛矿结构的铁电体都具有多个自发极化方向,例如四方相结构有 6 个自发极化方向,菱方相结构有 8 个自发极化方向,正交相有 12 个自发极化方向,故一般具有钙钛矿结构的压电陶瓷都具有较高的压电性能[10]；②在 PZT 系中,$PbZrO_3$ 是反铁电体，$PbTiO_3$ 是铁电体,二者可以无限固溶,结构为钙钛矿结构。而在 KNN 系中,$NaNbO_3$ 属于反铁电体 $KNbO_3$ 属于铁电体，两者也可以无限固溶,结构仍为钙钛矿结;③KNN 和 PZT 均有一个准同型相界(MPB),且在相界处压电性能较高。正是由于 KNN 与 PZT 具有上述相似的特征,因此 KNN 也吸引了国内外学者的广泛关注。

1959 年,Egerton 和 Dillon[11]首次报道了 KNN 陶瓷具有压电性,且当 $x=0.5$ 时,也有一个准同型相界(MPB)，此时，压电性能最好，压电常数 $d_{33}$ = 80 pC/N,$k_p$ = 36%，KNN 体系的居里温度也较高(420 ℃),也使其成为最有希望取代 PZT 基的新型压电陶瓷材料。但是,与 PZT 陶瓷相比,KNN 基陶瓷也有显著的缺点:①由 KNN 相图(图 1)[12]可以看出,KNN 陶瓷相稳定温度只有 1 140 ℃,较低的烧结温度难以使陶瓷致密化;②在烧结过程中,碱金属元素 K 和 Na 极易挥发,造成化学计量比的偏离,生成杂相 $K_4NbO_7$,极易潮解,所以使用传统烧结工艺很难制备出致密的 KNN 陶瓷,造成 KNN 陶瓷应用受到极大限制[13]。

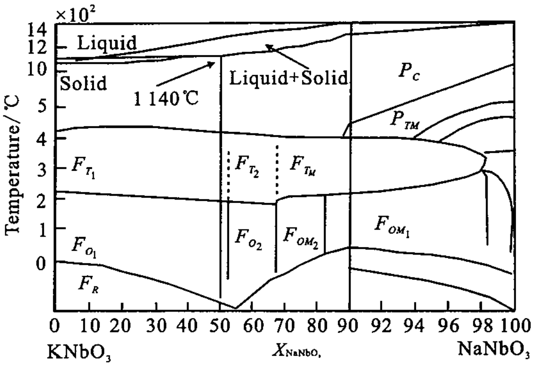

图 1 KNN 陶瓷相图

Fig. 1 KNN ceramics phase chart

## 2 研究热点

为了克服这些缺点,近年来国内外学者重点从提高性能和稳定性 2 个方面进行了大量研究。

### 2.1 引入新的组元

通过前面的分析,我们知道 PZT 陶瓷在 MPB 处具有高的性能,无论是由于两相共存的不稳定状态造成的,还是因为在 MPB 处出现了对称性更低的单斜或三斜相,总之,在准同型相界处 PZT 陶瓷具有优异的介电和压电性能是被广为认可的。因此在具有与 PZT 类似结构和相同特征的 KNN 陶瓷中引入新的组元,以形成 MPB,从而提高 KNN 陶瓷的电性能是可行的。近两年来国内外学者进行了广泛的研究,取得了显著效果。Ruzhong Zuo 等人[14]采用传统固态烧结法制备了$(1-x)(Na_{0.475}K_{0.475}Li_{0.05})NbO_3-x(Bi_{0.48}Na_{0.48}Ba_{0.04})TiO_3$ $(x=0-0.15)$压电陶瓷,当 $x=0.02$ 时,形成 MPB,在该相界处压电常数 $d_{33}$高达 328 pC/N,平面机电耦合系数 $k_p=0.48$,居里温度高达 415 ℃,但是没有给出铁电性能。表 1 给出了近几年来采用传统陶瓷工艺制备的具有较高介电、铁电和压电性能的 KNN 基陶瓷[14-17]。

表 1 KNN 基压电陶瓷在 MPB 处的介电、铁电和压电性能

Tab. 1 Dielectric, ferroelectric and piezoelectric properties of KNN - based piezoelectric ceramics

| Composition | MPB $x$ = mol | $d_{33}$ | $T_c$ | $k_p$ | $E_c$ /(kV · cm$^{-1}$) | $P_r$ /(μC · cm$^{-2}$) | $\varepsilon_r$ | tan $\delta$ |
|---|---|---|---|---|---|---|---|---|
| $(1-x)(Na_{0.475}K_{0.475}Li_{0.05})NbO_3-x(Bi_{0.48}Na_{0.48}Ba_{0.04})TiO_3$ | 0.02 | 328 | 415 | 0.48 | | | 702 | |
| $xLiNbO_3-(1-x)(Na_{0.535}K_{0.480})NbO_3$ | 0.058 | 314 | 490 | 0.42 | | 13.7 | | |
| $(1-x)(K_{0.4}Na_{0.6})NbO_3-xLiSbO_3$ | 0.05 | 280 | 364 | 0.494 | 14 | 30.8 | 1 463 | 0.023 |
| $KNN-xBiFeO_3$ | 0.01 - 0.02 | 185 | 370 | 0.46 | | 23.3 | | |

### 2.2 KNN 基陶瓷离子取代改性

离子取代作为陶瓷材料改性的重要手段,已广泛应用于各种体系材料的研究中,对于钙钛矿结构的材料,离子取代主要是指对 A、B 位的取代。近年来 KNN 陶瓷的离子取代已经引起了国内外学者的广泛关注。

表2列出了近年来采用传统陶瓷工艺制备的A、B位取代改性后的KNN基陶瓷的性能[18-21]。E. K. Akdoan等人[18]采用传统固相法制备了$K_{0.44}Na_{0.52}Li_{0.04}-Nb_{0.84}Ta_{0.1}Sb_{0.06}O_3$陶瓷，测得室温$d_{33}$高达345 pC/N，主要原因归结为通过离子取代，在室温附近出现了四方和正交相共存的结构，这种不稳定的多晶转变[22]（PPT）结构有利于压电性能的提高，但是正是因为高的压电常数来自于室温时的多晶转变（PPT），所以其性能的温度稳定性必然较差，制约其应用，这也应该成为将来的研究热点。

表2　A、B位取代改性后的KNN基陶瓷的性能

Tab. 2　Modified KNN - based ceramics properties

| Composition | $d_{33}$ /(pC·N$^{-1}$) | $T_c$ /℃ | $k_p$ | $E_c$ /(kV·cm$^{-1}$) | $P_r$ /(μC·cm$^{-2}$) | $\varepsilon_r$ | tan $\delta$ |
|---|---|---|---|---|---|---|---|
| $K_{0.44}Na_{0.52}Li_{0.04}-Nb_{0.84}Ta_{0.1}Sb_{0.06}O_3$ | 345 | 264 | | | | | |
| $K_{0.38}Na_{0.58}Li_{0.04}(Nb_{0.91}Ta_{0.05}Sb_{0.04})O_3$ | 306 | 337 | 0.48 | 11.3 | 34.9 | 1 327 | 0.025 |
| $(Na_{0.52}K_{0.433}Li_{0.047})Nb_{0.923}Sb_{0.047}Ta_{0.03}O_3$ | 308 | 339 | 0.51 | | | 1 009 | 0.02 |
| $[(K_{0.458}Na_{0.542})_{0.96}Li_{0.04}](Nb_{0.85}Ta_{0.1})O_3$ | 298 | 366 | 0.52 | 7.14 | 28.68 | 1 195 | 0.016 |

## 2.3　添加烧结助剂

添加烧结助剂目的是在烧结过程中产生液相，这是降低烧结温度的一种有效的方法。液相烧结中的晶粒重排、强化接触可提高晶界迁移率，使气孔充分排出，促进晶粒的发育，提高瓷体致密度，达到降低烧结温度的目的，但是这些液相在烧结的后期会留在陶瓷晶界处，恶化材料的介电和压电性能，所以为了降低烧结温度，同时又保持好的压电性能，必须选择合适的烧结助剂，使其在烧结的中间阶段存在液相，烧结后期全部进入晶粒，与基体材料完全形成固溶体。实验证实，少量的助烧剂可以在烧结过程中，产生液相，但是过量的烧结剂会恶化其电性能[23]。表3给出了近两年KNN基陶瓷添加烧结助剂后的性能[24-28]。

表3　KNN基陶瓷添加烧结助剂后的性能

Tab. 3　The properties of KNN - based ceramics with sintering reagent

| Composition | density /(g·cm$^{-2}$) | $d_{33}$ /(pC·N$^{-1}$) | $T_c$ /℃ | $k_p$ | $\varepsilon_r$ | tan $\delta$ |
|---|---|---|---|---|---|---|
| KNN - $0.05LiTaO_3$ + 1% $Li_2O$ | 4.51 | 250 | | 0.37 | 440 | 0.043 |
| KNN + $0.005K_{1.94}Zn_{1.06}Ta_{5.19}O_{15}$ | 4.34 | 126 | | 0.42 | 590 | |
| $(K_{0.5}Na_{0.5})NbO_3$ - 0.5 wt% $Bi_2O_3$ | 4.48 | 140 | | 0.46 | | |
| $(KN)(Nb_{0.97}Sb_{0.03})O_3$ + 2mol% CuO | 4.13 | 111 | 410 | 0.41 | 324 | |
| $100(KN)(Nb_{0.67}Ta_{0.33})O_3$ - 1.4Mn + $K_{4.1}CuTa_{7.7}O2_{2.3}$ + ZnO | | 240 | 193 | 0.45 | 1 490 | 0.017 |

## 2.4　KNN基陶瓷温度稳定性的研究

近年来，虽然KNN基陶瓷性能得到显著提高，传统陶瓷工艺制备的陶瓷室温压电系数已经大于300 pC/N[18-20]，居里温度也超过了400 ℃[14-15]，但是，高性能的原因主要是由于KNN基陶瓷经改性后在室温附近产生了一个多晶相变（PPT），正是由于多晶相变的不稳定性或者低对称性导致了KNN基陶瓷的异常，而当温度变化时，其性能极不稳定，甚至迅速降低，这完全不符合工业应用的要求。关于KNN基陶瓷温度稳定性，许多学者进行了研究。Shujun Zhang[29]等人利用$CaTiO_3$（CT）改性KNN - $LiSbO_3$（LS）陶瓷，使得PPT（四方相和正交相）的转变温度移至室温以下，图2中a、b、c分别表示KNN - $LiSbO_3$陶瓷、KNN - $LiSbO_3$中添加后量百分比为2%的$CaTiO_3$陶瓷、KNN - $LiSbO_3$中添加后量百分比为1% $CaTiO_3$陶瓷3种情况下压电常数随温度变化的情况。由图2可以看出，在 -50℃ -200℃，KNN - $LiSbO_3$陶瓷具有优异的温度稳定性，$d_{33}$ = 210 pC/N，$d_{15}$ = 268 pC/N，$k_{33}$ = 61%，$k_{15}$ = 56%；杜洪亮等人[30]把$BiScO_3$引入KNN陶瓷中，发现0.04BS - 0.96KNN陶瓷在100℃ -300℃，相对介电常数保持稳定（约2 500），同时介电损耗小于0.05。此外，Jiagang Wu[31]，Ling Wu[32]等人也进行了相关研究，取得了较好的结果。

经过国内外学者的共同努力,KNN 基陶瓷温度稳定性的研究取得了很好的成果,然而我们认为,目前对于 KNN 基陶瓷温度稳定性研究的基本思路是扩展 $T_{c-T}$和 $T_{T-O}$之间的距离,这样虽然温度稳定性得到提高,但是 KNN 基陶瓷在相变点处产生的高性能并没有被充分利用,所以我们认为在 KNN 基陶瓷中引入类似 PMN[33] 陶瓷的弛豫机制,造成在 $T_{T-O}$和 $T_{c-T}$处的弥散相变,这样既提高了温度稳定性,又保持了较高的介电和压电性能。

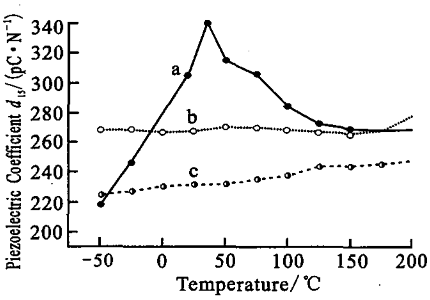

图 2 $CaTiO_3$ 改性的 KNN – $LiSbO_3$ 陶瓷压电常数温度稳定性

Fig. 2 The temperature stability of $CaTiO_3$ modified KNN – $LiSbO_3$ ceramics

## 3 KNN 基陶瓷研究展望

近年来,KNN 基陶瓷在制备和性能方面都取得了长足的进步,从目前的研究状况来看,主要存在以下几个问题,这些问题可能是下一步研究的重点:

1)KNN 基陶瓷的压电、介电和铁电性能还需进一步提高。为了满足目前工业生产中对材料在高温、高频等多领域的要求,还需要通过引入新组元,掺杂改性、工艺优化、添加烧结助剂等多种措施提高性能。

2)KNN 基陶瓷温度稳定性也可能成为下一阶段研究的热点。由于任何陶瓷在特定温度下的高性能对于工业应用是没有太大意义的,所以在宽广的温度范围内具有稳定的高性能应该成为研究的重点。这主要有 3 种途径:①通过掺杂改性扩展两个相变点间的距离;②把弛豫机制引入 KNN 基陶瓷中,造成在 $T_{T-O}$和 $T_{c-T}$处的弥散相变,这样既提高了温度稳定性,又保持了较高的介电和压电性能;③类比 PZT 相图,通过引入新的组元使得 KNN 相图(见图 1)中的正交相和四方相的相界倾斜,甚至尽量垂直于成分轴。

3)KNN 基陶瓷高性能的微观机制应该成为研究的热点,特别是人们使用最新的技术设备发现了导致 PZT 高性能的新的纳米微畴,那么对 KNN 基陶瓷也应该展开类似的深入研究。

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# Actuality and Prospect of Potassium Sodium Niobium Based Lead - free Piezoelectric Ceramics

ZHAO Jing - bo[1], QU Shao - bo[1], DU Hong - liang[2], ZHENG Yan - ju[3],MO Wei - dong[1],YANG ming[1]

(1. Science Institute Air Force Engineering University, Xi'an 710051, China; 2 State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an 710072, China; 3 The College of Chemistry & Environmental Science, Hebei University, Baoding 071000, Hebei ,China)

**Abstract:** With the development of science and technology and environment, lead - free piezoelectric ceramics has been a necessary trend, and potassium - sodium niobium (KNN) based lead - free piezoelectric ceramics has become a hotspot because of its high Curie temperature and piezoelectric properties. This paper firstly summarizes and analyzes the study direction and actuality of potassium - sodium niobium (KNN) based lead - free piezoelectric ceramics from new component, ions substitute, sintering reagent and temperature dependence in recent years, and then indicates the future hotspot and problem. We think it can improve the temperature stability to introduce diffusion mechanism into KNN based ceramics. Meanwhile, we also should study the effect of nano - sized domain on properties of KNN ceramics. At last, the paper forecasts the future study direction——the study of electric properties, of temperature stability and micro mechanism.

**Key words:** potassium - sodium niobium (KNN); lead - free piezoelectric ceramics; piezoelectric properties; nano - sized domain

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# Study of Intrusion Deception System Based on Network Proactive Defensive Security Model

ZHAO Hong - jing[1], ZHOU Chuang - ming[1], ZHAI Ping - li[2], YU Huan[3], ZHAO Ming - li[4]
(1. Missile Institute, Air Force Engineering University, Sanyuan 713800, Shaanxi, China; 2. Unit 93861, Sanyuan 713800, Shaanxi, China; 3. Siasun Robot & Automation Co. LTD, Shenyang 110168, China; 4. No. 631 Military Representative Room of PLA, Xi'an 710068, China)

**Abstract:** The situation of present network security is becoming rigorous day by day, the traditional security technologies such as firewall, intrusion detective system have some kinds of defects, that is, they cannot identify the unknown intrusion pattern effectively, the honeypot technology as a proactive defense method also has its own limitations. As to the defaults of the above every single technology and from the angle of active defense, the paper builds up an Intrusion deception architecture based on network active defensive security model, and simultaneously designs an interface system among the honeypot, firewall and the IDS to overcome the default that the firewall can not perform unreal time detection. This can decrease the false alarm and leaking alarm of IDS, make up the deficiency and unleash the superior of each method, thus, the proactive defense capacity of the network systems is enhanced. The paper also gives out a finite state auto - machine model, simulates the basic functions of the intrusion deception system, which provide a theory and reasoning supplement for the system's action description and architecture design.

**Key words:** proactive defense; intrusion deception; Honeypot; virtual network server; finite state auto - machine