Structure and properties of (Cu Ca Bi) doped KNN lead-free piezoceramics

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Lead free ceramics in the system (1-x)KNN·x(Bi_2O_3,CaO,CuO) with 0.0≤x≤0.1 were synthesized by the usual solid state reaction and their structural and piezoelectric properties were investigated. Dense samples with densities of about 4.68 g/cm^3 were prepared by sintering at an optimum temperature of 1150 ^{o}C for 6 h. Only perovskite phase was detected by X-ray investigation in all samples. A typical MPB where orthorombic-tetragonal phases coexist was detected for a doping level of 0.06 where the piezoelectric parameters showed maximum values. Planar coupling factor, as much as 0.46, piezoelectric charge constant of 270 pC/N and mechanical quality factor Q_m of 75 were recorded for the samples situated within the MPB.

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1. Introduction

Among the family of electroceramic materials the lead zirconate – lead titanate solid solutions, with their excellent properties, play the major role and the market is dominated by these lead-based PZT type materials. The main drawback of PZT is their high content (over 60%) of lead, a heavy toxic metal which by inhaling may provokes headaches, nausea, anaemia, reduced fertility. In addition, a continuous and uncontrolled exposure could cause more serious symptoms such as nerve, brain and kidney damage [1].

Consequently, great efforts are made in order to eliminate leads in many products and the recent UE directives put severe restriction on the use of hazardous substances in electronic equipments [2, 3]. Therefore, finding alternatives or replacements for the conventional lead based materials with lead free systems becomes the goals for almost all research centers in the world. In this regard, alkali niobates (K, Na)NbO_3 (denoted shortly as KNN), seem to offer comparable properties to that of PZT ceramics making them the most suitable for various applications. At present there are many works dealing with this subject [4-18]. Difficulties in obtaining good KNN ceramics arises from sintering since stoichiometric materials of high densities are extremely difficult to consolidate [1, 9, 13, 14]. Therefore some strategies have been used in the past to overcome this problem. Among them hot pressing or hot isostatic pressing, produced high density ceramic bodies [19, 20]. But the most common way to promote densification is the use of additives like Ba, Mg, Ca, Sr, or Nb in excess which introduce A site vacancies into the perovskite lattice which indeed promote densification [11, 21].

In this contribution we investigated the effect of Cu, Ca and Bi addition on the sinterability and the properties of KNN ceramics. The additives were chosen on the basis of their similar ionic radii to those of K and Na [22]. It is known [12, 14] that KNN exhibits a morphotropic phase boundary at around $K_{0.5}Na_{0.5}NbO_3$, separating two orthorombic phases where the properties show maximum values.

2. Experimental

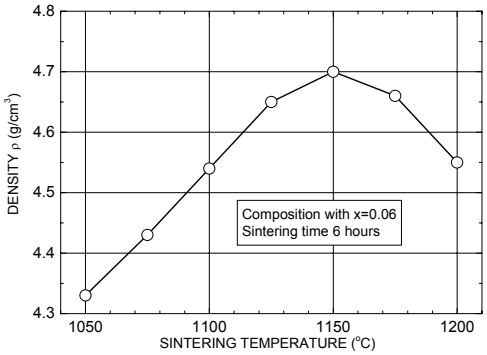
There are several problems involved in synthesising KNN ceramics like, for example, the stability of precursors (alkali elements), the milling process and the sintering temperature. The chemical formula of the material was as follows: (1-x)($K_{0.5}Na_{0.5}$)O_3·x($Cu_{1/3}CaO_{1/3}Bi_2O_{3\ 1/3}$).

The ceramics were prepared by the usual solid state synthesis using high purity grade (over 99.5%) raw materials oxides and carbonates from Fluka, Aldrich, Riedel de Haen and Merck. The particle size distribution of all raw materials were optimised firstly by milling them separately for 5 hours in acetone in a planetary ball mill Retsch PM400 in agate vessels. After drying the starting materials were weighted according to the desired composition and mixed in the same planetary ball mill for 6 hours. The milled powders were double calcinated at 850 ^{o}C and 900 ^{o}C for 3 hours with an intermediate milling of 10 minutes and a final milling of 6 hours.

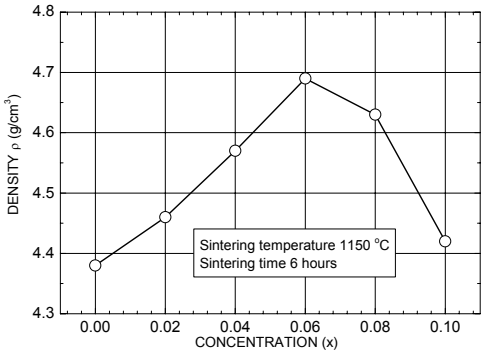
The milled powder was pressed in disc shaped pellets at a pressure of about 30 MPa and then sintered in sealed alumina crucibles for 6 hours at temperatures ranging between 1050 and 1200 ^{o}C. Densities were determined geometrically by measuring their masses and volumes and the piezoelectric properties by means of resonance-antiresonance method by making use of an Agilent 4294A Impedance/phase analyzer. SEM micrographs were recorded with an Zeiss Evo 50 XVP Scanning electron microscope. The structures were investigated with an BRUKER-AXS D8 ADVANCE X-ray diffractometer.

3. Results and discussion

Fig. 1 shows the effect of sintering temperature and concentration of dopants on the density of KNN ceramic samples. For example in Fig. 1 (a) the density of the composition with 0.06 is shown as a function of the sintering temperature. One can see that it increases with increasing temperature reaching a maxim value of 4.68 g/cm^3 at 1150 ^{o}C which can be considered as an optimum sintering temperature for such composition. Therefore, all sinterings were carried out at this temperature. Similar curves were also recorded for the other compositions as well, but the maxim values of the densities were lower up to about 10 % as can be seen in Fig. 1 (b).



(a)



(b)

Fig. 1 The behavior of density as a function of (a) sintering temperature and (b) composition.

The X-ray diffraction patterns of the KNN sintered samples containing different concentrations of dopants are shown in Fig. 2. One can see that for x≤0.06 the structure of the samples shows an orthorhombic symmetry characterised by the splitting of the reflections around 2θ = 45^{o} into (200) and (002) and having a little higher peaks for (200). For higher concentration, x>0.06 the splitting is completely reduced and a tetragonal phase appears, indicating that the dopant is incorporated into the perovskite structure. The coexistence of the orthorombic-tetragonal phase around x=0.06 can be identified as a typical morphotropic phase boundary indicating that the compositions within this MPB could exhibit maximum values for the piezoelectric parameters. Indeed this is confirmed experimentally as it will be shown further. This MPB between orthorombic and tetragonal cannot be considered as a real MPB (like the MPB in PZT type material between orthorombic and rhomboedral symmetries) but it must be a thermodynamic phase transition identified as polymorphism behavior caused by the temperature of the polymorphic phase transition which decreases at lower temperature [23, 25].

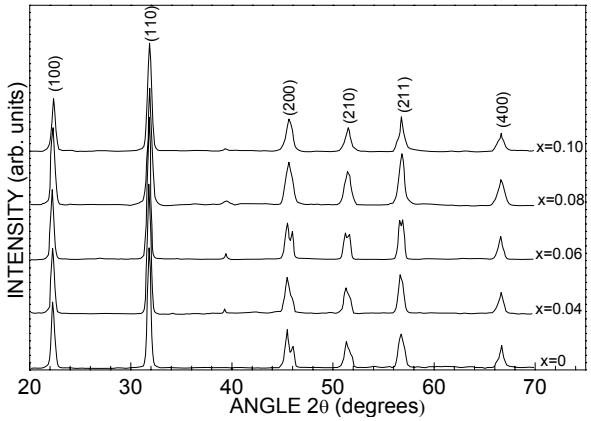


Fig. 2. X Ray difractograms for doped niobates for different compositions.

The morphostructure of sintered free surfaces of the KNN doped ceramics is illustrated in the sequences of the SEM micrographs shown in Fig. 3 for some compositions.

One observes that the crystallites are well formed, and rather cubic shaped. A slight increase of the grains with increasing dopant concentration can be noticed. The ceramics are dense enough and the density increased with x up to 0.06 then a coarsening accompanied by the decrease of the density was observed for higher x.

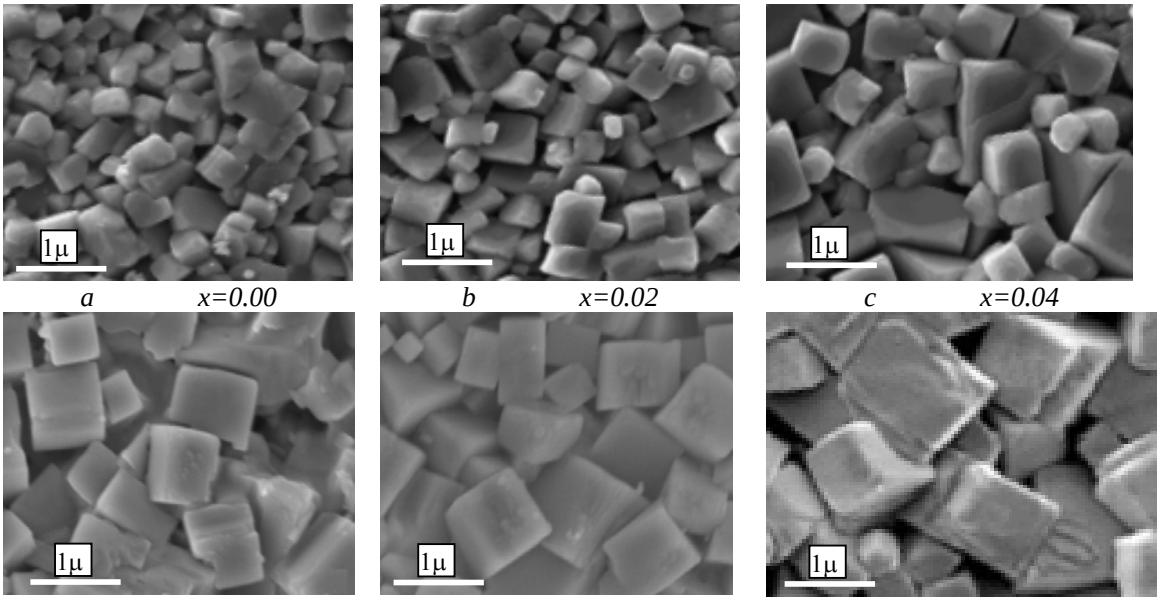


Fig. 3 SEM micrographs of free surfaces of sintered samples for dopedKNN with different compositions.

The density degrading effect may be associated with the evaporation of potasium oxide at higher temperature. Though the phase stability of pure KNN is limited to about 1140 ^{o}C, according to the phase diagram of $KNbO_3$-$NaNbO_3$ [2, 13, 26] the addition of proper dopants, (Bi, Ca and Cu in our case) may increase the melting point of the doped ceramic and at optimum sintering temperature of 1150 ^{o}C, and even higher, the ceramics were not melted. Therefore, one may assume that such dopants improve the phase stability and help densification, especially CuO which forms the benefic liquid phase for sintering and creates a number of oxygen vacancies, thus improving the piezoelectric properties as well.

The addition of dopants on KNN have a significant effect on piezoelectric properties of ceramics as well. Figs. 4 and 5 show the behaviour of the electromechanical planar coupling factor k_p and the charge constant d_{33} as a function of dopant concentration for ceramic samples sintered at optimum sintering temperature of 1150 ^{o}C.

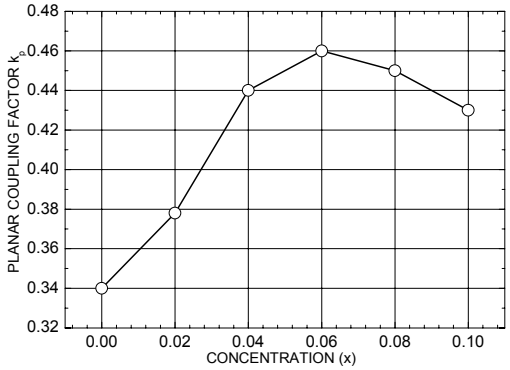


Fig. 4. Dependence of planar coupling factor k_p on dopant concentration.

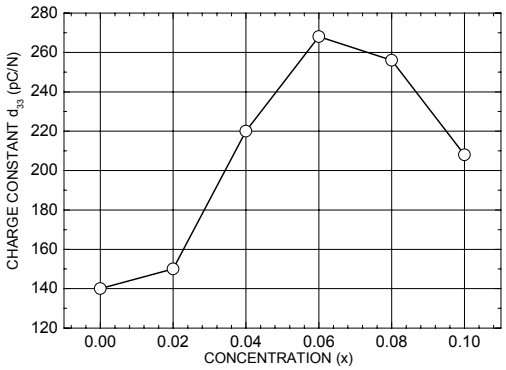


Fig. 5. Dependence of charge constant d_{33} on dopant concentration.

Both constants increases with increasing concentration reaching maximum values around x=0.06 suggesting that the MPB situates around these compositions. The planar coupling coefficient k_p increases from 0.34 for undoped samples to 0.46 for samples doped with 0.06 which represent a significant increase of about 25 %. The piezoelectric charge constant d_{33} show a more spectacular increase from 140 pC/N to 270 pC/N representing an increase of 48 %. These changes may be associated with a decrease of the amount of domain walls due to the increase of the grain size brought about by the addition of dopants which results in an easy movement of the domains and consequently in an increase of the piezoelectric constants. On the other hand Bi^{3+} ions which have a larger radius than Nb^{5+} (1.02 Å) compared with 0.64 Å), but very close to Na^{1+} (1.02 Å) and K^{1+} (1.33 Å) most probably enter the A site of the perovskite thus creating a surplus of positive charge and consequently A site vacancies. These vacancies facilitate the movement of the domain walls, thus improving the piezoelectric properties.

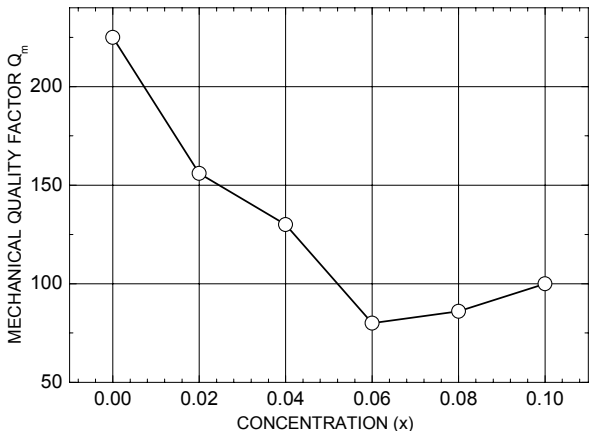


Fig. 6. Dependence of mechanical quality factor Q_m on dopant concentration.

The behaviour of the mechanical quality factor Q_m shown in figure 6 decreases with increasing dopant concentration from 240 to 75 (about 32 %), due probably to the inner stresses induced by the domain reorientation. Thus the presence of the dopants have a "softening" effect on doped KNN ceramics [27] making them suitable for sensitive US transducers.

4. Summary

KNN doped lead free piezoelectric ceramics were synthesized by solid state reaction and sintering at temperatures between 1050 – 1200 ^oC for 6 hours. All samples showed perovskite phase structure with a typical orthorhombic structure. At a doping level of around 0.06 a transition from orthorhombic to tetragonal symmetry was observed, the compositions laying within this doping range marking a specific MPB behaviour. Piezoelectric parameters for these compositions show maximum values of 0.46 for planar coupling factor, k_p, 270 pC/N for the piezoelectric charge constant d_{33} and 75 for the mechanical quality factor Q_m.

The Bi^{3+} dopant shows a typical donor like behaviour, entering on the A site position and creating A type vacancies.

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