1. INTRODUCTION

The PZT materials are the most important electroceramic materials, due to their excellent piezoelectric properties, thus making them the most used materials in almost all fields of activity. One of their main drawback is their high lead content (over 60 %). Consequently, during the last years, great efforts were being made to find alternatives for replacing the conventional lead containing materials with lead free systems, having similar properties. Sodium-potassium niobate solid solutions (shortly KNN ceramics) seem to offer the most appropriate alternative for PZT. There is one problem with KNN ceramics, namely the difficulties encountered in obtaining dense bodies during the sintering process. This problem can be overcome by using different dopants to form new solid solution within the KNN basic system. During the last few years there have been used a variety of additives like Cu, Ta, Ca, Sr, Mg. One of the main difficulties encountered were the high lead content (over 60 %). During the last few years, great efforts were being made to find alternatives for replacing the conventional lead containing materials with lead free systems, having similar properties. Sodium-potassium niobate solid solutions (shortly KNN ceramics) seem to offer the most appropriate alternative for PZT. There is one problem with KNN ceramics, namely the difficulties encountered in obtaining dense bodies during the sintering process. This problem can be overcome by using different dopants to form new solid solution within the KNN basic system. During the last few years there have been used a variety of additives like Cu, Ta, Ca, Sr, Mg.

2. OBJECTIVES

The main objectives:
- To prepare dense ceramic bodies of a lead free material in the sodium-potassium niobate solid solutions using proper additives.
- The additive used was an equimolar mixture of CuO and Bi2O3 chosen on the basis of their ionic radii (0.98 Å for CuO and 0.93 Å for Bi2O3) that of Na+ (0.95 Å) thus being possible that all these ions to enter the B position in the perovskite structure without affecting too much the lattice.
- Another reason to use these additives was that they help to decrease the orthorhombic to tetragonal MPB phase transition temperature and at the same time they may enhance the densification by forming a liquid phase at lower temperatures.

3. EXPERIMENTAL

The compositions investigated in this experiment were (1-x)(0.95KNN 0.05BT)⋅x(0.5CuO 0.5 Bi2O3) with x = 0.0; 0.5; 1.0; 1.5 and 2 mol %. They were prepared by conventional solid state synthesis. Stoichiometric amounts of K2O3, Na2CO3, Nb2O5, BaCO3 and TiO2, to form 0.95 KNN-0.05BT were mixed together for 6 hours in a PM400 Retsch planetary ball mill in agate jars in methanol. After drying the powder was calcined at 950 °C for 5 h. CuO and Bi2O3 were added to the calcined powder of KNN-BT and were milled for 5 hours in the planetary ball mill in methanol. After milling and drying the powders were uniaxially pressed as discs of 12 mm diameter and 2 mm thickness and prepared for sintering. The sintering were carried out between 1000 and 1200 °C for 10 hours. Densities were determined geometrically by measuring their masses and volumes and the piezoelectric properties by means of resonance-anteresonance method.

4. RESULTS AND DISCUSSION

Figure 1 illustrates the effect of (Cu-Bi) dopant concentration on the density of KNN-BT ceramic samples sintered at different temperatures. One can notice an increase of density with concentration and maximum values for the doping level of 1 mol %, the highest one being obtained for the sintering temperature of 1150 °C. The behavior of these maximum values of density with sintering temperature for samples doped with 1 mol % is shown in figure 2. One can see a rather steady increase of density with increasing sintering temperature up to a value of 4.45 g/cm3 representing more than 98 % of TD. More additive may form foreign phases, as it becomes evident from figure 3. The presence of this phase, not yet identified, may be an indication of the solubility of these additive into KNN-BT materials. The structure of the samples with x ≤ 1.0 mol % have orthorhombic symmetry. For higher concentration (x > 1.0 mol %) the tetragonal phase appears, indicating the incorporation of the dopants into the perovskite structure. The morphology of the sintered free surfaces is illustrated in the SEM micrographs shown in figure 4 for some compositions sintered at 1150 °C for 10 hours. It seems that Cu enhances the grain growth while Bi hindered it and reduces the grain size so that the presence of both Cu and Bi compensates each other and the result is no modification of the crystallite size. But when the dopant overcomes the optimum amount, the effect of Bi becomes predominant and the crystallite size decreases. Figure 5 shows, for example, the behavior of the planar coupling coefficient kp as a function of the dopant content. The coupling factor increases with increasing dopant content from 0.34, up to a maximum value of 0.46. The total increase is about 25 %. A similar behavior shows also the piezoelectric charge constant d33 with an increase of nearly 50 %. These changes may be associated both with the slight increase of the grain size brought about by the addition of BiCu dopant which make possible an easy switch and movement of the domains. The CuBi dopant proved to have a softening effect on the KNN ceramics. This is obvious from figure 7 which shows a decrease of the mechanical quality factor Qm from 215 to 70.

5. CONCLUSIONS

Dense ceramic lead free samples of 0.95KNN-0.05BT doped with an equimolar mixture of CuO and Bi2O3 were synthesized by the conventional mixed oxide route and sintered at temperatures between 1000 and 1200 °C for 10 hours. The doping level was from zero up to 2 mol % and the optimum amount of dopant was 1 mol %. At this level the density shows a maximum value of 4.45 g/cm3, as well as high values for piezoelectric parameters were obtained at 1150 °C. Thus the highest values for the planar coupling coefficient kp was 4.6, for the charge constant d33 it was 270 pC/N while the mechanical quality factor Qm showed a mininum value of 65 indicating the soft character of CuBi doped KNN based lead free ceramics. Such materials seem to be very promising as replacement of lead containing counterparts for many applications.