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Molten Hydroxide Synthesis as an Alternative to Molten Salt Synthesis for Producing $K_{0.5}Na_{0.5}NbO_3$ Lead Free Ceramics

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Abstract

Lead-free piezoelectric materials have grown in importance through increased environmental concern and subsequent EU and worldwide legislation, with the aspiration to reduce the use of Pb-based materials in all sectors. Integration of the next generation of lead-free piezoelectric materials with substrates to form functional micro devices has received less attention. Low temperature synthesis methods for $K_{0.5}Na_{0.5}NbO_3$ powder were developed to overcome the issue of poor purity of the final product during high temperature sintering. Molten hydroxide synthesis (MHS), derived from molten salt synthesis (MSS), has been developed to overcome a Na ion preference in the molten salt synthesis reaction that leads to $NaNbO_3$ production instead of $K_{0.5}Na_{0.5}NbO_3$ when stoichiometric amounts of precursors are used. MHS makes use of a KOH molten reaction aid in place of the NaCl/KCl molten salt mix of the MSS. In a two stage reaction K rich intermediate niobates are produced and subsequent reactions with Na species produce KNN.

Keywords – Lead-free, piezoelectric, KNN, low temperature synthesis, molten salt synthesis

1. Introduction

Due to environmental legislation, both in the EU and around the world, aimed at reducing the use of hazardous substances in electrical products and appliances and control of the resultant waste, there has been an exponential growth in the research and development of Pb-free materials in the piezoelectric field, with emphasis placed on potentially one of the more successful materials in this area, $K_{0.5}Na_{0.5}NbO_3$ (KNN) [1]. The advantages of KNN over other Pb-free materials include its low toxicity [1], relative low cost with respect to other biomedical compatible Pb-free piezo-electrics, a PZT comparable level of piezoelectric performance [1] and the relative ease of processing [1]. This has led to continued research and deeper understanding of KNN production, electrical characteristics and incorporation into MEMS. Advanced research into KNN has highlighted issues that may affect the production and electrical characteristics of the material.

Focussing on powder production, initially the favoured method of KNN powder production involved high temperature mixed oxide calcination of KNN precursors with a long soak time. The main difficulty faced with the use of high temperature calcined KNN powders involved the precursor volatility that led to poor compositional control which in turn led to a ceramic with varied grain sizes and poor piezo-electric activity [2]. The precursor volatility and the related issues are due to the volatility of K_2O at calcination (800-950°C) [3] and sintering (>1000°C) temperatures which lead to low density materials and the resultant production of non-perovskite structures of potassium niobate [4] with poor piezoelectric characteristics. To counter these deficiencies low temperature synthesis routes were adapted and employed. Examples of low temperature powder production methods to produce KNN include the molten salt synthesis (MSS) [4], sol-gel method [5], citrate method [6], hydrothermal process [7] and the microwave hydrothermal process [8]. Besides the MSS the other methods lack the low cost, simplicity [9], robustness and ease required for effective scale up. Compared to conventional mixed oxide synthesis, MSS represents a low temperature route that is suitable for scale up. The MSS is a short soak time, low temperature based method (due to the low melting points of the salts), thus reducing the issue of K_2O volatility. In addition it makes use of relatively inexpensive precursors, which are non toxic, does not require specialist equipment and is scalable making it suitable for use in commercial environments.

The MSS involves mixing the reactants with a low melting point salt or combination of salts and allowing the KNN precursors to interact in the molten salt(s) to produce highly reactive single phase KNN powders. The MSS method allows for greater control of the desired morphology from the choice of salt used [9]. $BaTiO_3$ [10], $Bi_4Ti_3O_{12}$ [11], PZT [12], and Pb-based niobates [13] are some of the single phase electronic ceramics that have utilized molten chlorides, sulphates and carbonates in their synthesis [9]. MSS proceeds by two mechanisms depending on if all the reactants are soluble or if some are not [12]. In the case of KNN where K_2CO_3, Na_2CO_3 and Nb_2O_5 are used, only the K_2CO_3 and Na_2CO_3 are expected to be soluble. In this case the soluble species should dissolve and then react with and diffuse into the insoluble Nb_2O_5 to produce KNN. K ions are known to exhibit a lower diffusion rate compared to Na ions (an order of magnitude lower [4,15]) which would favour the initial formation of a Na rich alkali niobate when stoichiometric ratios of the precursors are used.

In this paper the issue of a sodium rich niobate production at the expense of KNN is explored and an alternative method of KNN powder synthesis is introduced; which is a MSS derived low temperature method of KNN production that overcomes the issue of low potassium reactivity with the niobium oxide. The work presents a simple, low temperature method to produce KNN powder.

2. Experimental

The Molten Salt Synthesis (MSS) method, involves mixing stoichiometric ratios of K_2CO_3, Na_2CO_3, Nb_2O_5 with an excess of salt (NaCl/KCL mix). These were ball milled in a propan-1-ol for 12 hours with zirconia balls to evenly distribute the reagents throughout the salt mix. The slurry was then dried at 120°C and placed in an alumina crucible and heat treated at between 650°-800°C for 2 hours. On cooling the powder was washed with de-ionized water and filtered to remove the salts and dried at 120°C.

The Molten Hydroxide Synthesis (MHS) method, involves mixing stoichiometric ratios of K_2CO_3 and Nb_2O_5 with an excess of KOH in the first stage. These were crushed and mixed using a pestle and mortar and placed in an alumina crucible and heat treated at 500°C for 2 hours to form K rich niobates. An excess of NaCl or Na_2CO_3 was then added to the mixture which was again crushed and mixed using a pestle and mortar. The mixture was then heat treated at 700°C for 2 hours. The resultant powder cake was washed with de-ionized water to remove the water soluble materials and dried at 120°C.

The phase composition and crystalline structure of the powders were analyzed using X-Ray diffraction (Siemens D-5005). SEM-EDX was used to analyse the composition of the powder.

3. Results and Discussion

When the NaCl/KCl salt mix was used in the MSS, this resulted in the formation of $NaNbO_3$ and related derivatives in place of the desired $K_{0.5}Na_{0.5}NbO_3$ despite starting with equimolar amounts of Na_2CO_3 and K_2CO_3, as seen in the XRD trace shown in *Fig.1*. A similar behaviour was also observed in studies of the hydrothermal synthesis (H.S.) of KNN, where to achieve a 1:1 ratio of K-Na in the final product the ratio of the precursors needed to be greater than 3:1 of K-Na [7]. The observation that in the mixed oxide synthesis, $K_{0.5}Na_{0.5}NbO_3$ is produced with the use of equimolar quantities of K and Na precursors whereas in the low temperature synthesis methods (i.e. MSS and H.S.), potassium deficient species are produced, indicates that there is an issue associated with K diffusion or reactivity. Indeed as indicated earlier it is known that potassium ions have a lower diffusion rate with respect to sodium ions [4,15].

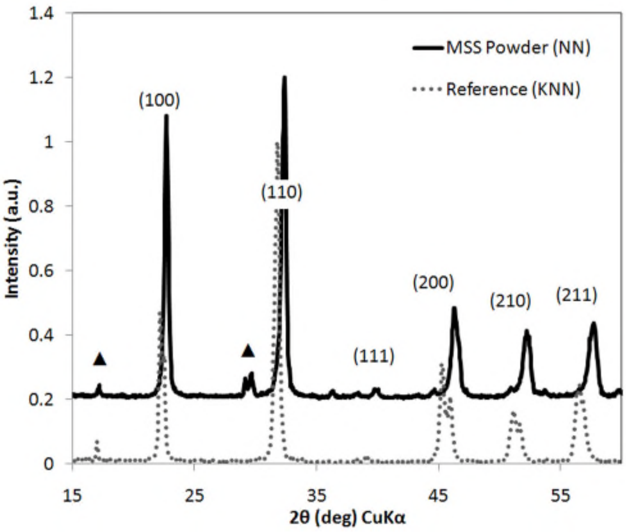

Fig.1 XRD patterns of powder made from MSS method (that formed $NaNbO_3$) compared with KNN reference powder sample. ▲= unreacted Nb_2O_5.

The XRD analysis shows the absence of K containing phase and the presence of residual Nb_2O_5 in the end product as seen in *Fig.1.* The MSS XRD powder trace correlates with that of $NaNbO_3$. SEM-EDX analysis supports this observation showing a K-Na ratio of 1:14 as seen in *Table 1*.

Table 1: EDX Analysis of powder made using MSS showing atomic percentages of constituent parts.

SEM EDX Analysis - Molten Salt Synthesis (MSS) Powder				
Element	Nb	Na	K	Total
Atomic Ratio	58.9	38.3	2.8	100.0

Increasing reaction temperature (700°C – 800°C) and reaction soak time (2hrs – 4hrs) failed to produce any significant changes in reaction products. Equally increasing the potassium ion excess up to 3:1 K-Na, as with hydrothermal synthesis (HS), also failed to increase the level of K incorporation into the final product implying that, unlike in HS, the difficulty in incorporating K into the structure during MSS is not entirely due to diffusion related issues. Instead it is proposed that a non-diffusion based phenomena occurs that prevents diffusion of K ions or limits the availability of K ions.

Repeating the synthesis with only Nb_2O_5, NaCl and KCl did not result in the formation of any metal niobates showing that Na and K from the molten salts are not available to diffuse into the Nb_2O_5. When K_2CO_3 was added to the reaction (i.e. Nb_2O_5, NaCl and KCl), a Na rich niobate was produced instead of the anticipated K rich niobate. This indicates that a substitution mechanism has occurred whereby K_2CO_3 is able to liberate the previously unavailable Na ions from the NaCl. These liberated Na ions are then able to interact with the Nb_2O_5 to form $NaNbO_3$. This shows that unlike with HS, overloading the system with K reagent will still not yield a KNN powder. A proposed reaction is shown below.

$$K_2CO_3 + 2NaCl \rightarrow 2KCl + Na_2CO_3$$
$$Na_2CO_3 + Nb_2O_5 \rightarrow 2NaNbO_3 + \uparrow CO_2$$

Given the preferential incorporation of Na from the NaCl (at the expense of K ions) in the MSS at the expense, to overcome this issue, the MSS process was modified to remove the NaCl/KCl and replace it with NaOH/KOH which offers an alternative low temperature molten phase. KOH (mp 420°C) and NaOH (mp 318°C) have lower melting points with a eutectic melting point of 170°C; compared to KCl (mp 770°C) and NaCl (mp 801°C) with a eutectic melting point of 657°C. Simply removing the NaCl from the MSS is impractical due to the need to employ much higher temperatures when the eutectic liquid is not formed.

The reactants were heat treated for 2 hours at 500°C and this reaction resulted in the formation of $KNbO_3$ as seen in *Fig.2* rather than the desired KNN or the $NaNbO_3$ that the MSS favoured. Whilst not yielding KNN, the results did show that the K-Na substitution could be avoided by using molten hydroxides in place of molten salts. Furthermore removal of NaOH did not affect the resultant product, so KOH was used in isolation to ensure the production of pure KN. At 500°C all water based moisture is removed [15].

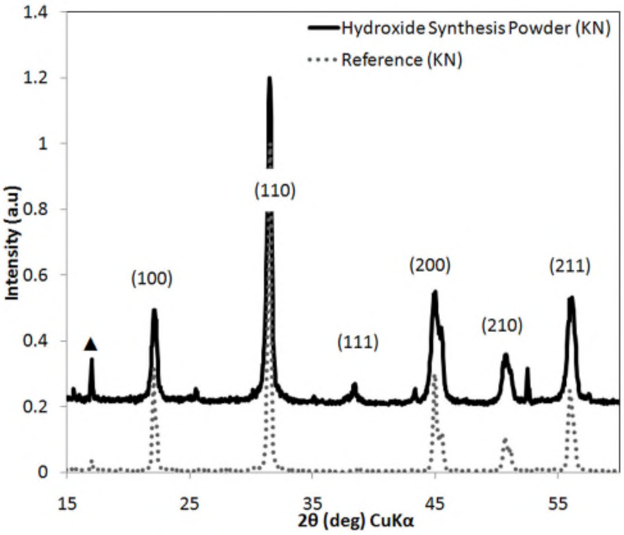

Fig.2 is the XRD pattern of the powder with dual NaOH/KOH molten solvent that formed K rich alkali niobate, compared with a reference $KNbO_3$ powder sample. ▲= unreacted Nb_2O_5.

Following the formation of $KNbO_3$ a two step procedure was investigated with the aim of first forming $KNbO_3$ using KOH as the molten solvent and then incorporating Na ions with the aim of synthesizing $K_{0.5}Na_{0.5}NbO_3$.

Examination of the reaction products at each stage has led to a two stage reaction process

Stage 1 - K_2CO_3 + KOH + Nb_2O_5

The initial reaction is thought to lead to the formation of multiple potassium niobate compounds including $KNbO_3$ as well as KNb_3O_8 [14], $K_4Nb_{16}O_{17}.3H_2O$ [3,16,17] and water soluble potassium hexaniobates of the general formula $K_{8-x}H_x[Nb_6O_{19}].nH_2O$, x = 0-3 [3,16,17] depending on the temperature and quantity of KOH used [16]. *Fig.3* shows the XRD pattern for both the unwashed and washed powders after the stage 1 synthesis. Comparison between the two clearly shows that there are significant water soluble species present in the unwashed sample that cannot be attributed to the starting reagents. As these water soluble species are required for the formation of KNN it is imperative that the system is not washed at this stage. The reaction of K_2CO_3 and Nb_2O_5 is known to progress through various stages before $KNbO_3$ [14] is produced, which accounts for the phases observed.

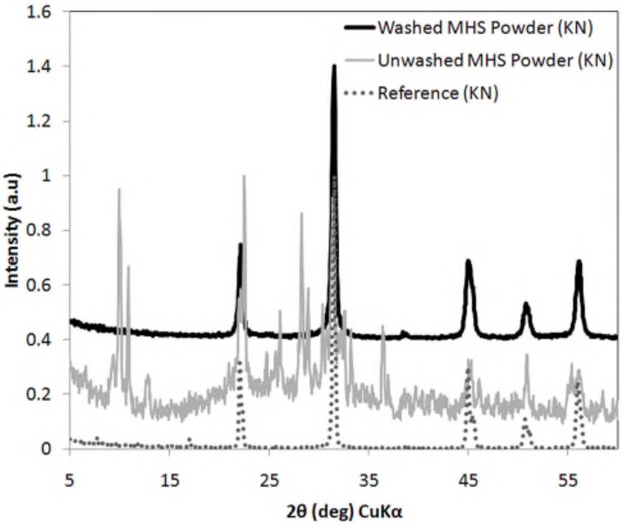

Fig.3 is the XRD pattern of the powder with the single KOH molten solvent that formed $KNbO_3$, compared with a Reference $KNbO_3$ sample.

Stage 2 – $K_xNb_yO_z$ products + Na source (NaCl or $NaCO_3$)
On the introduction of Na ions in the second stage the Na ions are thought to diffuse into the various potassium niobate derivatives and also react with any unreacted Nb_2O_5 to form KNN as seen in *Fig.4.* From the SEM EDX analysis results shown in *Table 2*, the ratios of each element can be seen to agree with the stoichiometric ratio of the formula $K_{0.5}Na_{0.5}NbO_3$. *Fig.5* shows the SEM image of MHS prepared KNN powder. To differentiate it from the standard MSS, this process was named the Molten Hydroxide Synthesis method (MHS).

Table 2: EDX Analysis of powders made using MHS showing atomic percentages of constituent parts.

SEM EDX Analysis - Molten Hydroxide Synthesis (MHS) Powder				
Element	Nb	Na	K	Total
Atomic Ratio	53.9	22.6	23.5	100.0

While KNN was successfully produced it was found that a molar excess of Na ions with respect to niobium oxide was required for the reaction to proceed to the desired conclusion. Tests of the 2nd stage of the MHS showed that stoichiometric amounts of Na ions were not sufficient for the reaction to progress to completion. A level of between 1.5 – 2.9 molar excess of Na ions with respect to Nb_2O_5 was found to be needed to produce $K_{0.5}Na_{0.5}NbO_3$.

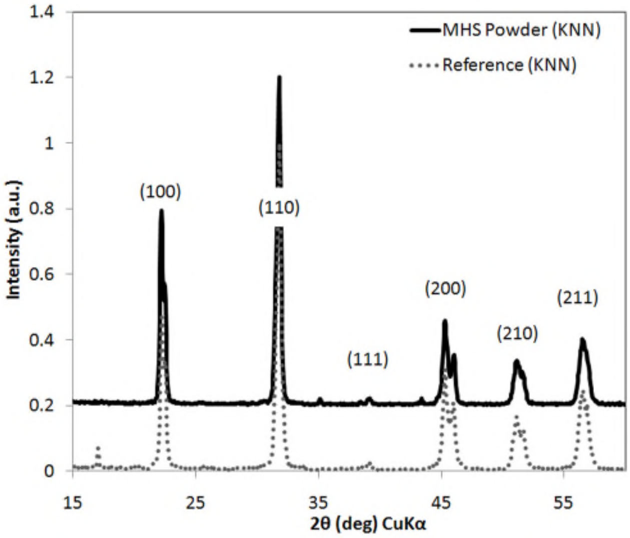

Fig.4 XRD patterns of MHS KNN powder compared with KNN reference powder

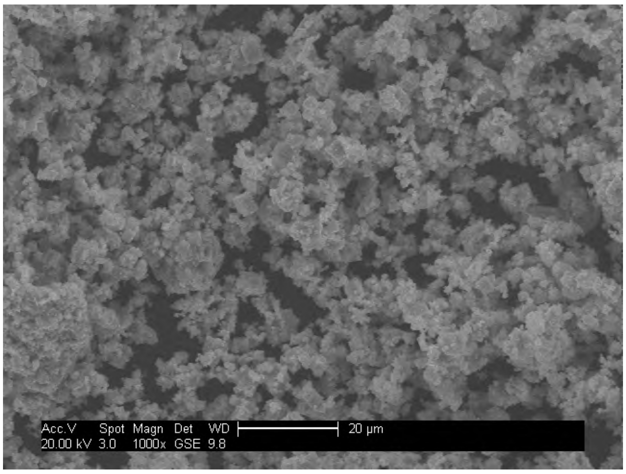

Fig.5 SEM image of MHS KNN powder

4. Conclusion

The use of equal molar amounts of the perovskite A-site starting materials in the molten salt synthesis (NaCl/KCl) of KNN led to the favourable release and diffusion of sodium ions at the expense of potassium ions; leading to the formation of $NaNbO_3$ in place of $K_{0.5}Na_{0.5}NbO_3$. Conversely when a NaOH/KOH mix or KOH on its own were used as the molten phase, potassium rich niobates were produced. The production of KNN using a two stage Molten Hydroxide Synthesis (MHS) with KOH as the sole molten reaction aid was successfully carried out using a stoichiometric amount of potassium with an excess of sodium in the second stage of the synthesis. The maximum processing temperature used during the MHS was 700°C. While the MSS is a simpler one step process, it is unable to produce KNN despite several modifications; the MHS has the advantage of producing a fully reacted KNN product with no unreacted niobium oxide present which tends to be seen in the MSS and hydrothermal synthesis methods.

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