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Observing the in-situ formation of the lead-free piezoceramic potassium sodium niobate (KNN) with SAED

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Background incl. aims

The use of PZT has continued despite the restriction of hazardous substances (RoHS) directives being passed by the European union (EU) to limit the use of hazardous materials – such as lead (PZT) – in electronic equipment. This is influenced by a lack of available substitutes that can be implemented and scaled in a reasonable time to eliminate the use of PZT (RoHS Annex III). The lead-free alkali-niobate, potassium sodium niobate (KxNa1-xNbO3, KNN), is a potential replacement for PZT, since it can exhibit equivalent, if not better, piezoelectric properties without compromise at temperatures >120 °C. The challenges in the synthesis of KNN, however, have hindered its use as an alternative. Notable challenges include difficulty in achieving the 50% K+ and Na+ occupancy required to make stochiometric KNN (i.e., K0.5Na0.5NbO3) and a lack of control in the formation of phase boundaries. Therefore, developing a reproducible method for synthesising stoichiometric KNN, bodes well for the implementing KNN as a commercial piezoceramic.

Methods

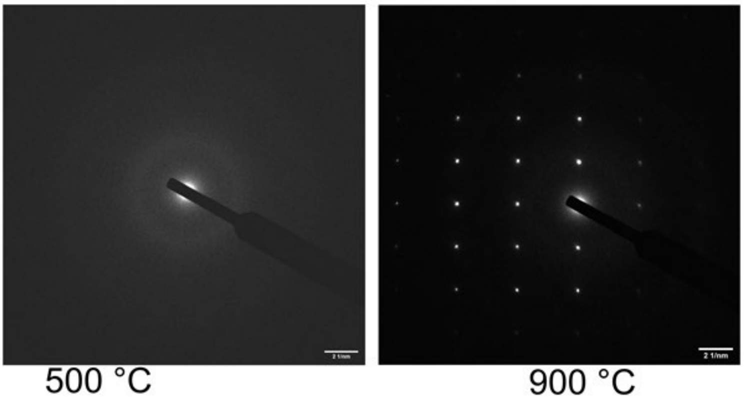
A simple and robust method for synthesis of the lead-free piezoceramic material KNN has been developed via an aqueous route. Stochiometric KNN (K0.5Na0.5NbO3) was prepared by combining alkali-nitrate solutions (NaNO3 and KNO3) with the nano-sized, water-soluble, niobium precursor hexaniobate ([HxNb6O19]8-x, Nb6), followed by sintering at elevated temperatures. Ex-situ studies on the formation of solid-state niobium oxides from Nb6 indicate formation of amorphous niobium oxides ca 400–500 °C. However, observing the dynamics accompanying this crystallization process are limited with conventional solid-state methods. We therefore probed the transformation of Nb6 in the presence of alkali-cations, to yield crystalline KNN from an amorphous oxide precursor. This was possible via in-situ heating with simultaneous selected area electron diffraction (SAED). Whereby, the amorphous Nb6-KNN precursor was mounted on a micro-electromechanical systems (MEMs) chip (Norcada Inc.), which is heated via a tungsten filament coil. In-situ heating experiments proceeded with heating from 400 to 1000 °C, at ramping rate of ca 0.25 °C s-1 in vacuum.

Results

KNN can be synthesised with heating NaNO3 and KNO3, with the water-soluble hexaniobate (Nb6) precursor. The results from SAED indicate the amorphous Nb6-KNN precursor becomes crystalline above ca 550 °C, without degradation after further heating up to 1000 °C. The SAED patterns at 800, 900 and 1000 °C, were acquired along the (101) axis, and agreed with the simulated diffraction pattern of stoichiometric KNN reported previously. The SAED patterns <800 °C exhibited sporadic spots which were incongruent with the simulated diffraction pattern. However, below ca 550 °C there were no obvious spots in SAED patterns, which is consistent with the presence of an amorphous oxide. These findings merit the use of a water-soluble niobium precursor, such as Nb6, as an alternative to accessing KNN in the solid-state.

Conclusion
In-situ heating with SAED is a suitable technique for monitoring the real-time transformation of amorphous precursor oxides, to yield crystalline lead-free piezoceramics. Formation of the lead-free piezoceramic KNN is achievable using the water-soluble, niobium precursor Nb6, which is advantageous compared to conventional solid-state methods. This makes it an attractive alternative approach for developing lead-free piezoceramic materials.

Graphic:



Keywords:

Lead-free, hexaniobate, KNN, in-situ, TEM

Reference:

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