

Low-temperature combustion synthesis of $K_{0.5}Na_{0.5}NbO_3$ powders

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Pure $K_{0.5}Na_{0.5}NbO_3$ powder was prepared at low temperature by a combustion method using Na_2CO_3 , K_2CO_3 and Nb_2O_5 as raw materials and urea as fuel. The crystal structure and morphology of the powder were characterized by X-ray diffraction and scanning electron microscope. The XRD patterns reveal that single-phase $K_{0.5}Na_{0.5}NbO_3$ powder can be obtained at 550 °C by the method, and the SEM photographs show that the powder is fine and well-developed. The synthesis parameters (e. g., the calcination temperature, dwelling time, and $(Na_2CO_3 + K_2CO_3 + Nb_2O_5)$ -to- urea weight ratio) are studied to reveal the optimized synthesis conditions for preparing pure $K_{0.5}Na_{0.5}NbO_3$ powders.

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1. Introduction

Piezoelectric ceramics are the most important and widely used materials for piezoelectric transducers, transformers, sensors, actuators, buzzers and other electronic devices due to their excellent electrical properties [1-3]. However, these piezoelectric ceramics are mostly $Pb(Zr, Ti)O_3$ (PZT)-based ceramics, which contain more than 60 wt% lead [4]. However the toxicity of lead is a serious threat to human health and environment and thus lead-free piezoelectric ceramics have attracted great attention recently. Recently, much attention for lead-free piezoelectric ceramics has been paid to $(K_{0.5}Na_{0.5})NbO_3$ (abbreviated as KNN) based piezoelectric ceramics because of its high piezoelectric properties, high Curie temperature and compatibility with human tissue [5-7]. However, a major problem concerning this material is reported to be the difficulty of obtaining high density by conventional solid-state preparation and sintering in air. So some dense KNN ceramics were synthesized by the different preparing methods such as the hot pressing and spark plasma sintering [8, 9]. However, these ways could not adapt to industrial production because of high cost. To overcome this disadvantage preparation of uniform fine powder of $KNbO_3$ was attempted. Contrary to the solid-state method, wet chemical routes become an excellent technique for the synthesis of high-purity multi-component oxides because of their inherent superior qualities, which include the better homogeneity, compositional control, and lower processing temperature that result in more reactive powders [8]. Among the wet chemical routes, sol-gel method is usually employed to prepare KNN powders, and alkoxides of niobium are generally used as Nb sources. However, certain inherent problems are associated with Nb alkoxides, including their inflammability, relatively high cost, and great sensitivity to moisture [8]. Therefore, powders preparation technique is a promising topic in the

field of chemical syntheses of oxides. Although a lot of work on powders preparation using wet chemical routes has been done, the outstanding capability has been widely demonstrated, only limited efforts have been made to improve the preparation efficiency of KNN powders by employing the wet chemical process [8-10].

In the present work, we employ a fast and energy-efficient route for the direct synthesis of KNN powders, which may be regarded as a kind of high quality and environmental friendly chemical processes. Urea is added into raw materials to improve the heat efficiency in the conventional solid-state reaction [11]. On the basis of the optimized synthesis parameters (e.g., the calcination temperature, calcination time, and the composition of raw materials etc.), an efficient one-step synthesis route of the pure KNN powders with a well-crystalline structure is developed. At the same time, the possible mechanism of the present combustion synthesis of KNN powders is proposed.

2. Experimental procedure

Reagent-grade Nb_2O_5 (99.9%), K_2CO_3 (99.9%), Na_2CO_3 (99.9%) and urea (A.P.) are used as starting materials. With a molar ratio of $[K]/[Na]/[Nb]=1:1:2$, Nb_2O_5 , K_2CO_3 and Na_2CO_3 are ground with a mortar and pestle in ethanol for 1 h to obtain uniformly distributed oxide mixtures. Then the obtained oxide mixtures are mixed with urea with a weight ratio varying from 1:1 to 1:3 by wet ball-milling for 4 h. The mixed slurry is dried at 80 °C for 2 h for the complete removal of ethanol. The mixed powders are placed in alumina crucibles and then reacted at different temperatures ranging from 500 °C to 700 °C. The synthesized products were typically fine powders.

The phase composition of the powders as-prepared at different temperatures was analyzed by X-ray diffraction (XRD, D/max-2200PC, Rigaku). The thermal decomposition and crystallization of the precursor were investigated by differential Scanning Calorimeter (TG-DSC, STA404, NETZSCH). The morphology of the KNN powder was investigated by SEM (JSM-6700F, JEOL).

3. Results and discussion

Fig.1 shows the powders diffraction patterns of the powder prepared at different temperatures, from 500 °C to 700 °C, for 6 h. As shown in Fig. 1, properties (e.g., the phase composition, purity and crystallinity) of the synthesized KNN powders are sensitive to the variation of temperature. At lower temperature (500 °C), besides the main phase of KNN, the diffraction peaks of Nb-rich $Na_2Nb_4O_{11}$ phase are also detected, while the K-rich phase cannot be detected since it takes complicated reactions with urea and converts into the amorphous under heating. Then increasing the temperature to 550 °C, the phase of $Na_2Nb_4O_{11}$ disappears, and the single-phase KNN powders can be obtained. With the continuous increase of temperature, the diffraction peaks of KNN phase gradually and slightly strengthen.

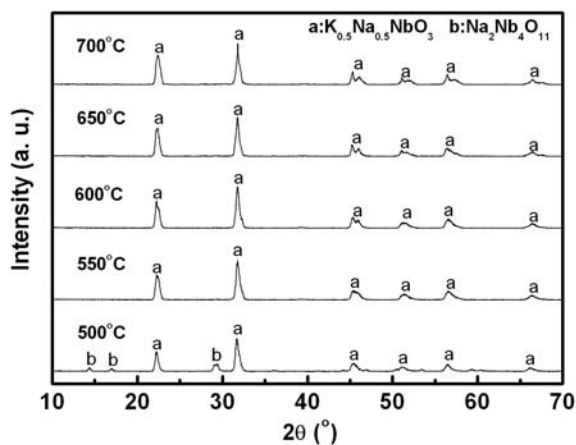


Fig. 1 XRD patterns of the powders prepared at different temperature for 6 h.

Fig. 2 displays the SEM micrographs of the as-prepared powders obtained at different temperatures for 6 h. It can be seen that the powder obtained at 650 °C is very fine, with the diameter of about 1-2 μm . With the increase of temperature the grain size increases and the grain develops better and better, which is well corresponded with the above XRD analysis. It also can be found most of grains is cuboid-like and some of them is rod-like, which is due to the obtained KNN phase (JCPDS No. 33-1270) belonging to orthorhombic syngony.

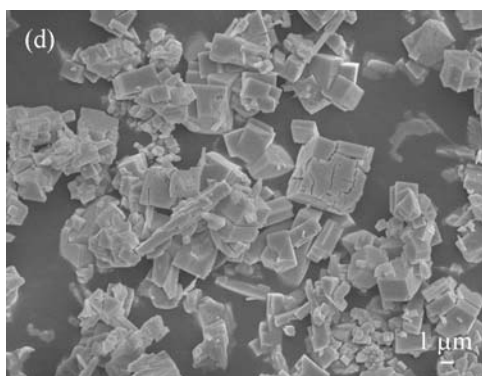
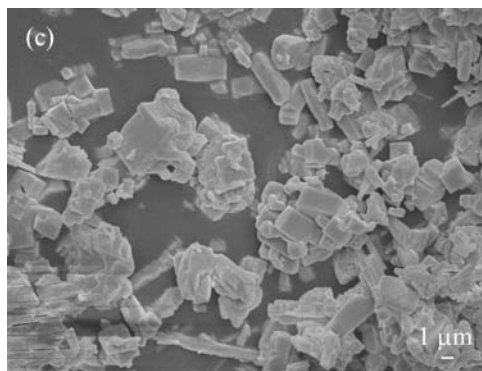
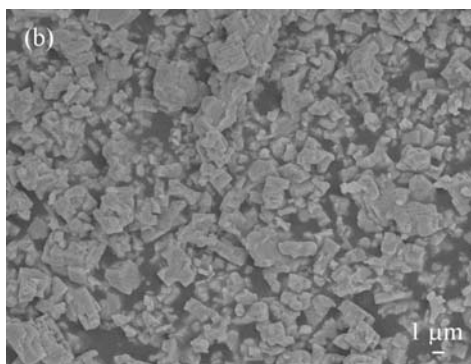
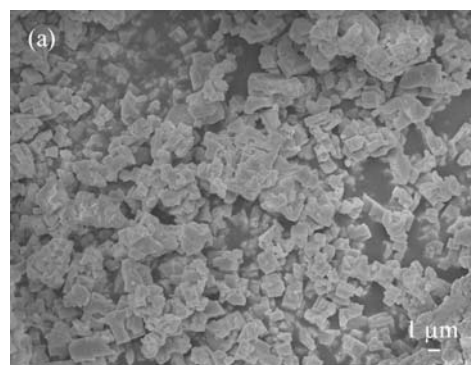


Fig.2 SEM micrographs of the powders prepared at different temperature for 6 h (a) 550 °C; (b) 600 °C; (c) 650 °C; (d) 700 °C;

Fig. 3 shows the TG-DSC curve of the precursor mixture. The first endothermic peak centered at about 167 °C can be attributed to the polymerization reaction of urea (as the Eqs.(1) and (2)). The second endothermic one at about 211 °C may be assigned to the organic compounds reacted with sodium and potassium ions. The endothermic peaks centered at about 381 °C correspond to the decomposition reaction of organic materials and the solid-state reactions between niobium and sodium complexions. The last exothermic peak at about 533 °C can be assigned to the nucleation of KNN, which can be verified by the above XRD analysis.

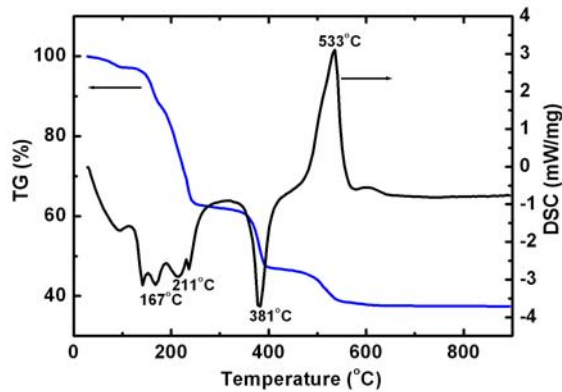
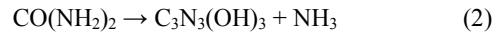


Fig. 3 TG-DSC curve of the precursor mixture.

Fig. 4 displays the powders diffraction patterns of the powder prepared at 550 °C for different time. As the dwelling time is less than 6 h, besides the main phase of KNN, the diffraction peaks of $\text{Na}_2\text{Nb}_4\text{O}_{11}$ phase are also detected. As prolonging the dwelling time to 6 h, the phase of $\text{Na}_2\text{Nb}_4\text{O}_{11}$ disappears, and the single-phase NaNbO_3 powders can be obtained. This indicates that the nucleation of KNN needs enough time to carry out.

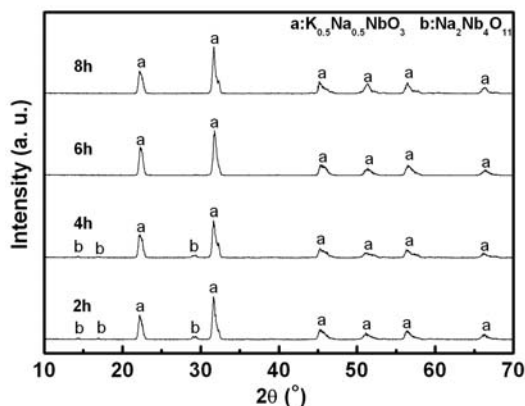


Fig. 4 XRD patterns of the powders prepared at 550 °C for different time

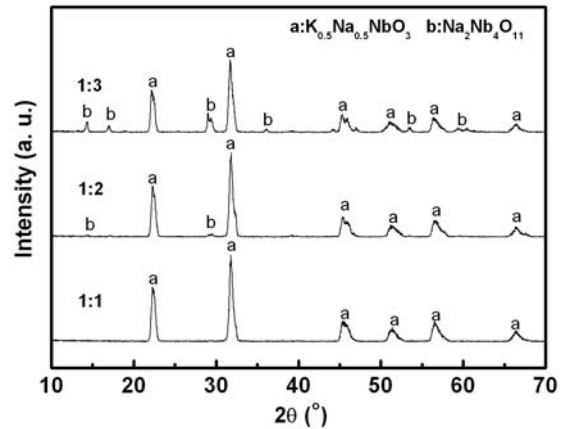


Fig. 5 XRD patterns of the powders prepared at 550 °C for 6 h by adding different amount of urea

Fig. 5 displays the powders diffraction patterns of the powder prepared at 550 °C for 6 h by adding different amount of urea. It can be found that as the weight ratio of oxide mixture and urea is 1:1 the single-phase KNN powders can be obtained. However with the increase of the amount of urea, the second phase $\text{Na}_2\text{Nb}_4\text{O}_{11}$ gradually occurs. This may be due to the fact that as urea is too much, the uniformity of oxide mixture decrease and the second phase $\text{Na}_2\text{Nb}_4\text{O}_{11}$ occurs.

4. Conclusions

Pure KNN powder can be prepared by a combustion method using urea as fuel. The optimized conditions are found in the present work. The urea/ $(\text{Na}_2\text{CO}_3 + \text{Nb}_2\text{O}_5)$ ratio of 1 and calcination at 550 °C for 6 h can produce pure LN powders. Moreover, the possible mechanism of the whole reaction is discussed, which shows that urea plays an important role in the whole reaction process. Firstly, urea leads to complicated reactions to form intermediate organic compounds and subsequently, it triggers a vigorous combustion reaction.

Acknowledgements

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