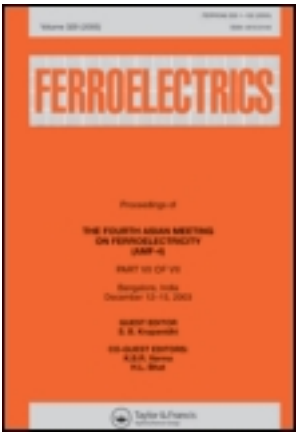

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HYDROTHERMAL SYNTHESIS OF LEAD MAGNONIOBATE POWDER

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Lead Magnoniobate (designated as PMN) is the most promising ferroelectric relaxor material. Hydrothermal synthesis of PMN under low temperature demonstrated positive results with niobium oxide as one of the starting materials. The as-prepared nanometer crystallized pyrochlore phase can be transformed into perovskite phase by heat treatment at elevated temperatures. Both of the powders before and after heat treatment were analysed by means of X-ray diffractometry (XRD), differential thermal analysis (DTA) and X-ray photoelectron spectroscopy (XPS).

Keywords: hydrothermal synthesis, lead magnoniobate, XPS

INTRODUCTION

Perovskite lead Magnoniobate is the most promising ferroelectric relaxor with ultrahigh dielectric permittivity and field induced strain. It should have been widely used already if there was no pyrochlore phase PMN, which is liable to nuclear, appearing during the PMN fabrication process. Numerous studies of the pyrochlore phase elimination have been carried out[1-9]. The columbite method has been presented by Swartz and Shrout in 1982[1], where a two-step solid reaction route was employed to synthesize pure perovskite PMN phase. A newly developed method, which is called "mechanochemically synthesis" by Wang[4], offers a direct way to get pure perovskite PMN. Melting salt method was proved to be another effective way by Xia[5] and Wan[6]. Sol-gel and coprecipitation have been done yet with good effect[7-8].

Hydrothermal synthesis is quite an unordinary chemical method with hyper-crisis aqueous circumstance under high pressure. It can provide new access for chemical substance synthesis. Yamamoto has

reported that pyrochlore PMN powder could be produced directly by hydrothermal synthesis with niobium chlorate as one of the staring materials[9]. In this paper, the common niobium oxide powder was employed as one starting material instead of the chlorate. And we found that pyrochlore phase is directly available after hydrothermal route and can be partially transformed into perovskite by heat treatment in the temperature range from 700 to 850°C.

EXPERIMENTAL PROCEDURE

The autoclave used is stainless steel vessel about 40 milliliter in volume with screwed cap to seal it off. It has PTFE isolation mounted inside to prevent the vessel from basic or acid corrosion. At the beginning, 6M $Pb(NO_3)_2$ water solution was prepared carefully by heating the aqueous mixture to 70°C with stirring, keep this condition unchanged during the following preparation procedure; then 6M $Mg(NO_3)_2$ water solution was dropped into the previous one; followed excessive 6M NaOH water solution was added in carefully, colored deposition appeared at this step; after stirring for 30 minutes, niobium oxide powder was mixed in; finally the mixture was poured into the autoclave. The relative atomic ratio of the three cations is constricted by the chemical stoichiometry of perovskite PMN. Then the autoclave was heated to 160°C for 2 hr to make the included chemicals react. After cooling down, the precipitation was filtered and washed, then dried in infrared chamber, and heat-treated at 550-850°C for 1hr.

The as-prepared powder was analysed by DTA to find the heat transformation behavior. Both the as-prepared and heat-treated powders was characterized by means of XRD(Rigaku 2400 MAX, Rigaku Corp.) and XPS(ESCALAB MKII, VG Corp.). The Cu kα radiation beam with its wave length λ=1.5418Å and Mg kα radiation beam with the photon energy =1253.6eV were used for XRD and XPS analysis respectively. And the static charge was calibrated by shifting the contamination carbon peak C1s to 284.6eV for XPS samples.

RESULTS AND DISCUSSIONS

Figure 1 shows the powder X-ray diffractometry results of as-prepared powder and that of heat-treated at elevated temperature in the range from 550 to 850°C. It can be seen from figure1 that the as prepared

powder is of nearly pure pyrochlore phase. The average grain size along crystalline face (hkl) D_{hkl}, which is of nano-scale, can be calculated by Scherrer Equation:

$$D_{hkl} = \frac{k\lambda}{\beta \cos\theta}$$

Where k is a constant, λ is the X-ray wave length, β is the peak width increment caused by grain fining, θ is the diffraction angle. The calculated grain size of the as-prepared pyrochlore phase is about 14nm. For this nanometer grain scale, the powder has high reactivity under moderate temperature heat treatment.

Figure1 also demonstrates the variation of pyrochlore to perovskite phase transition. Approximately, we suppose that the relative percentage of the two phases can be represented by the main peak intensity ratio of the two phases, then the percent of perovskite phase would be calculated as the following equation:

$$\text{Perovskite } \% = I_{pero}/(I_{pero}+I_{pyro})$$

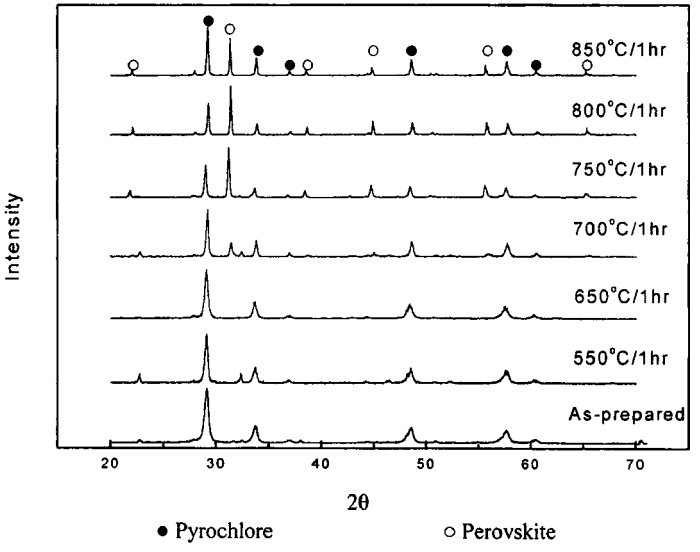

Figure 1 XRD patterns of the as-prepared and heat-treated PMN powders

Here I_{pero} means the diffraction peak intensity of crystalline face (110) for perovskite, and I_{pyro} means that of crystalline face (202) for pyrochlore. The calculated percentage data was shown in table 1. From this table, we can see that the percentage of perovskite varied with the increasing temperature. There is no perovskite phase formed when heat-treated under 650°C, and a small percent formed at 700°C, then reached a maximum with a percentage more than 60% at 750 °C, and keep this maximum to 800 °C, and then a little decrease at 850 °C. This tells us that: (1) The phase transition may start at a temperature within 650-700°C. (2) More and more perovskite phase forms with the elevated temperature up till 750-800°C. (3) The higher temperature as 850°C could not increase the perovskite content anymore, on the contrary it decreases the percentage. This is could be explained by lead evaporation at that higher temperature. Perovskite has more lead content than pyrochlore, so the lead loss move the equilibrium between the perovskite and pyrochlore phases to the latter one.

TABLE 1 The calculated relative content percentage of perovskite phase

Heat treatment Temperature	None	550 °C	650 °C	700 °C	750 °C	800 °C	850 °C
Perovskite %	0	0	0	23	61	61	42

Yamamoto reported that the hydrothermal synthesized pyrochlore can be fully transformed into perovskite by heat treatment[9], while it's something different in the present study, where the maximum perovskite percentage is just more than 60%. This is attributed to that the composition of the as-prepared powder has deviated from the stoichiometry of perovskite phase PMN due to water soluble composition loss in the filtering and washing steps, although the starting composition is of perovskite type.

Figure 2 shows the DTA curve of as-prepared PMN powder. The uncommon exothermic dome in the temperature range from RT to 900°C reveals that the hydrothermal synthesis at relatively low temperature may not completely run, and it continues at elevated temperature during heat treatment. The small endothermic peak at 380.25°C is believed to be an indicator of niobium hydroxide thermal decomposition.

Figure 3 show XPS curves of O1s peaks of the powders before and after heat treatment. Both of the peaks could be separated into two child peaks, peak 1 with binding energy ≈ 529.2eV and peak 2 with binding

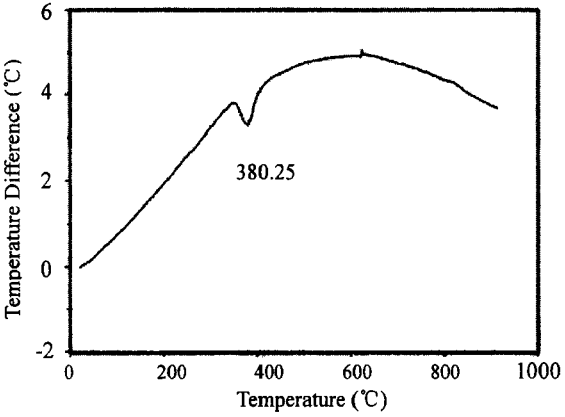

Figure 2 DTA curve of the as-prepared powder

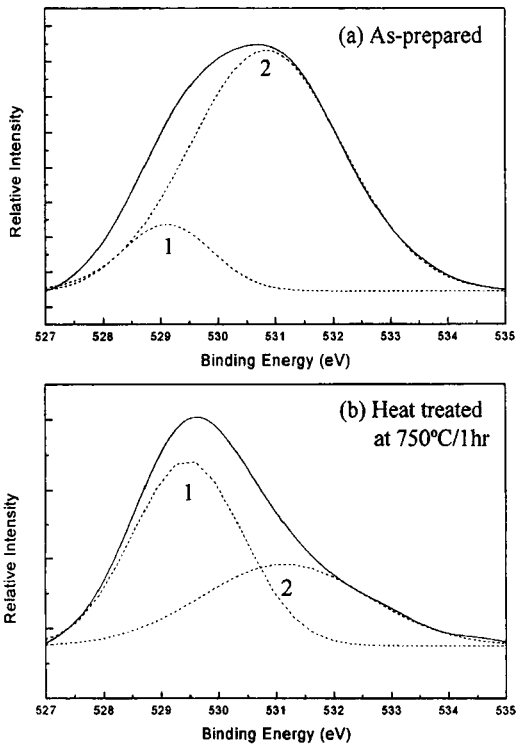

Figure 3 XPS spectrum of O1s

energy ≈ 531.1eV. These two peaks indicated that oxygen atoms has two kinds of chemical status, i.e., peak 1 and 2 represent the well structured oxygen located in crystal lattice and the partially structured oxygen in grain boundary or defects respectively. For the as-prepared PMN shown in figure 3a, peak 2 is much higher than peak 1. This could be attributed to the incomplete reaction and the powder's nanometer scale, which has a big amount of disordered atoms. While the heat-treated PMN at 750°C as shown in figure 3b, peak 2 is lower than peak 1. This may exhibits that there is mainly the well crystallized structure, the grain has grown bigger and the portion of the grain boundary decreased. This presumption agrees with the results of XRD and DTA.

CONCLUSION

Hydrothermal synthesis was proved to be an effective preparation method of lead magnoniobate ceramic powder. The low temperature synthesized pyrochlore powder is incompletely reacted and of nanometer scale, it has high reactivity under moderate temperature heat treatment. Perovskite PMN powder can be derived in the temperature range from 700 to 850°C, the intensity ratio of perovskite to pyrochlore varied with the treating temperature. In the present study, the maximum percentage of perovskite content is just above 60% due to composition deviation. The two child peaks derived from the O1s XPS spectrum may represent the fully and partially structured oxygen atoms respectively.

Acknowledgements
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