Synthesis and structural characterization of some Pb(B\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} type materials by two-stage solid-state route

MUKUL PASTOR, P K BAJPAI* and R N P CHOUDHARY
School of Pure & Applied Physics, Guru Ghasidas University, Bilaspur 495 009, India
†Department of Physics & Meteorology, Indian Institute of Technology, Kharagpur 721 302, India

MS received 27 January 2004

Abstract. Two-stage columbite solid state reaction route has been used for the preparation of Pb(B\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} materials (B' = Mg, Ni and Cd). The columbite precursor phase was structurally characterized using diffraction data. MgNb\textsubscript{2}O\textsubscript{6}, NiNb\textsubscript{2}O\textsubscript{6} and CdNb\textsubscript{2}O\textsubscript{6} show orthorhombic structures i.e. pure columbite phase. Final phase materials get stabilized in mixed phase. The diffraction pattern shows that it is a mixture of cubic pyrochlore and perovskite phase. Percentage of perovskite phase was calculated using the band intensities of (110) perovskite and (222) pyrochlore peaks. The calculated percentages show the dominant perovskite phase. Possible reasons for mixed phase are discussed.

Keywords. Relaxor ferroelectrics; perovskite phase; pyrochlore phase; XRD pattern; columbite precursor.

1. Introduction

Lead based perovskite structures are being synthesized vigorously and many of them show relaxor properties. They have drawn attention during last couple of years owing to their industrial applications such as multilayer capacitors, electro-mechanical coupling devices and actuators due to their low temperature sinterability, high permittivity and low temperature coefficient of capacitance (Chen et al 1997) and excellent optical and electrostrictive properties (Kuwata et al 1979). It has been reported that usual solid state reaction route does not stabilize the perovskite phase in these materials (Furukawa et al 1985). Attempts have been made to synthesize the pure perovskite phase using solid state (Swartz and Shrot 1982; Rao et al 1996), sol–gel (Chaput et al 1989; Choy et al 1990), combustion (Sekar and Halliyal 1998) and soft mechanical (Back et al 1997) techniques. Stabilizers such as BaTiO\textsubscript{3}/PbTiO\textsubscript{3} are also used to increase the tolerance factor (Chen et al 1991; Halliyal et al 1987) and electronegativity difference to get pure perovskite phase in some relaxors (Shrot and Halliyal 1987). Even though a number of preparation routes are tried, the two-stage columbite and B-oxide route are generally used for the lead based relaxors. Recently, it has been reported that the perovskite phase content in the final material depends on the type of pyrochlore phase sequence formed (Chaput et al 1989; Villegas et al 1995). Accordingly, the formation of a perovskite phase within PMN relaxors requires the presence of either rhombohedral pyrochlore (Pb\textsubscript{3}Zn\textsubscript{2}O\textsubscript{7}) or cubic pyrochlore (Pb\textsubscript{3}Nb\textsubscript{2}O\textsubscript{6}) and only slightly depend on the presence of stabilizer, whereas in PZN it requires a cubic pyrochlore phase and stabilizer (Chen et al 1997). It is, therefore, important to know what kind of pyrochlore phase is present along with the perovskite phase in the final phase synthesis in two-stage solid state route. Further, the columbite phase that is used as precursor is pure or is also not important. This should provide a clue about the calculations and sintering parameters optimization. We, therefore, planned a systematic study of structural content of first- and second-stage materials formed during the preparation of some lead based relaxor materials using two-stage columbite route. The X-ray diffraction data are used to characterize the materials. Content of perovskite phase in the final materials is quantitatively estimated along with the density of prepared materials.

2. Experimental

All the raw materials used were of highest purity (> 99.5%). Materials were prepared by pre-reacting the Nb\textsubscript{2}O\textsubscript{5} with divalent metal oxides, MgO, NiO and CdCO\textsubscript{3}, to form columbite structure. The calcination was performed in a closed alumina crucible at 1150°C for 12 h. Calcined powder was characterized by X-ray diffraction pattern. This material was then reacted with excess amount of PbO (2% excess weight) in a closed crucible at 950°C. The calcination was repeated two times and the calcined powder was pelletized using PVA binder. The pellets were fired first at 500°C to remove the binder and then sintered at 1075°C for 12 h. The prepared phases (both first and second) are structurally characterized using XRD

*Author for correspondence (bajpai_pk@yahoo.com)
pattern. XRD peaks were indexed using standard POWD program. Experimental density of final phases were measured and compared with calculated density.

3. Results and discussion

X-ray diffraction patterns for three columbite precursors, MgNb$_2$O$_6$, NiNb$_2$O$_6$, and CdNb$_2$O$_6$, are shown in figure 1. Three materials do not show similar reflections. All columbite phases are orthorhombic; there are significant differences in the lattice parameters. Indexing does not involve significant error as the standard deviation calculated is very small. The XRD peaks observed in the final phase materials are shown in figure 2. All the three materials show similar reflections. Attempts of indexing peaks in any one structure failed indicating that the phase is a mixed phase. We then attempted the fitting by first indexing the peaks due to cubic perovskite structure. Remaining peaks were indexed as due to pyrochlore structure. Out of the three pyrochlore phases, the peaks could be fitted with cubic pyrochlore phases. These data are shown in table 1. The lattice constants obtained for perovskite phase match very well with earlier reports for PMN and PNN (Sharma et al 1993; Lu and Wu 1996). We have not come across any earlier report on PCN. The value of lattice constants changes in a systematic manner and has a direct correlation with the ionic radii of B-site substituent ion, the lattice constant decreases with increase in ionic radii (ionic radii are 0.66, 0.69 and 0.97 for Mg$^{2+}$, Ni$^{2+}$ and Cd$^{2+}$, respectively).

The prepared materials are of mixed phase. It has been reported that the % of perovskite phase depends upon the nature of the pyrochlore phase. For example, in PMN,