

Synthesis and structural characterization of some $\text{Pb}(\text{B}'_{1/3}\text{Nb}_{2/3})\text{O}_3$ type materials by two-stage solid-state route

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Abstract. Two-stage columbite solid state reaction route has been used for the preparation of $\text{Pb}(\text{B}'_{1/3}\text{Nb}_{2/3})\text{O}_3$ materials ($\text{B}' = \text{Mg}, \text{Ni}$ and Cd). The columbite precursor phase was structurally characterized using diffraction data. MgNb_2O_6 , NiNb_2O_6 and CdNb_2O_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 Shrouf 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 $\text{BaTiO}_3/\text{PbTiO}_3$ 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 (Shrouf 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

($\text{Pb}_2\text{Nb}_2\text{O}_7$) or cubic pyrochlore ($\text{Pb}_3\text{Nb}_2\text{O}_8$) 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 calcinations 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_2O_5 with divalent metal oxides, MgO , NiO and CdCO_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

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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_2O_6 , NiNb_2O_6 and CdNb_2O_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,

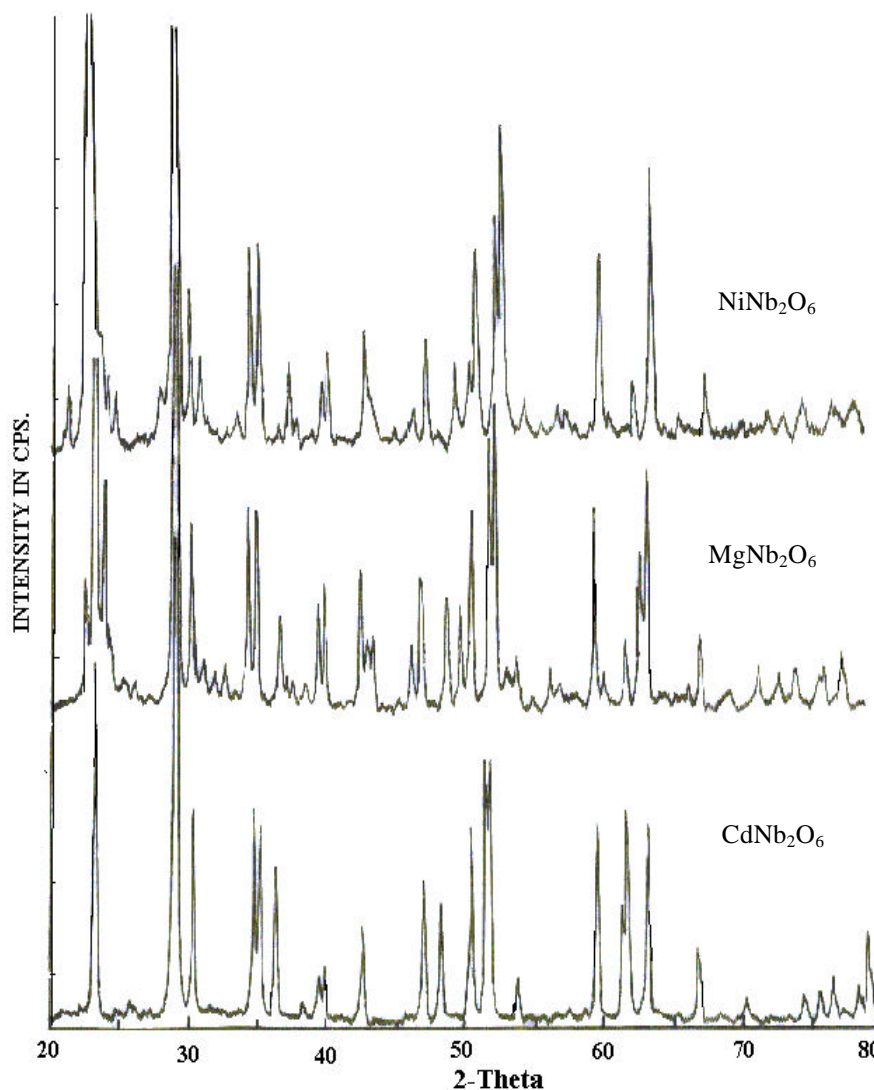


Figure 1. X-ray diffraction of columbite precursor phases of MgNb_2O_6 , NiNb_2O_6 and CdNb_2O_6 .

pyrochlore phases could be rhombohedral ($Pb_2Nb_2O_6$), cubic, $Pb_3Nb_4O_8$, and a stoichiometric phase, $Pb_2Nb_2O_7$, as identified by XRD method. The presence of a particular pyrochlore phase sequence is shown to influence the final perovskite content. It is, therefore, possible to identify the type of pyrochlore phase present when sintered at a particular temperature in the second stage of columbite process. The relative amount of perovskite phase could also be determined using the method described earlier

(Klug and Alexander 1974). The percentage of perovskite is

$$\% \text{ perovskite} = 100 * I_{\text{pero}} / (I_{\text{pero}} + I_{\text{pyro}}), \quad (1)$$

where I_{pero} and I_{pyro} are the integrated band intensities of perovskite (110) and pyrochlore (222) XRD peaks, respectively. The observed pyrochlore phase in final phase of prepared materials is cubic ($Pb_3Nb_4O_8$). Accordingly, the calculated perovskite phase percentages are 72%,

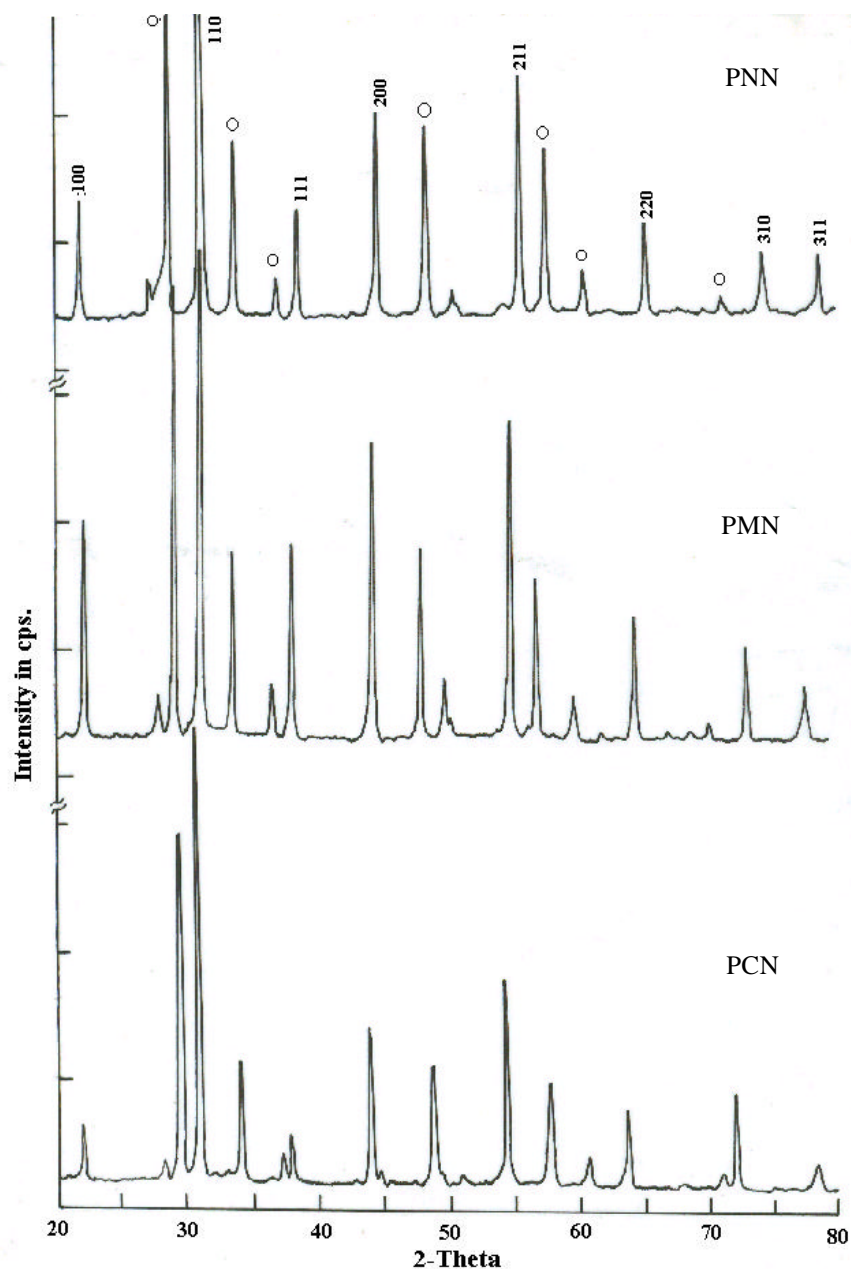


Figure 2. X-ray diffraction of PNN, PMN and PCN. Peaks indexed are due to perovskite phase. Peaks of cubic pyrochlore phase are marked by ellipse (O). The average density of each material and the percentage of perovskite phases in each sample are also shown.

76% and 72%, respectively in PMN, PNN and PCN. Earlier, the percentage of perovskite phase in PMN sintered at 1100°C was calculated as 89% (Das and Pramanik 1999). Our results show relatively small perovskite phase. The cubic pyrochlore gets stabilized along with the perovskite phase, hence, it may be possible to obtain pure perovskite phase when sintered at higher temperature.

For the PCN no such reports are available to the best of our knowledge. Densities of mixed phase were calculated and compared with the theoretical densities. Densities were calculated taking both perovskite and pyrochlore unit cells in respective percentages and thus represent the average densities of mixed phase. The experimental densities are almost 90% to that of theoretical ones.

Table 1. X-ray diffraction data, lattice parameter, a , and volume of unit cell along with standard deviation obtained for perovskite and pyrochlore phases of PMN, PNN and PCN.

PMN-perovskite: $a = 4.0378 \text{ \AA}; V = 65.83 \text{ \AA}^3; \text{S.D.} = 0.06192$				PMN-pyrochlore: $a = 10.6654 \text{ \AA}; V = 1213.18 \text{ \AA}^3; \text{S.D.} = 0.01156$			
d -spacing (obs.)	d -spacing (cal.)	Intensity I/I_0	hkl	d -spacing (obs.)	d -spacing (cal.)	Intensity	hkl
4.0212	4.0580	45	100	3.1989	3.2157	9	311
2.8564	2.8694	100	110	3.0844	3.0788	94	222
2.3429	2.3429	11	111	2.6407	2.6663	38	400
2.0371	2.0290	60	200	2.4396	2.4468	11	331
1.6622	1.6567	64	211	1.8895	1.8854	38	440
1.4400	1.4347	25	220	1.8241	1.8291	12	530
1.2896	1.2832	19	310	1.6129	1.6079	33	622
1.2229	1.2235	11	311	1.5418	1.5394	9	444
				1.3353	1.3332	4	800
PCN-perovskite: $a = 4.0014 \text{ \AA}; V = 64.07; \text{S.D.} = 0.04224$				PCN-pyrochlore: $a = 10.4141 \text{ \AA}; V = 1129.44; \text{S.D.} = 0.01767$			
d -spacing (obs.)	d -spacing (cal.)	Intensity	hkl	d -spacing (obs.)	d -spacing (cal.)	Intensity	hkl
3.9672	3.9940	13	100	3.1561	3.1412	8.1	311
2.8507	2.8242	76	110	3.0124	3.0074	59	222
2.0367	1.9970	28	200	2.6264	2.6045	23	400
1.6842	1.6306	36	211	2.3720	2.3901	11	331
1.4661	1.4121	16	220	1.8602	1.8417	22	440
1.3104	1.3313	18	310	1.6006	1.6075	20	541
1.2214	1.2042	7.6	311	1.5259	1.5361	9	631
PNN-perovskite: $a = 4.0344 \text{ \AA}; V = 65.67; \text{S.D.} = 0.00937$				PNN-pyrochlore: $a = 10.8374 \text{ \AA}; V = 1272.85; \text{S.D.} = 0.01752$			
d -spacing (obs.)	d -spacing (cal.)	Intensity	hkl	d -spacing (obs.)	d -spacing (cal.)	Intensity	hkl
4.0212	4.0395	23	100	3.2676	3.2676	8	311
2.8564	2.8564	100	110	3.0844	3.1285	95	222
2.3276	2.3322	20	111	2.6407	2.6285	35	410
2.0257	2.0198	46	200	2.4229	2.4233	8	420
1.6477	1.6491	48	211	1.8438	1.8319	38	531
1.4296	1.4282	18	220	1.5994	1.5979	33	631
1.2817	1.2774	13	310	1.5297	1.5326	9	550
1.2194	1.2180	12	311	1.3267	1.3240	3	733
Samples	Density (observed) g/cm^3	Theoretical density (calculated) g/cm^3	% Perovskite				
Pb(Mg _{1/3} Nb _{2/3})O ₃	5.786	6.36	72				
Pb(Ni _{1/3} Nb _{2/3})O ₃	6.51	6.85	76.2				
Pb(Cd _{1/3} Nb _{2/3})O ₃	6.413	6.9	72				

4. Conclusions

Lead based relaxors, PMN, PNN and PCN, prepared by two-stage columbite process show dominant perovskite phase along with cubic pyrochlore phase when sintered at 1075°C. The columbite precursor phase is structurally characterized and found to be orthorhombic with significantly different unit cells in three materials. It is suggested that at relatively high temperature sintering pure perovskite phase could be achieved.

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