Preparation and Characterization of Lithium Doped Silver Niobate Perovskite System

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Abstract   Ceramic pellets of lithium doped silver niobate, $Ag_{1-x}Li_xNbO_3$ (x = 0, 0.3, 0.5 and 0.7), were prepared by solid-state reaction and sintering process. Niobium penta-oxide Nb_2O_5, silver oxide (Ag_2O) and lithium carbonate (Li_2CO_3) were the starting materials. The prepared samples were characterized by XRD and SEM techniques. Grain sizes and lattice parameters were calculated by SEM and X-ray diffraction data for mixed $Ag_{1-x}Li_xNbO_3$ system. The variations in grain sizes and lattice parameters with composition at room temperature have been reported. All the samples show orthorhombic structure at room temperature.

Keywords   Silver Lithium Niobate, Perovskite Ceramics, Ferroelectrics, XRD, SEM

1. Introduction

The perovskite niobate ($ANbO_3$) constitutes an interesting structural family, which undergoes several sequences and mechanisms of structural phase transitions. Silver lithium niobate ($Ag_{1-x}Li_xNbO_3$) system shows interesting properties[1, 2]. The constituents of this system are silver niobate ($AgNbO_3$) and lithium niobate ($LiNbO_3$). Silver niobate is known to exhibit several sequences and mechanisms of structural phase transitions as a function of the temperature[3-5]. Silver niobate $AgNbO_3$ undergoes a sequence of phase transitions[6-8] observed at the following temperatures:

(i) At 67 ^{0}C, orthorhombic M_1[FE] $\rightarrow$ orthorhombic $M_{2[}$AFE];

(ii) At 267 ^{0}C, orthorhombic M_2[AFE] $\rightarrow$ orthorhombic $M_{3[}$AFE];

(iii) At 353 ^{0}C, orthorhombic M_3[AFE] $\rightarrow$ orthorhombic $O_{1[}$PE];

(iv) At 361 ^{0}C, orthorhombic $O_{1[}$PE] $\rightarrow$ orthorhombic $O_{2[}$PE];

(v) At 387 ^{0}C, orthorhombic O_2[PE] $\rightarrow$ tetragonal T[PE];

(vi) At 567 ^{0}C, tetragonal T[PE] $\rightarrow$ cubic C[PE].

where M_1, M_2 & M_3 denote the phases with orthorhombic symmetry in rhombic orientation, while O_1 & O_2 are the phases with orthorhombic symmetry in parallel orientation. The parallel orientation means the orthorhombic axes are parallel to the pseudo cubic directions, whereas in the case of rhombic orientation the orthorhombic a- and b-axes are parallel to diagonals contained inside the faces of the same pseudo cubic axes[6]. It was established that M_1 phase exhibit, weak ferroelectric[FE] properties, phase M_2 & M_3 are antiferroelectric[AFE] and phases O_1, O_2, T and C are paraelectric[PE][9]. The temperature evolution of the lattice parameters and the sequence of phase transitions are similar to those observed in sodium niobate ($NaNbO_3$)[10, 11].

Lithium niobate, $LiNbO_3$ undergoes the phase transition at 1210 ˚C, from the trigonal[Ferroelectric] to the trigonal[Paraelectric]. Bhatt and Semwal[12] have reported dielectric properties of $LiNbO_3$. The non- linear acoustical properties of $LiNbO_3$ have led to the observation of a new physical effect. An acoustical tone burst stores energy with in the crystal that is re emitted at a later time of order of 70 μs. This effect can be characterized as an 'acoustic memory'. This phenomenon is dependent on frequency and temperature[13]. X-ray investigations of $Ag_{1-x}Li_xNbO_3$ solid solution ceramics ($0 \leq x \leq 0.15$) showed that small Li substitution causes a change of symmetry[14]. At room temperature, a phase boundary between orthorhombic and rhombohedral symmetry is observed for x = 0.05; this phase boundary is indicated also by dielectric properties. The Li- substitution, leads to a gradual rise and shift of diffuse ε' (T) maximum which is observed for (AN) as 227^{0}C. Instead of this diffuse maximum, a sharp one at 197 ^{0}C is already observed for $Ag_{0.94}Li_{0.06}NbO_3$[14].

2. Material and Methods

The final physical and electromechanical properties of

ferroelectric material components greatly depend upon the preparation method used. For studies of fundamental properties of materials, large homogeneous single crystals are usually desirable to minimize the effects of surfaces and imperfections. However, single crystals are very expensive and difficult to grow, whereas ceramics have the advantage of being a great deal easier to prepare compare to their single crystal.

2.1. Sample Preparation

The starting materials used for preparing silver lithium niobate $Ag_{1-x}Li_xNbO_3$ system were silver oxide (Ag_2O), purity 97% (Qualigens Fine Chemicals); lithium carbonate (Li_2CO_3), purity 99% (Qualigens Fine Chemicals) and niobium pentaoxide (Nb_2O_5), purity 99.9% (Loba Chemie). Similar to preparation of silver niobate[7], silver sodium niobate[15,16], holmium doped lithium niobate[17] and silver potassium niobate[18,19], the samples of silver lithium niobate were prepared by solid-state reaction method. The starting materials were initially dried at 200ºC for 2h to remove the absorbed moisture and then quantities of the reagent required to prepare silver lithium niobate were weighed in stoichiometric proportion. All the samples were prepared according to following reaction:

(1-x) Ag_2O + x Li_2CO_3 + Nb_2O_5 → 2 $Ag_{1-x}Li_xNbO_3$ + x CO_2
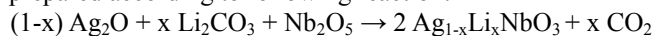
Each composition was manually dry ground into fine powder for two and half hours and then wet mixed using reagent methyl alcohol and pestle for two hrs. The mixture was calcined in a silica crucible, in air, at 650 ºC for 2h, at 850 ºC for 2h and at 950 ºC for 1 ½ h.

The pre-sintered mixture was ground again for 2h and pressed into pellets of 11 mm diameter applying the pressure of 3 tons. All pellets of a composition were placed on a silica crucible and sintered in air at 1000 ºC for 14h. All the samples were taken out from furnace when they cooled to room temperature. The sintered pellets of all compositions were gold polished for characterization (SEM) and electroded in metal-insulator-metal (MIM) configuration using air-drying silver paste for dielectric measurements. Prepared samples were characterized using XRD and SEM.

2.2. Characterization

X-ray diffraction (XRD) patterns of all the prepared samples at room temperature have been obtained on a D-8 ADVANCE X-ray diffractometer (Bruker) using Cu-K$_\alpha$ radiation of 1.540598Å wavelength. The instrument was well calibrated with the silicon standard sample. Peak indexing was done by using JCPDS data. From the observed diffraction pattern, lattice spacing *d* was determined which was used to determine the lattice parameters. Surface topography of the samples was studied by scanning electron micrographs (SEM) using LEO-440 scanning electron microscope.

3. Results and Discussion

The prepared ceramic samples of $Ag_{1-x}Li_xNbO_3$ for x = 0,

0.3, 0.5 and 0.7 were analyzed for phase and crystallinity by powder X-ray diffraction technique. X-ray diffraction pattern for all the samples were recorded at room temperature. The diffraction data were collected in the 2θ ranges of 10–70º with a scan step of 0.02º. X-ray diffraction patterns of obtained for all prepared samples is shown in Figure. 1. From the observed diffraction patterns the lattice spacing was determined which was used to determining the unitcell parameters. The unit-cell parameters were determined using the 'WinPLOTR' computer software (2005 version), which includes CRYSFIRE and FULLPROF software. From X-ray patterns, it was found that at room temperature all the compositions are in orthorhombic phase. Lattice parameters (Table 1) also reveal the structures of present systems.
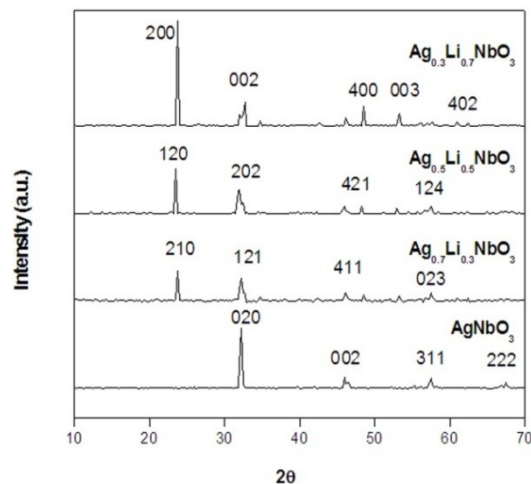

Figure 1.   Powder X-ray diffraction pattern of $Ag_{1-x}Li_xNbO_3$ for different x values.

Table 1.   Lattice parameters and average grain sizes of $Ag_{1-x}Li_xNbO_3$ for different x values at room temperature

S. no.	Compositions	Lattice Parameters			Grain Size (SEM) (µm)
		a (Å)	b (Å)	c (Å)	
1.	AgNbO$_3$	5.5972	5.5423	3.9100	5.127
2.	Ag$_{0.7}$Li$_{0.3}$NbO$_3$	8.8653	7.0365	5.3847	3.873
3.	Ag$_{0.5}$Li$_{0.5}$NbO$_3$	8.7997	8.3403	7.2954	3.711
4.	Ag$_{0.3}$Li$_{0.7}$NbO$_3$	7.4974	6.6379	5.1534	2.573

Surface morphology and grain sizes of the prepared samples were studied by SEM technique. Scanning Electron Micrographs for $Ag_{1-x}Li_xNbO_3$ (x = 0, 0.3, 0.5 and 0.7) are shown in Figs 2(a) - (d) respectively. The grains of different sizes are randomly distributed with large inter-granular porosity. The grains of different sizes with orthorhombic shape grow in the prepared samples. Smaller grains (~ 1 to 2 µm) occupy the space between the bigger grains (~ 4 to 8 µm), and thus reducing the porosity. Variation of average grain size with different composition of $Ag_{1-x}Li_xNbO_3$ is shown in Table 1. Average grain size of AgNbO$_3$ is found 5.127 µm, on doping of Li grain size decreased to 3.873 µm, on further increasing the doping percentage of Li, grain size further decreased. The decrease in grain sizes is due to the smaller

size of lithium.

4. Conclusions

In the present study, formation and characterization of lithium doped silver niobate perovskite system, $Ag_{1-x}Li_xNbO_3$ (x = 0, 0.3, 0.5, 0.7) have been investigated. Ceramic samples were prepared by solid state reaction and sintering method. The sintered samples were investigated for phase and crystallinity by powder X-ray diffraction. From X-ray diffraction patterns and SEM studies, it has been observed that at room temperature all the compositions are in orthorhombic phase. It was also found that average grain size of $Ag_{1-x}Li_xNbO_3$ decrease on increasing the value x, i.e., doping of Li. As Li is smaller than Ag, it causes a decrease in grain size on increasing concentration of lithium.
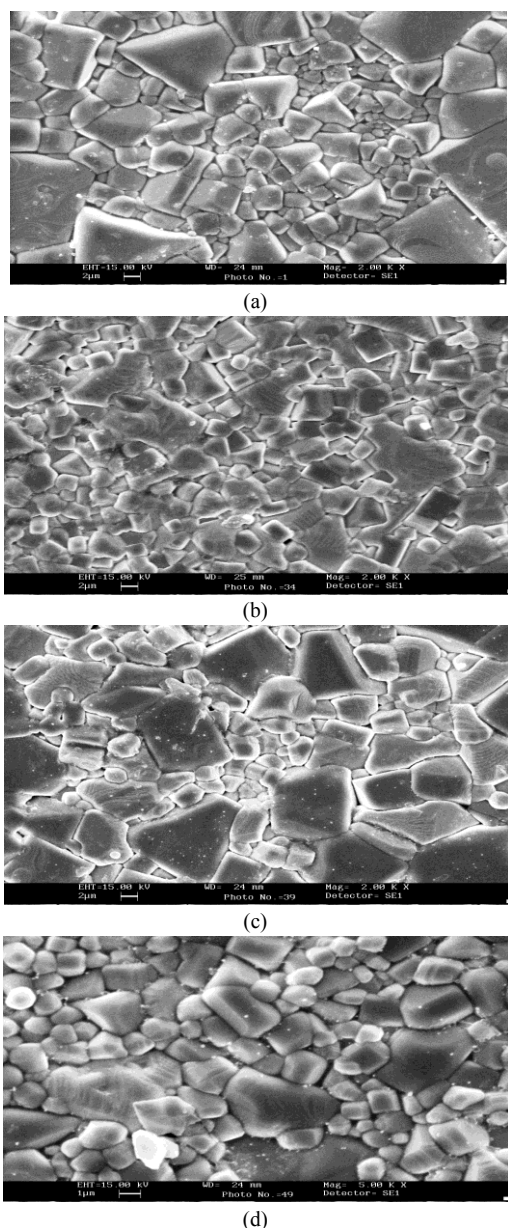

(a)

(b)

(c)

(d)

Figure 2. Scanning Electron Micrographs of $AgNbO_3$ (a), $Ag_{0.7}Li_{0.3}NbO_3$ (b), $Ag_{0.5}Li_{0.5}NbO_3$ (c) and $Ag_{0.3}Li_{0.7}NbO_3$ (d) samples.

REFERENCES

[1] Wada S., Saito A., Hoshina T., Kakemato H., Tsurumi T., Moriyoshi C., and Kuroiwa Y., 2007, Ferroelectrics 346, 64-71.

[2] Kania A., and Miga S., 2001, Mater. Sci. Eng. B 86, 128-133.

[3] Nautiyal O.P., Bhatt S.C., Pant R.P., and Semwal B.S., 2010, Indian J. Pure & Appl. Phys. 48, 357-362.

[4] Kityk I.V., Makowska-Janusik M., Fontana M.D., Aillerie M. and Fahmi A., 2001, J. Applied Physics, 90, 5542.

[5] Kania A., Roleder K., Kugel G.E., and Fontana M.D., 1986, J. Phys. C: Solid state Physics 19, 9.

[6] Sciau Ph., Kania A., Dkhil B., Suard E., and Ratuszna A., 2004, J. Phys.: Condens. Matter 16, 2795.

[7] Nautiyal O.P., Bhatt S.C., and Bartwal K.S., 2010, J. Alloys and Compouds, 505, 168-171.

[8] Valant M., and Sarvorov D., 2006, J. Appl. Phys. 99, 124109.

[9] Levin I., Krayzman V., Woicik J. C., Karapetrova J., Proffen T., Tucker M. G., and Reaney I. M., 2009, Phys. Rev., B 79, 104113 (14pp).

[10] Bhatt S.C., Singh K., Uniyal M., Om Prakash, Singh P.K., Saxena R., and Semwal B.S., 2007, Indian J. Pure Appl. Phys. 45, 609.

[11] Glazer A.M., and Megaw H., 1973, Acta Crystallogr.A 29, 489.

[12] Bhatt S.C., and Semwal B.S., 1987, Indian J. Pure and Appl. Phys. 25, 174.

[13] Michael S., Pherson Mc, Ostrovskit Igor, and Breazeale M.A., 2002, Phys. Rev. Lett. 89, 115506.

[14] Nalbandinan V.B., Medviediev B.S., and Bieliayev I.N., 1980, Izv AN SSSR: Neorg. Mater. 16, 1819.

[15] Nautiyal O.P., Bhatt S.C., Pant R.P., Bourai A.A., Singh P.K., Saxena R., and Semwal B.S., 2009, Indian J. Pure Appl. Phys. 47, 282.

[16] S. C. Bhatt, O. P. Nautiyal, and B. S. Semwal, Processes and Characterisation of advanced nanostructured materials, Macmillan Publisher India Ltd, 2010, pp. 9-14.

[17] Fadil F.Z., Aillerie M., Lamcharfi T., and Abdi F., 2011, Ceramics International, 37 (7), 2281.

[18] Nautiyal O.P., Bhatt S.C., and Semwal B.S., 2009, Indian J. Pure Appl. Phys. 47, 719.

[19] O. P. Nautiyal, S. C. Bhatt, and B. S. Semwal, Processes and Characterisation of advanced nanostructured materials, Macmillan Publisher India Ltd, 2010, pp. 3-8.