

Preparation and characterization of ceramic samples of silver sodium niobate mixed system

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Ceramic pellets of $\text{Ag}_{1-x}\text{Na}_x\text{NbO}_3$ ($x = 0, 0.3, 0.5$ and 0.7), system have been prepared by solid-state reaction method and sintering process. The prepared samples are characterized by XRD and SEM techniques. Lattice parameters and crystallite size have been calculated by XRD pattern and grain size has been calculated by SEM. It has been observed that all the prepared samples show orthorhombic structure at room temperature.

Keywords: Dielectrics, Ceramics, X-ray diffraction, Scanning electron micrographs

1 Introduction

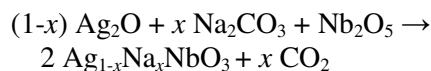
The ABO_3 type niobate perovskite compounds constitute an important group of oxide crystals with broad ranges of scientifically and technologically important dielectric, piezoelectric, ferroelectric and electro-optic properties¹. Silver niobate (AgNbO_3) is a member of the perovskite niobate. AgNbO_3 and NaNbO_3 are isostructural antiferroelectric compounds². At room temperature, they exhibit the orthorhombic symmetry with the $Pbcm$ space group². The electro-physical properties of AgNbO_3 differ from those of NaNbO_3 and KNbO_3 , which is probably due to the presence of silver ions occupying d-shells near the top of the valence band, in contrast to sodium and potassium^{2,3}.

Because of recent developments in telecommunications, electro-optics and piezoelectric components, perovskite niobates have been considered as functional materials for future technologies. 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 easier to prepare than their single crystal counterparts¹.

2 Material and Methods

The starting materials used for preparing silver sodium niobate ($\text{Ag}_{1-x}\text{Na}_x\text{NbO}_3$) system were silver

oxide (Ag_2O), of purity 97% (Qualigens Fine Chemicals); sodium carbonate (Na_2CO_3), purity 99.8% (Qualigens Fine Chemicals); and niobium pentaoxide (Nb_2O_5), purity 99.9% (Loba Chemie). The sample of silver niobate was prepared by conventional sintering method, i.e., solid-state reaction method. The starting materials were initially dried at 200°C for 2 h to remove the absorbed moisture and then quantities of the reagent required to prepare silver sodium niobate were weighed in stoichiometric proportion. All the samples were prepared according to following reaction:



Each composition was manually dried mixed for two and half hours and then wet mixed using reagent methyl alcohol and pestle for next 2 h. The mixture was calcined in a silica crucible, in air, for carbonate removal and reaction at $800, 850$ and 950°C each for 2 h respectively.

After cooling to room temperature, above mixture was ground for about 2 h and pressed in to pallets of 11 mm diam using a palletizer at 3 t pressure. All pellets of composition were placed on a silica crucible and sintered in air at $1080-1100^\circ\text{C}$ for 12 h. The sintered pellets were gold polished for characterization (SEM) and electroded using air-drying silver paste for dielectric measurements.

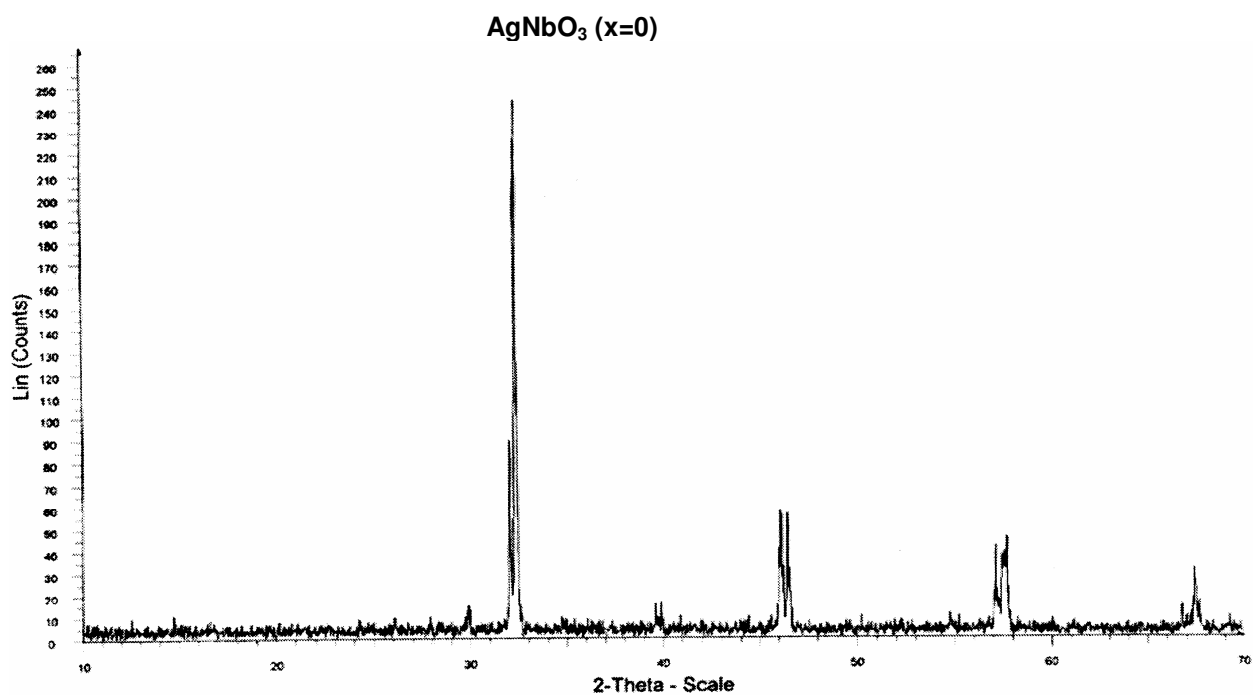


Fig. 1 — X-ray diffraction pattern of AgNbO₃

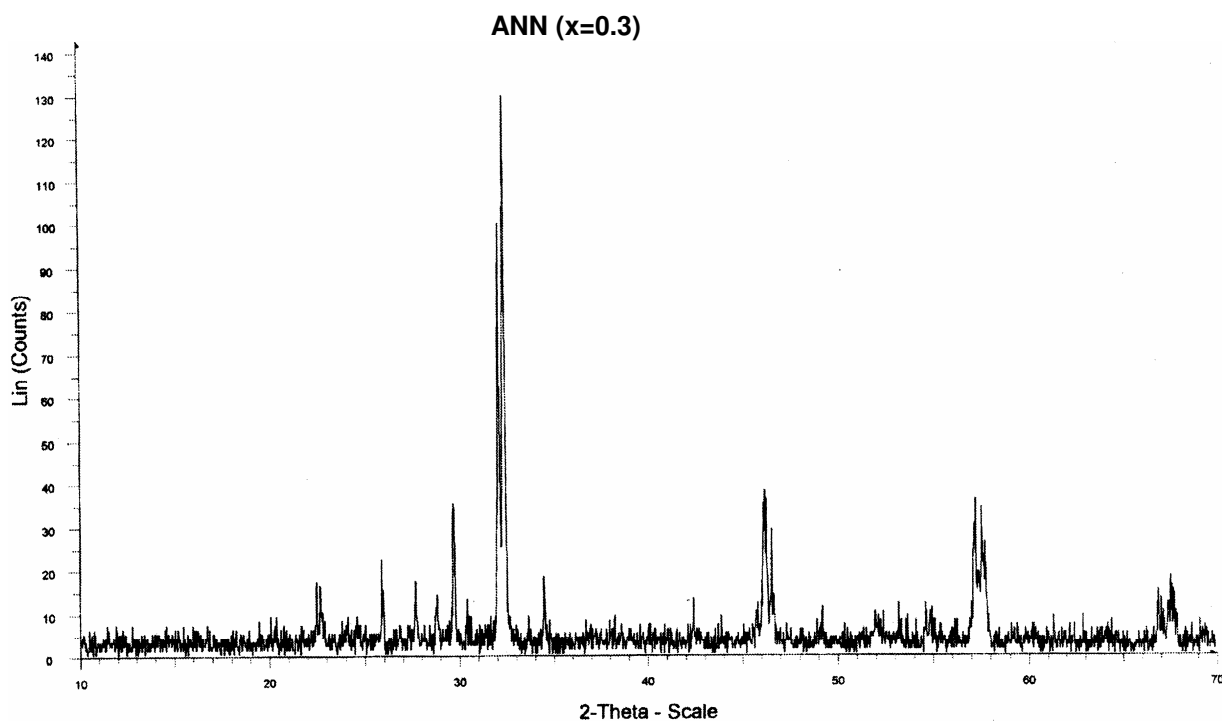
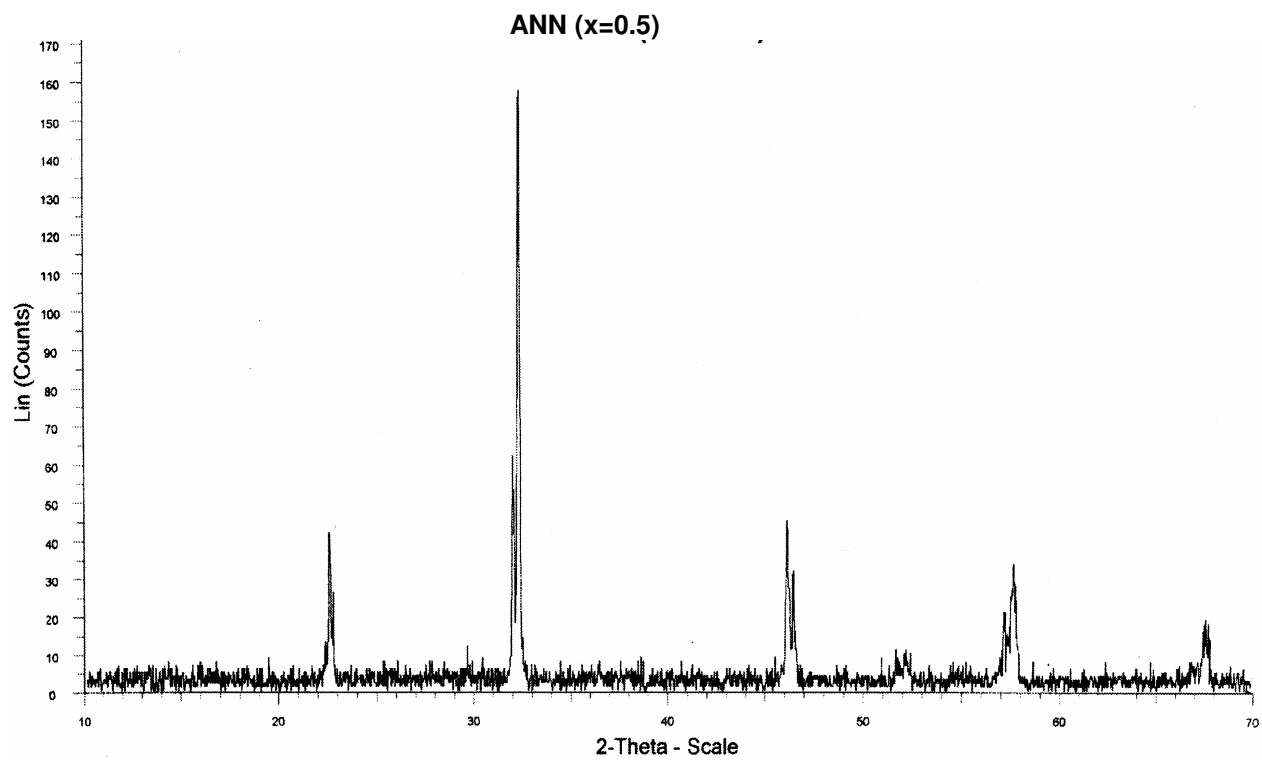
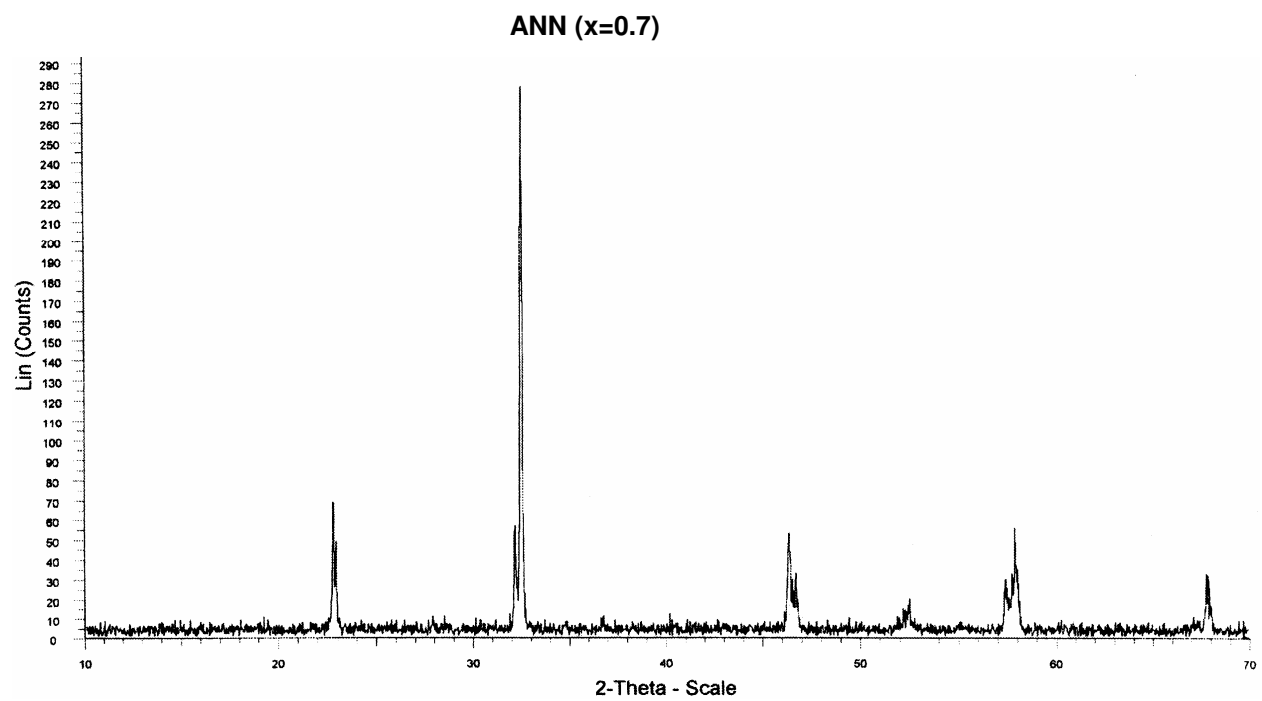


Fig. 2 — X-ray diffraction pattern of Ag_{0.7}Na_{0.3}NbO₃

Fig. 3 — X-ray diffraction pattern of $\text{Ag}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ Fig. 4 — X-ray diffraction pattern of $\text{Ag}_{0.3}\text{Na}_{0.7}\text{NbO}_3$

2.1 Characterization

2.1.1 X-ray diffraction patterns

To characterize the material in the present study, X-ray diffraction pattern of all the samples at room temperature were obtained on a D-8 ADVANCE X-ray diffractometer made by Bruker, using Cu-K α filter radiation of 1.540598 Å wavelength. The instrument is well calibrated with the silicon standard sample. The diffraction data were collected in the 2 θ range of 10-70° with a scan step of 0.025° and step time 1 s. Peak indexing was done by using Joint Committee on Powder Diffraction Standards (JCPDS) data cards. From the observed diffraction pattern, lattice spacing d was determined, which was used to determining the perovskite lattice parameters. The unit-cell parameters were determined using the WinPLOTR computer software (2005 version), which includes CRYSFIRE and FULLPROF software.

The X-ray diffraction patterns obtained from all the prepared samples have been shown in Figs 1-4. The comparison of the present study for AgNbO $_3$ ceramic system, with Joint Committee on Powder Diffraction Standards (JCPDS) data card and other workers data of d -values are given in Table 1. The values of change in intensity of reflected X-ray beam with angle of incidence in Ag $_{1-x}$ Na $_x$ NbO $_3$ systems are presented in Tables 2-5 respectively.

The lattice parameters for all the prepared compositions have been presented in Table 6 and the variation of lattice parameters with compositions is shown in Figs 5 and 6.

Crystallite size — Crystallite size of the samples is calculated by Scherrer formula from the full width at half maximum (FWHM) of the highest intensity peak in the XRD pattern and is given in Table 7. Its variation with compositions has been shown in Fig. 7.

2.1.2 Scanning Electron Micrographs (SEM)

Surface topography of the samples was studied by Scanning Electron Micrographs (SEM) using LEO-440 scanning electron microscope. Figures 8-11 show typical electron micrographs of silver sodium niobate Ag $_{1-x}$ Na $_x$ NbO $_3$ mixed system.

Grain size — Variation of average grain size with the different compositions of Ag $_{1-x}$ Na $_x$ NbO $_3$ has been shown in Fig.12 and Table 8.

Table 1 — The comparison of data for d -values of AgNbO $_3$ ceramic with JCPDF data cards and other workers data

d^*	d^{**}	$d^\#$
2.780	2.800	2.8004
2.260	2.770	2.7743
1.970	1.977	2.2627
1.957	1.955	1.9712
1.609	1.609	1.9553
1.603	1.599	1.6128
1.599	1.594	1.6018
1.401	1.399	1.5982
1.386	1.383	1.3882

* JCPDS data, File No. 22-0471, Ref.: Brusset *et al.*, *Bull Soc Chim France*, (1976) 2276-83

** Lukaszewski and Ratuszna⁶

Present study results for ceramic sample

Table 2 — Change in intensity of reflected X-ray beam with angle of incident in AgNbO $_3$

2 θ	d	I	h	k	l
31.93162	2.8004	41.4	2	0	0
32.24039	2.7743	247.1	0	2	0
39.80608	2.2627	12.7	0	2	1
46.00604	1.9712	47.7	2	2	0
46.40102	1.9553	75.4	0	0	2
57.06031	1.6128	19.2	3	1	1
57.48738	1.6018	48.5	1	3	1
57.62886	1.5982	44.6	0	2	2
67.40459	1.3882	28.0	2	2	2

Table 3 — Change in intensity of reflected X-ray beam with angle of incident in Ag $_{0.7}$ Na $_{0.3}$ NbO $_3$

2 θ	d	I	h	k	l
25.851	3.4436	14.0	1	0	1
27.616	3.2275	16.0	1	1	1
28.738	3.1039	13.0	2	1	1
32.045	2.7908	100.0	0	2	1
32.324	2.7674	128.0	1	2	1
34.437	2.6022	19.0	5	0	1
46.168	1.9646	35.0	9	2	0
57.195	1.6093	26.0	6	5	0
66.905	1.3974	15.0	2	6	1

Table 4 — Change in intensity of reflected X-ray beam with angle of incident in $\text{Ag}_{0.5}\text{Na}_{0.5}\text{NbO}_3$

2θ	d	I	h	k	l
22.554	3.9392	37.0	2	1	0
22.698	3.9145	12.0	0	0	1
30.398	2.9381	9.0	2	0	1
31.970	2.7972	51.0	3	1	0
32.254	2.7731	157.0	2	1	1
46.436	1.9539	25.0	0	0	2
51.354	1.7778	07.0	5	0	0
57.193	1.6093	19.0	0	3	2
57.653	1.5976	29.0	4	3	1

Table 5 — Change in intensity of reflected X-ray beam with angle of incident in $\text{Ag}_{0.3}\text{Na}_{0.7}\text{NbO}_3$

2θ	d	I	h	k	l
22.724	3.9100	68.0	0	1	1
27.647	3.2239	08.0	2	2	0
30.325	2.9451	07.0	5	0	1
32.128	2.7838	54.0	0	2	1
32.437	2.7580	265.0	1	2	1
46.319	1.9586	53.0	3	3	1
57.405	1.6039	11.0	11	0	1
57.880	1.5919	40.0	2	4	1

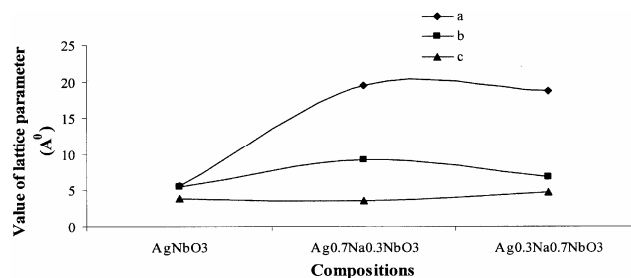
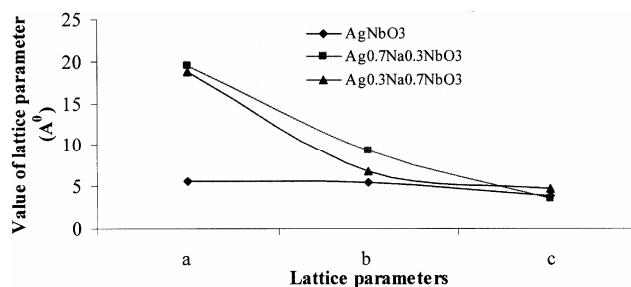
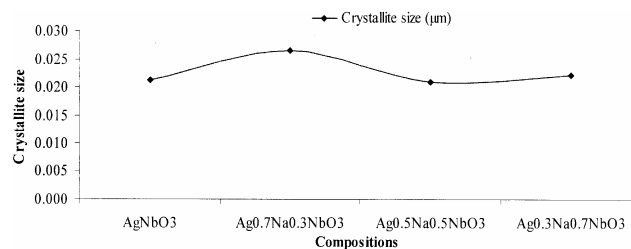
Table 6 — Lattice parameters of $\text{Ag}_{1-x}\text{Na}_x\text{NbO}_3$ for different x values

Compositions	Lattice Parameters		
	a (Å)	b (Å)	c (Å)
AgNbO_3	5.5972	5.5423	3.9100
$\text{Ag}_{0.7}\text{Na}_{0.3}\text{NbO}_3$	19.5127	9.2598	3.4990
$\text{Ag}_{0.5}\text{Na}_{0.5}\text{NbO}_3$	8.8926	8.5154	3.9080
$\text{Ag}_{0.3}\text{Na}_{0.7}\text{NbO}_3$	18.7492	6.8689	4.7578

3 Results and Discussion

X-ray diffraction patterns obtained for all prepared samples show characteristic lines corresponding to the orthorhombic along with some impurities and are shown in Figs 1-4. The comparison of the present study for AgNbO_3 ceramic system, with Joint Committee on Powder Diffraction Standards (JCPDS) data card and other workers data of d -values are given in Table 1.

From X-ray patterns, it was found that at room temperature all the compositions are in orthorhombic phase, which is in agreement with the previously reported results⁴⁻¹⁴. Lattice parameters (Table 6 and Figs 5 and 6) also reveal the structures of present systems.

Fig. 5 — Effect of Na on the lattice parameters of AgNbO_3 Fig. 6 — Lattice parameters of different compositions of $\text{Ag}_{1-x}\text{Na}_x\text{NbO}_3$ Fig. 7 — Crystallite size for different composition of $\text{Ag}_{1-x}\text{Na}_x\text{NbO}_3$ Table 7 — Crystallite Size for different composition of $\text{Ag}_{1-x}\text{Na}_x\text{NbO}_3$

Compositions	Crystallite Size (μm)
AgNbO_3	0.0212
$\text{Ag}_{0.7}\text{Na}_{0.3}\text{NbO}_3$	0.0265
$\text{Ag}_{0.5}\text{Na}_{0.5}\text{NbO}_3$	0.0209
$\text{Ag}_{0.3}\text{Na}_{0.7}\text{NbO}_3$	0.0222

Crystallite size of the samples has been given in Table 7 and shown in Fig 7. It is observed that addition of sodium (Na) in silver niobate (AgNbO_3) system shows an increase in the crystallite size. The SEM pictures of $\text{Ag}_{1-x}\text{Na}_x\text{NbO}_3$ samples have been shown in Figs 8-11. The average grain size with the different compositions of $\text{Ag}_{1-x}\text{Na}_x\text{NbO}_3$ has been given in Table 8 and shown in Fig 12. The grain of different sizes $\sim 1 \mu\text{m}$, $4 \mu\text{m}$, $10 \mu\text{m}$ with orthorhombic shape grow in the prepared samples of

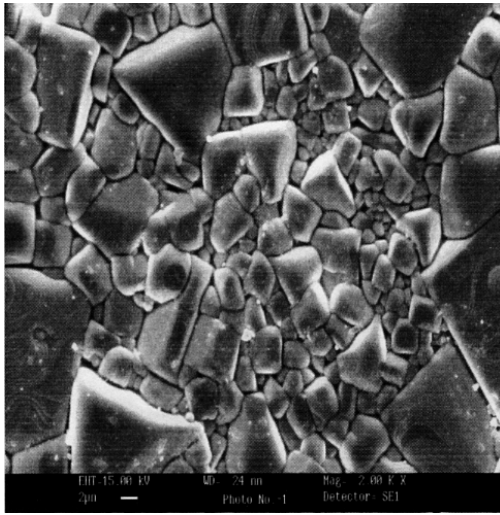


Fig. 8 — Scanning Electron Micrographs of AgNbO_3

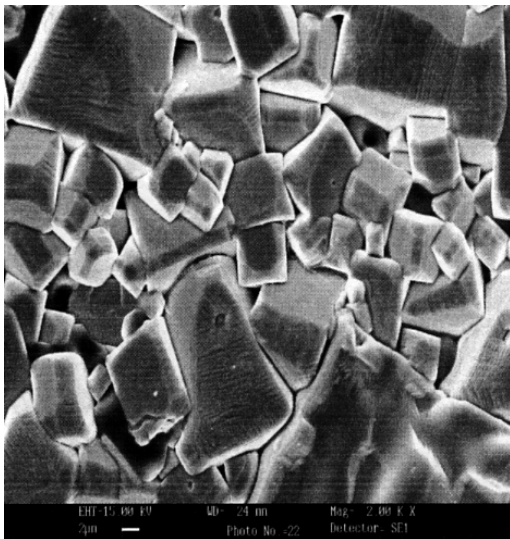


Fig. 9 — Scanning Electron Micrographs of $\text{Ag}_{0.7}\text{Na}_{0.3}\text{NbO}_3$

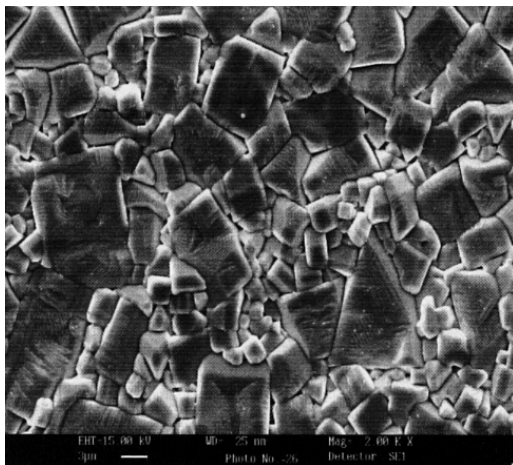


Fig. 10 — Scanning Electron Micrographs of $\text{Ag}_{0.5}\text{Na}_{0.5}\text{NbO}_3$

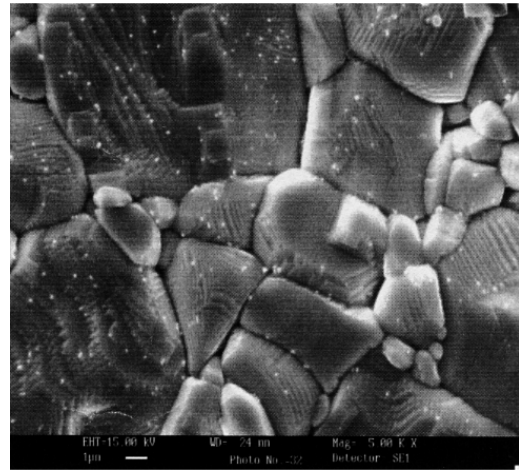


Fig. 11 — Scanning Electron Micrographs of $\text{Ag}_{0.3}\text{Na}_{0.7}\text{NbO}_3$

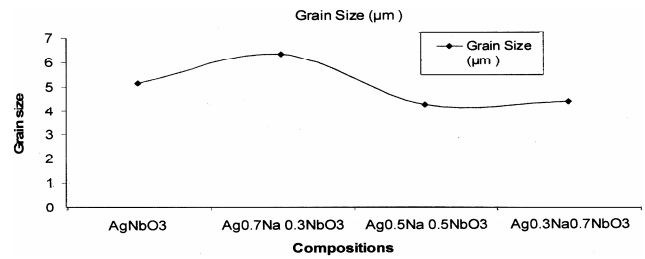


Fig. 12 — Variation of average grain size with the different compositions of $\text{Ag}_{1-x}\text{Na}_x\text{NbO}_3$

Table 8 — Variation of average grain size with the different compositions of $\text{Ag}_{1-x}\text{Na}_x\text{NbO}_3$

Compositions	Grain Size (μm)
AgNbO_3	5.127
$\text{Ag}_{0.7}\text{Na}_{0.3}\text{NbO}_3$	6.285
$\text{Ag}_{0.5}\text{Na}_{0.5}\text{NbO}_3$	4.220
$\text{Ag}_{0.3}\text{Na}_{0.7}\text{NbO}_3$	4.315

$\text{Ag}_{1-x}\text{Na}_x\text{NbO}_3$ for $x = 0, 0.3, 0.5$ and 0.7 . Smaller grains occupy the space between the bigger grains and thus reducing the porosity.

From XRD and SEM studies, it has been observed that for composition $\text{Ag}_{0.7}\text{Na}_{0.3}\text{NbO}_3$ crystallite size and average grain size increase. As Na is lighter and smaller than Ag, at low concentration Na could not replace Ag but occupy interstitial position and hence, cause an increase in crystallite size and grain size.

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